Platinum Complexes of Naphthalene-1,8-dichalcogen and Related Polyaromatic Hydrocarbon Ligands

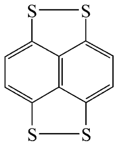
Stephen M. Aucott, Heather L. Milton, Stuart D. Robertson, Alexandra M. Z. Slawin, Greg D. Walker, and J. Derek Woollins*[a]

Abstract: Platinum bisphosphine complexes bearing dichalcogen-derivatised naphthalene, acenaphthene or phenanthrene ligands have been prepared by either oxidative addition to zero-valent platinum species or from $[PtCl_2(PPhR_2)]$ (R = Ph or Me) and the disodium or dilithium salts of the parent disulfur, diselenide or mixed S/Se species. The parent naphthalene, acenaphthene and phenanthrene chalcogen compounds were treated with either $[Pt(PPh_3)_4]$ or $[Pt(C_2H_4)(PMe_3)_2]$ (prepared in situ from $[PtCl_2(PMe_3)_2]$, ethene and sodium naphthalide or super hydride $[LiBEt_3H]$) to give the appropriate platinum(II) species. The dilithium salts of 1,8-E_2-naphthalene (E = S or Se) prepared in situ by reduction of the E–E bond with $[LiBEt_3H]$ were treated with $[PtCl_2(PPh_3)_2]$ to give $[Pt(1,8\text{-}E_2\text{-nap})(PPh_3)_2]$. The tetraoxides $[Pt(1,8\text{-}(S(O)_2)_2\text{-nap})(PR_3)_2]$ ($PR_3 = PPh_3$ or PMe_2Ph) were prepared in a similar metathetical manner from the appropriate $[PtCl_2(PR_3)]$ complexes and the disodium salt of naphthalene 1,8-disulfinic acid (1,8-$(S(O)ONa)_2$-nap). The X-ray structures of selected examples reveal bidentate coordination with the naphthalene-E_2 unit hinged (111–137°) with respect to the coordination plane. The naphthalene ring suffers significant distortion from planarity.

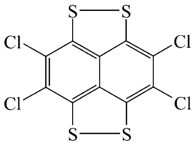
Keywords: chalcogens • metathesis • oxidative addition • platinum • structure elucidation

Introduction

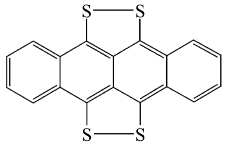
The coordination chemistry of naphtho[1,8-*cd*][1,2]dichalcogenoles and the structurally related compounds described herein has been largely overlooked. The notable exceptions to this statement being a series of publications by B. K. Teo in the late 1970s and early 1980s on the oxidative addition of tetrathionaphthalene (TTN), tetrachlorotetrathionaphthalene (TCTTN) and tetrathiotetracene (TTT) to a variety of low-valent metal substrates, for which a number of diverse structural motifs were reported.[1–8] The only other reported example of complexes containing this type of ligand system is an unusual trinuclear nickel(II) complex $[Ni_3(PPh_3)_3(S_2C_{10}Cl_6)_3]$ (**A**), which was also obtained by oxidative addition by reaction of hexachlorodithionaphthalene (hcdtn) with $[Ni(cod)_2]$ in the presence of triphenylphosphine (PPh_3).[9] The trimeric nature of the nickel species is in contrast to the mononuclear square-planar compounds $[M(PPh_3)_2(hcdtn)]$ (M = Pd or Pt) obtained by reaction of $[Pd(PPh_3)_3]$ or $[Pt(PPh_3)_4]$ with the same ligand.[9] More recently oligomeric, dimeric and monomeric zinc complexes, with no co-ligands, with pyridine or with neocuproin, respectively, of sterically crowded and electron-poor naphthalene-1,8-dithiolate derivatives were reported.[10] Complexes in which the chalcogen–chalcogen bond remains unbroken have also been described, examples of which are a series of Group 6 pentacarbonyl systems bearing monodentate naphtho[1,8-*cd*][1,2]dichalcogenole ligands (M = Cr or Mo, E and E′ = S or Se) (**B**)[11] and a binuclear Re^I carbonyl complex with bridging bromides and a naphtho[1,8-*cd*][1,2]dithiole ligand (**C**).[12] Although the literature pertaining to complexes of naphtho[1,8-*cd*][1,2]dichalcogenoles or naphthalene-1,8-dichalcogenates and related compounds is sparse, there are no examples of naphthalene-1,8 mixed thiolato–sulfenato (-S–M–S(=O)-), thiolato–sulfinato (-S–M–S(=O)$_2$-), sulfenato–sulfinato (-(O=)S–M–S(=O)$_2$-) and disulfinato



TTN



TCTTN



TTT

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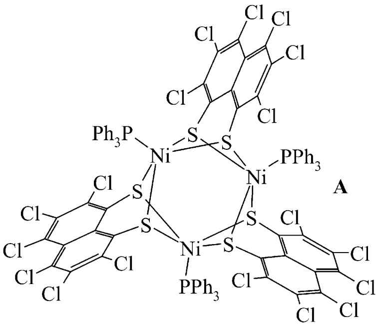

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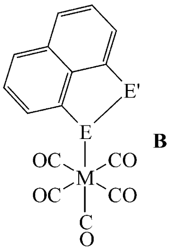

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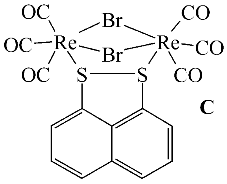
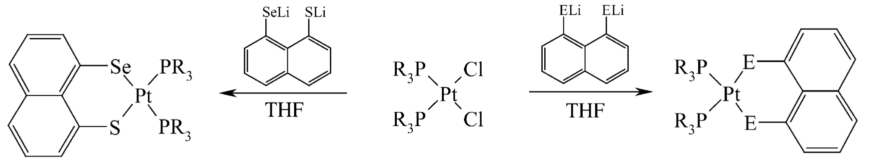


C

(-(O=)$_2$S–M–S(=O)$_2$-) metal complexes. In more general terms transition-metal complexes of sulfenato (-S(=O)R) or sulfinato (-S(=O)$_2$R) ligands are uncommon,[13] when compared to the vast number of known thiolate complexes. Of those that are known only the mixed thiolato–sulfenato complexes have been obtained by oxidative addition reactions and examples of this seem to be limited to reactions of cyclic thiosulfinates with Pt^0 precursors[14–20] and dithiirane 1-oxides.[21] Thiolato–sulfenato (-S–M–S(=O)-) complexes have also been prepared through the mono-oxidation of dithiolate complexes of which the diiron compounds [{(OC)$_3$Fe}$_2$SCH$_2$CH$_2$S(=O)] and [{(OC)$_3$Fe}$_2$SC$_6$H$_{10}$S(=O)] containing bridging 1,2-ethanesulfenatothiolato and 1,2-cyclohexylsulfenatothiolato ligands are illustrative examples.[22,23] This preparative method has also been utilised by Darensbourg and co-workers in the preparation a series of thiolato–sulfenato, disulfenato, thiolato–sulfinato, sulfenato–sulfinato and disulfinato complexes of nickel(II) and palladium(II) from bis(2-mercaptoethyl)-1,5-diazacyclooctane-M^{II} (M = Ni, Pd) and *N,N'*-bis(2-methyl-2-mercaptopropyl)-1,5-diazacyclooctane-Ni^{II}.[24–28] Some further examples of thiolato–sulfenato, thiolato–sulfinato and disulfinato complexes formed by oxidation of thiolate complexes are known.[29–34] This paper describes the preparation of platinum bisphosphine complexes of naphtha-1,8-dichalcogenates and related ligand systems by both oxidative and metathetical methods and the oxidative addition reactions of the oxides of naphtho[1,8-*cd*][1,2]dithioles. Furthermore platinum complexes bearing the naphthalene-1,8-disulfinate ligand have been prepared. All complexes from these reactions have been fully characterised, principally by multi element NMR spectroscopy and in selected cases by single-crystal X-ray diffraction studies.



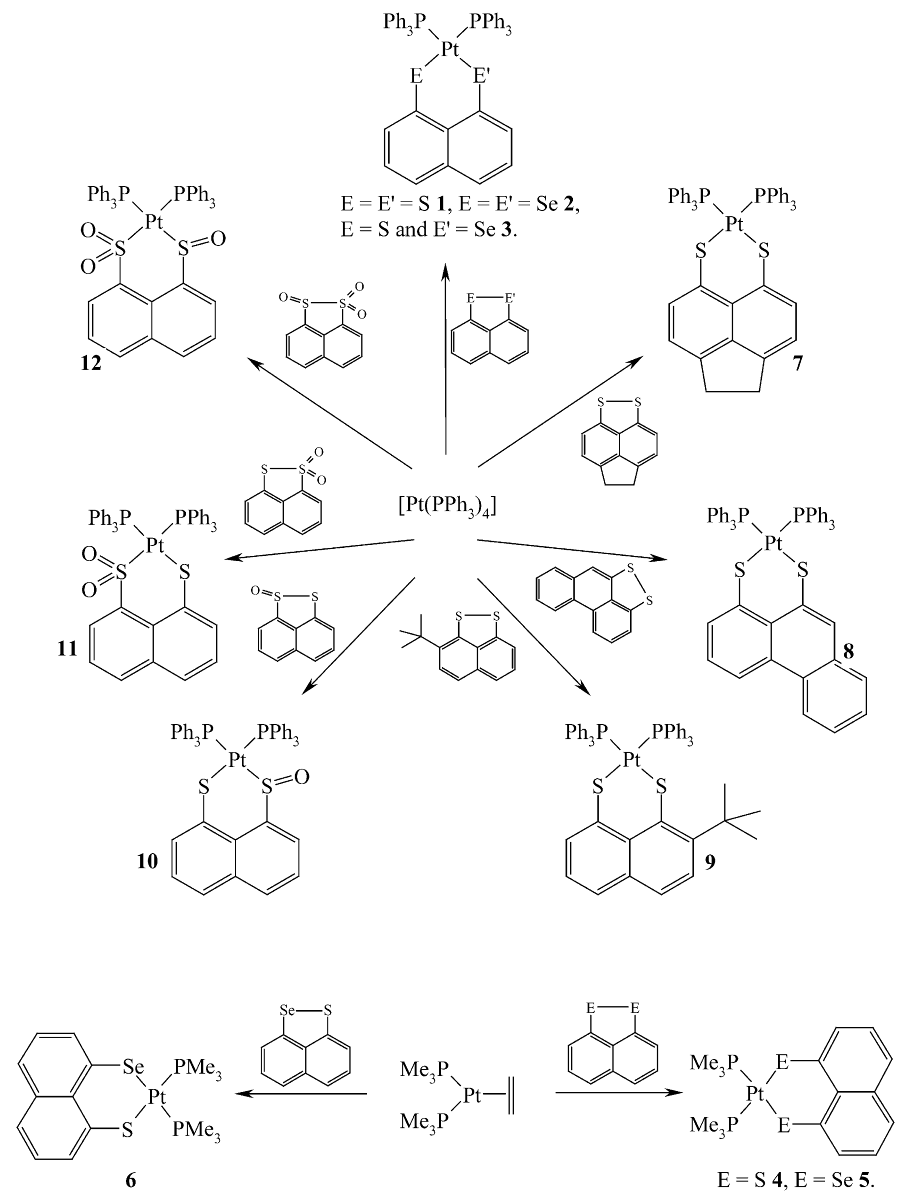
R = Ph **3**,
R = Me **6**.

R = Ph, E = S **1**, E = Se **2**,
R = Me, E = S **4**, E = Se **5**.

(1)

Results and Discussion

Platinum complexes of naphthalene-1,8-dichalcogenole ligands: Oxidative addition reactions (method A) of naphtho[1,8-*cd*][1,2]dithiole, its selenium analogue naphtho[1,8-*cd*][1,2]diselenole and the mixed chalcogen derivative naphtho[1,8-*cd*][1,2]selenathiole with [Pt(PPh$_3$)$_4$] all proceed smoothly in toluene at room temperature (Scheme 1) to give [Pt(1,8-S$_2$-nap)(PPh$_3$)$_2$] (**1**), [Pt(1,8-Se$_2$-nap)(PPh$_3$)$_2$] (**2**) and [Pt(1-S,8-Se-nap)(PPh$_3$)$_2$] (**3**), respectively, in good to excellent yields (84–95 %). The purification and isolation of these compounds was straight forward; it was achieved by filtration through a shallow pad of silica and elution with dichloromethane followed by evaporation of the filtrate and precipitation of the product with diethyl ether and hexane. An alternative synthetic approach (method B), which furnished compounds **1**–**3** in slightly lower yields (73–85 %), involved the in situ generation of dilitho-1,8-dichalcogenato naphthalenes, by reduction of the parent dichalcogen compound with two equivalents of lithium triethylborohydride (LiBEt$_3$H) followed by reaction with *cis*-[PtCl$_2$(PPh$_3$)$_2$] [Eq. (1)]. The ^{31}P{^{1}H} NMR spectra (CD$_2$Cl$_2$) of complexes **1** and **2** display the anticipated single resonances with platinum satellites at δ(P) = 23.4 ppm (^1J(^{31}P,^{195}Pt) = 2966 Hz) and δ(P) = 20.5 ppm (^1J(^{31}P,^{195}Pt) = 3016 Hz), respectively, with additional ^{77}Se satellites (^2J(^{31}P,^{77}Se) = 51 Hz) observed in the spectra of complex **2**. The ^{31}P{^{1}H} NMR spectra (CD$_2$Cl$_2$) of **3** is of the AX type with both platinum and selenium satellites. Although it is impossible to assign the two distinct phosphorus doublets as being *trans* to either sulfur or selenium with absolute certainty, the similarity of the two shifts when compared to those of complexes **1** and **2** led us to designate the phosphorus signal at δ(P) = 20.1 ppm (^1J(^{31}P$_{(A)}$,^{195}Pt) = 2984 Hz, ^2J(^{31}P$_{(A)}$,^{77}Se) = 58 Hz) as being *trans* to the selenium and that at δ(P) = 22.6 ppm (^1J(^{31}P$_{(X)}$,^{195}Pt) = 2989 Hz, ^2J(^{31}P$_{(X)}$,^{77}Se) = 47 Hz) *trans* to the sulfur of the (1S,8Se-nap) ligand. An additional ^2J(^{31}P$_{(A)}$,^{31}P$_{(X)}$) coupling constant of 25 Hz is typical for platinum complexes bearing two inequivalent phosphine ligands in a *cis* configuration. The ^{195}Pt NMR spectra (CD$_2$Cl$_2$) show triplets at δ(Pt) = −4799 ppm and δ(Pt) = −4912 ppm for **1** and **2**, respectively, while that of **3** is a double doublet at δ(Pt) −4820 ppm. The spectrum of **2** also containes seleni-



Scheme 1. Oxidative addition reactions of dichalcogen ligands to platinum species.

um satellites with ${}^{1}J({}^{195}\mathrm{Pt},{}^{77}\mathrm{Se}) = 165$ Hz, which is within the range of previously reported examples of ${}^{1}J({}^{195}\mathrm{Pt},{}^{77}\mathrm{Se})$ couplings of 61–298 Hz.[35–39] The ^{77}Se NMR spectra (CD_2Cl_2) for complexes **2** and **3** are complex and appear as an approximate 'septet' centred at $\delta(\mathrm{Se}) = 189$ ppm and a second-order double doublet at $\delta(\mathrm{Se}) = 278$ ppm, respectiely. The δ(Se) NMR (57.2 MHz) resonances for the two selenium starting materials for complex **2** (naphtho[1,8-*cd*][1,2]diselenole) $\delta(\mathrm{Se}) = 402$ ppm and **3** (naphtho[1,8-*cd*][1,2]selenathiole) $\delta(\mathrm{Se}) = 542$ ppm appear as well-resolved singlets.

The trimethylphosphine derivatives **4–6** were also prepared by two methods, oxidative addition (method A) and metathesis (method B). Method A entails the in situ preparation of the zero-valent platinum–ethene species $[\mathrm{Pt(C_2H_4)(PMe_3)_2}]$ by reduction of the dichloride *cis*-$[\mathrm{PtCl_2(PMe_3)_2}]$ with either two equivalents of sodium naphthalide or lithium triethylborohydride in THF under an ethene atmosphere followed by addition of the appropriate 1,8-dichalcogenole naphthalene (Scheme 1) to give **4–6** in yields of 75–89 %. Method B is the metathetical route, whereby *cis*-$[\mathrm{PtCl_2(PMe_3)_2}]$ is treated with preformed dilitho-1,8-dichalcogenato naphthalenes in an identical manner to the method described above for the synthesis of the triphenylphosphine derivatives, again giving the products in lower yields than those of method A (70–75 %). The trimethylphosphine analogues are unstable in chlorinated solvents; especially in chloroform in which almost complete decomposition occurs overnight (observed by ${}^{31}\mathrm{P}\{{}^{1}\mathrm{H}\}$ NMR spectroscopy), solutions in dichloromethane decompose in around four days to give new products, which we did not try to isolate and identify. We found that the addition of small quantities of triethylamine (Et_3N acts as an acid scavenger) to workup and NMR solvents prevented decomposition leading us to surmise that free HCl in the solvent was responsible for the breakdown process. The majority of the ${}^{31}\mathrm{P}\{{}^{1}\mathrm{H}\}$, ^{195}Pt and ^{77}Se NMR data (CD_2Cl_2/Et_3N) for complexes **4–6** is as anticipated and is comparable to those obtained for complexes **1–3** (Table 1). In addition to the ${}^{2}J({}^{31}\mathrm{P},{}^{77}\mathrm{Se})$ coupling constant observed in the diselenato complex **2**, the ${}^{31}\mathrm{P}\{{}^{1}\mathrm{H}\}$ NMR spectra (CD_2Cl_2/Et_3N) for the trimethylphosphine analogue $[\mathrm{Pt(1,8\text{-}Se_2\text{-}nap)(PMe_3)_2}]$ (**4**) displays two sets of ^{77}Se satellites with ${}^{2}J({}^{31}\mathrm{P},{}^{77}\mathrm{Se})$ values of 47 and 53 Hz, which we believe correspond to *cis* and *trans* couplings.

Platinum complexes of related dithiole ligands: The acenaphthylene-, phenanthrene- and *tert*-butyl-substituted naphthalene dithiolate complexes $[\mathrm{Pt(1,2\text{-}S_2\text{-}acenap)(PPh_3)_2}]$ (**7**), $[\mathrm{Pt(4,5\text{-}S_2\text{-}phenan)(PPh_3)_2}]$ (**8**) and $[\mathrm{Pt(1,8\text{-}S_2\text{-}2\text{-}}t\mathrm{Bu\text{-}nap)(PPh_3)_2}]$ (**9**) were prepared by oxidative addition of the relevant parent disulfide compound to $[\mathrm{Pt(PPh_3)_4}]$ in toluene at room temperature (Scheme 1). All were isolated in good to excellent yields (76–94 %) as yellow/orange powders or crystalline solids. The complexes are all very soluble in chlorinated solvents especially complex **8**, which is also soluble in benzene and toluene. The ${}^{31}\mathrm{P}\{{}^{1}\mathrm{H}\}$ NMR (CD_2Cl_2)

Table 1. $^{31}P\{^1H\}$, ^{195}Pt and ^{77}Se NMR data for complexes **1**–**14**.

	Chemical shifts [ppm]				Coupling constants [Hz]		
Complex	$\delta(^{31}P_A)$	$\delta(^{31}P_X)$	$\delta(^{195}Pt)$	$\delta(^{77}Se)$	$^1J(P_A,Pt)$	$^1J(P_X,Pt)$	$^2J(P_A,P_X)$
1[a,b]	23.4	–	−4799	–	2966	–	–
2[a–e]	20.5	–	−4912 [165]	189	3016 (51)	–	–
3[a–c,e]	20.1	22.6	−4820	278	2984 (58)	2989 (47)	25
4[f,g]	−23.1	–	−4663	–	2801	–	–
5[c,d,f–h]	−28.7	–	−4767 [215]	133	2840 (47, 53)	–	–
6[c,f–h]	−27.3	−23.6	−4716	354	2805 (44)	2834 (63)	27
7[a,b]	23.3	–	−4836	–	2981	–	–
8[a,b]	21.9	24.6	−4736	–	2944	2984	26
9[a,b]	19.5	25.5	−4664	-	2923	3017	27
10[a,b]	20.8	26.4	−4530	-	2451	3587	19
11[a,b]	18.4	22.4	−4529	–	2451	3197	23
12[a,b]	20.0	22.1	−4097	–	3094	2554	16
13[f,g]	−10.6	–	−4352	–	2599	–	–
14[f,g]	14.2	–	−4250	–	2672	–	–

[a] ^{31}P NMR spectra (109.4 MHz) measured in CD_2Cl_2. [b] ^{195}Pt NMR spectra (58.1 MHz) measured in CD_2Cl_2. [c] Values in parentheses denote $^2J(^{31}P,^{77}Se)\,Hz^{-1}$. [d] Values in square brackets denote $^1J(^{195}Pt,^{77}Se)\,Hz^{-1}$. [e] ^{77}Se NMR spectra (57.2 MHz) measured in $CDCl_3$. [f] ^{31}P NMR Spectra (109.4 MHz) measured in CD_2Cl_2/Et_3N. [g] ^{195}Pt NMR Spectra (58.1 MHz) measured in CD_2Cl_2/Et_3N. [h] ^{77}Se NMR spectra (51.5 MHz) measured in CD_2Cl_2/Et_3N.

data for complexes **7**–**9** are consistent with the proposed structures; that of **7** consisting of a singlet with platinum satellites at $\delta(P) = 23.0$ ppm $^1J(^{31}P,^{195}Pt)$ 2981 Hz, while the unsymmetrically substituted complexes **8** and **9** display AX-type spectra with resonances in the range of $\delta(P) = 19.5$ and 25.5 ppm, and $^1J(^{31}P,^{195}Pt)$ and $^2J(^{31}P_{(A)},^{31}P_{(X)})$ coupling constants with typical values of around 3000 and 26/27 Hz, respectively. ^{195}Pt NMR (CD_2Cl_2) $\delta(Pt)$ values are in accordance with those of complexes **1**–**6** and characteristically lie within the −4900 to −4700 Hz range and appear as a well-resolved triplet for **7** and as a doublet of doublets for **8** and **9**.

Platinum complexes of naphthalene-1,8-dithiolate oxide ligands: Complexes **10**, **11** and **12** were also prepared by oxidative addition of the S−S-bridged mono-, di- and trioxides of naphtho[1,8-*cd*][1,2]dithiole to $[Pt(PPh_3)_4]$ in toluene at room temperature. The yellow/orange microcrystalline solids were obtained in almost quantitative yields (91–96 %). The $^{31}P\{^1H\}$ NMR (CD_2Cl_2) data (Table 1) for all three complexes are similar in that the spectra are all of the AX type with corresponding platinum satellites. The phosphorus resonances and $^1J(^{31}P,^{195}Pt)$ coupling constants of complex **10**, $\delta(P_A) = 20.8$ ppm (2451 Hz) and $\delta(P_X) = 26.4$ ppm (3587 Hz), have been assigned to the phosphine groups *trans* to the sulfenato (-S(O)R) and the thiolato (-SR) groups, respectively. In previously characterised examples of $[(PPh_3)_2Pt]$ complexes bearing thiolato/sulfenato ligand systems, phosphine groups *trans* to the sulfenato moiety have much smaller $^1J(^{31}P,^{195}Pt)$ coupling constants due to the larger *trans* influence of the (-S(O)R) ligand.[13–21] Assuming that (-S(O)_2R) ligands have a higher *trans* influence than (-SR) (see crystallographic discussion below) the phosphine ligands of complex **11** can been assigned thus, P *trans* to (-S(O)_2R) $\delta(P_A) = 18.4$ ppm, $^1J(^{31}P_{(A)},^{195}Pt) = 2451$ Hz and P *trans* to (-SR) $\delta(P_X) = 22.4$ ppm, $^1J(^{31}P_{(X)},^{195}Pt) = 3197$ Hz. The assignment of the $^{31}P\{^1H\}$ NMR spectra of **12** is more complicated, but we believe that the signal at $\delta(P_A) = 20.0$ ppm ($^1J(^{31}P_{(A)},^{195}Pt) = 3094$ Hz) corresponds to the Ph_3P group *trans* to the (-S(O)_2R) and that at $\delta(P_X) = 22.1$ ppm ($^1J(^{31}P_{(X)},^{195}Pt) = 2554$ Hz) is the Ph_3P ligand *trans* to the (-S(O)R) function. This assignment was based upon a quantitative comparison of the $^1J(^{31}P,^{195}Pt)$ coupling constants of complexes **1**, **10**, **11**, **12** and **14** (Figure 1). The $^1J(^{31}P,^{195}Pt)$ of the dithiolate complex **1** is 2966 Hz, while that of the PPh_3 ligand *trans* to the thiolate group of **10** is 3587 Hz, 600 Hz larger than in **1**, an increase we believe that is due to an effect of the *cis* ligand (-S(O)R) in **10**. In complex **11** the coupling constants are 2451 Hz for $P_{(A)}$, PPh_3 *trans* to (-SO)_2R) and 3197 Hz for $P_{(X)}$, PPh_3 *trans* to (-SR). Once more there is an increase, although smaller than in **10**, in the coupling constant magnitude for the PPh_3 *trans* to the (-SR) ligand; this is again a consequence of the "*cis* effect" of a ligand with a higher *trans* influence. If this argument is

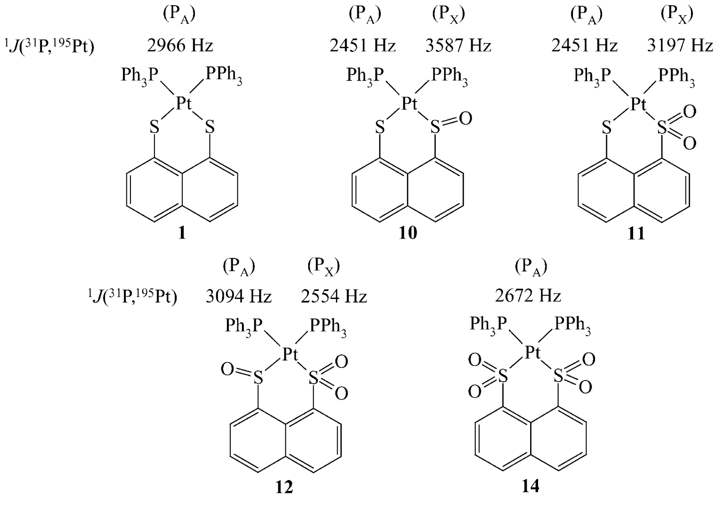
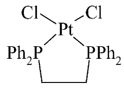


Figure 1. Comparison of $^1J(^{31}P,^{195}Pt)$ coupling constants for complexes **1**, **10**, **11**, **12** and **14**.

applied to **12** then the ligand *trans* to (-S(O)$_2$R) should have a coupling constant that is substantially higher than that observed in **11**, which is what we find in **12**, 3094 versus 2451 Hz, an increase of over 640 Hz. There is also an increase in the *trans* to (-S(O)R) $^1J(^{31}P_{(X)},^{195}Pt)$ coupling of **12** (2554 Hz) relative to that of **10** (2451 Hz) and which we also observe in **11**. Further evidence for the proposed “*cis* effect” of highly *trans*-influencing ligands can be seen by comparison of the $^{31}P\{^1H)$ NMR data (CD$_2$Cl$_2$) for a series of Pt^{II} complexes bearing DPPE (1,2-bis(diphenylphosphino)ethane), Me and Cl ligands. The $^1J(^{31}P,^{195}Pt)$ coupling constant of the chloride complex **D** is 3620 Hz,[40] while that of **F** with Me ligands (the *trans* effect of Me is much greater than that of Cl ligands) has a coupling of 1797 Hz.[41] The couplings in **E** are 1738 Hz for the phosphorus *trans* to the Me ligand and 4211 Hz for phosphorus *trans* to Cl, an increase of nearly 600 Hz relative to that of dichloride **D**.[41] The $^{31}P\{^1H\}$ NMR spectra of **10**, **11** and **12** also show the characteristic $^2J(^{31}P_{(A)},^{31}P_{(X)})$ couplings of 19, 23 and 16 Hz, respectively, which are consistant with unsymmetrically substituted *cis*-platinum diphosphine complexes. The ^{195}Pt NMR data (CD$_2$Cl$_2$) is also consistent with the proposed structures, each spectra being displayed as a doublet of doublets in the expected range −4529 to −4097 ppm. The tetraoxide derivatives **13** and **14** were prepared from the appropriate *cis*-[PtCl$_2$(PR$_3$)$_2$] complex and the Na$_2$ salt of naphthalene-1,8-disulfinic acid [Eq. (2)] as attempted oxidative addition reactions of naphtho[1,8-*cd*][1,2]dithiole 1,1,2,2-tetraoxide[42] failed. Compound **13** was isolated as yellow crystals, which were found by microanalysis and X-ray crystallography to contain a half molecule of dichloromethane per molecule of product. The triphenylphosphine analogue **14** was isolated as a yellow solvent-free powder. In common with complexes **4**, **5** and **6**, the tetraoxide derivatives were prone to degradation in chlorinated solvents—the decomposition products in both cases were identified as *cis*-[PtCl$_2$(PR$_3$)$_2$] (PR$_3$ = PMe$_2$Ph **13**, PPh$_3$ **14**) confirmed by comparison of the $^{31}P\{^1H\}$ $\delta(P)$ and $^1J(^{31}P,^{195}Pt)$ values to those of authentic samples. The addition of triethylamine to chlorinated solvents used in their preparation prevented decomposition. The $^{31}P\{^1H\}$ NMR spectra (CD$_2$Cl$_2$/Et$_3$N) of **13** and **14** are both single resonances with platinum satellites at $\delta(P) = -10.6$, ($^1J(^{31}P,^{195}Pt) = 2599$ Hz) and 14.2 ppm, ($^1J(^{31}P,^{195}Pt) = 2672$ Hz), respectively, and the ^{195}Pt NMR spectra (CD$_2$Cl$_2$/Et$_3$N) contain triplets centred at $\delta(Pt) = -4352$ and −4250 ppm for **13** and **14**, respectively. IR (KBr disc) data for complexes **10**–**14** were consistent with the structural assignments showing $\nu(S{=}O)$ bands for complexes **10** and **12** at about 1100 cm^{-1} and $\nu(S({=}O)_2)$ bands for **11**, **12**, **13** and **14** at approximately 1200 and 1060 cm^{-1}. Satisfactory microanalyses were obtained for all of the new complexes (Table 2) and FAB$^+$ MS data in all cases showed *m/z* corresponding to [M]$^+$ or [M+H]$^+$ and mass peak profiles matching [Pt(PR$_3$)$_2$]$^{2+}$ (PR$_3$ = PPh$_3$, PMe$_3$ or PMe$_2$Ph).



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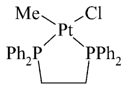

E

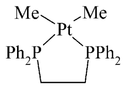

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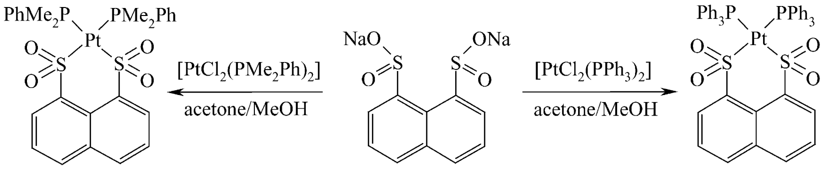
Table 2. Microanalytical data for complexes **1** to **14** (calculated values in parentheses).

	Compound	C	H	S
1	[Pt(1,8-S$_2$-nap)(PPh$_3$)$_2$]	60.45 (60.72)	4.00 (3.99)	6.88 (7.05)
2	[Pt(1,8-Se$_2$-nap)(PPh$_3$)$_2$]	54.89 (55.04)	3.66 (3.62)	–
3	[Pt(1-S,8-Se-nap)(PPh$_3$)$_2$]	57.63 (57.74)	3.82 (3.79)	3.19 (3.35)
4	[Pt(1,8-S$_2$-nap)(PMe$_3$)$_2$]	35.61 (35.75)	4.46 (4.50)	11.91 (11.93)
5	[Pt(1,8-Se$_2$-nap)(PMe$_3$)$_2$]	30.51 (30.44)	3.89 (3.83)	–
6	[Pt(1-S,8-Se-nap)(PMe$_3$)$_2$]	32.64 (32.88)	4.04 (4.14)	5.45 (5.49)
7	[Pt(1,2-S$_2$-acenap)(PPh$_3$)$_2$]	61.64 (61.60)	4.05 (4.09)	6.65 (6.85)
8	[Pt(4,5-S$_2$-phenan)(PPh$_3$)$_2$]	62.24 (62.56)	4.11 (3.99)	6.53 (6.68)
9	[Pt(1,8-S$_2$–2-*t*Bu-nap)(PPh$_3$)$_2$]	62.61 (62.16)	4.50 (4.59)	6.23 (6.64)
10	[Pt(1-S,8-{S(O)}-nap)(PPh$_3$)$_2$]	59.45 (59.67)	3.84 (3.92)	6.72 (6.93)
11	[Pt(1-S,8-{S(O)$_2$}-nap)(PPh$_3$)$_2$]	58.44 (58.66)	3.80 (3.85)	6.42 (6.81)
12	[Pt(1-{S(O)},8-{S(O)$_2$}-nap)(PPh$_3$)$_2$]	57.61 (57.68)	3.57 (3.79)	6.43 (6.70)
13	[Pt(1,8-{S(O)$_2$}$_2$-nap)(PMe$_2$Ph)$_2$]·0.5CH$_2$Cl$_2$	41.79 (41.46)	3.71 (3.81)	8.46 (8.34)
14	[Pt(1,8-{S(O)$_2$}$_2$-nap)(PPh$_3$)$_2$]	56.42 (56.73)	3.43 (3.73)	6.60 (6.59)



13 **14** (2)

X-ray crystallography: The crystal structures of complexes **2**, **4**, **10**, **11**, **12** and **13** are shown in Figures 2 and 3 and selected bond lengths and angles are given (Table 3). The X-ray analyses show that in every example the platinum core lies at the centre of a distorted square-planar coordination sphere, consisting of two phosphorus and two sulfur or selenium atoms. The P(1)-Pt(1)-P(2) angles are typically 97–98°, showing considerable deviation from idealized 90° square-planar geometry and are directly comparable to those of the related compound [(PPh$_3$)$_2$Pt(ttn)Pt(PPh$_3$)$_2$] (ttn = tetrathiolatonaphthalene) at 98.5°.[3] The P(1)-Pt(1)-P(2) angle of complex **12** lies outside the typical range and has a significantly larger P(1)-Pt(1)-P(2) angle of 103.6°. The corresponding E(1)-Pt(1)-E(9) angles are typically 86–87° and are similar to those of [(PPh$_3$)$_2$Pt(ttn)Pt(PPh$_3$)$_2$] 88.2°.[3] Again the E(1)-Pt(1)-E(9) angle of **12** (81.7°) falls outside the typical range, as does that of **10** with the smallest E(1)-

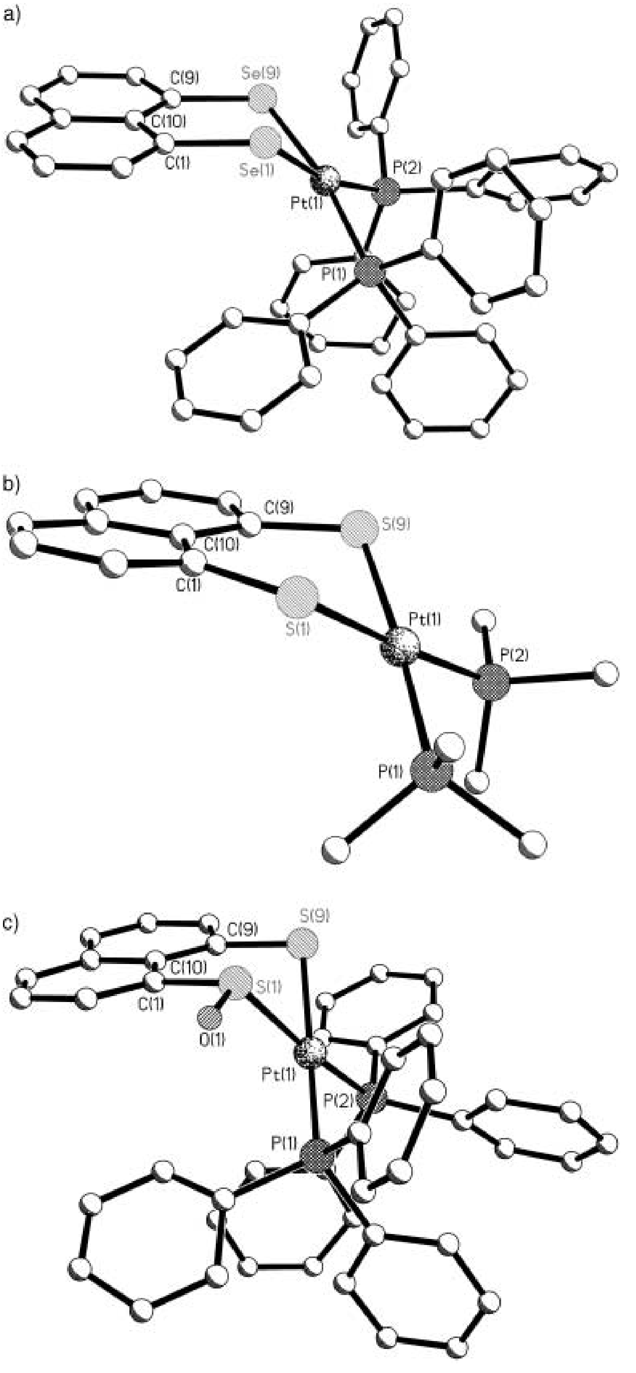


Figure 2. a) Crystal structure of [Pt(1,8-Se_2-nap)$(PPh_3)_2$]·0.25 CH_2Cl_2 (**2**). The solvent molecule has been omitted and only a single molecule from the asymmetric unit is shown for the sake of clarity. b) Crystal structure of [Pt(1,8-S_2-nap)$(PMe_3)_2$] (**4**). c) Crystal structure of [Pt(1-S,8-{S(O)}-nap)$(PPh_3)_2$] (**10**).

Pt(1)-E(9) angle of 77.9°. The *cis* P(1)-Pt(1)-E(1), P(2)-Pt(1)-E(9) 85.88(4)–92.99(6)° and *trans* P(1)-Pt(1)-E(9), P(2)-Pt(1)-E(1) 152.29(6)–176.83(4)° angles lie within the expected ranges and are unremarkable; however, they serve to highlight the distorted square-planar coordination environments within **2**, **4**, **10**, **11**, **12** and **13**. The P(1)-P(2)-Pt(1)-E(1)-E(9) and E(1)-E(9)-naphthalene mean planes deviate from planarity to a greater or lesser degree; in all cases the maximum deviations from these planes are occupied by a chalcogen atom, the largest distortion observed in the P(1)-P(2)-Pt(1)-E(1)-E(9) plane is by the S(9) atom of **12** at 0.49 Å and in the E(1)-E(9)-naphthalene plane by $E(9)_{(molecule\ 2)}$ atoms of **2** and **11** at 0.42 and 0.43 Å, respectively. The asymmetric unit of the diselenato complex **2** is composed of two independent molecules with similar geometries. The Pt(1)−P(1) (2.289(2), 2.292(2) Å) and Pt(1)−P(2) (2.283(2),

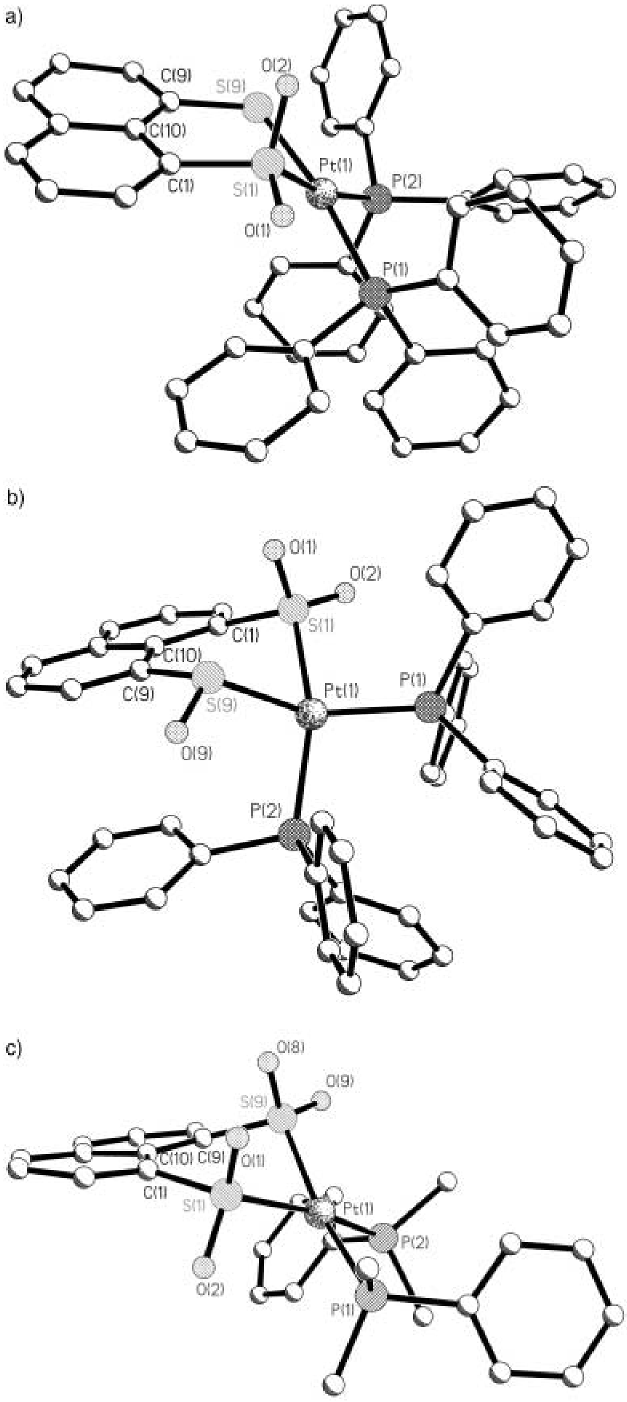


Figure 3. a) Crystal structure of [Pt(1-S,8-{$S(O)_2$}-nap)$(PPh_3)_2$] (**11**). The solvent molecule has been omitted and only a single molecule from the asymmetric unit is shown for the sake of clarity. b) Crystal structure of [Pt(1-{S(O)},8-{$S(O)_2$}-nap)$(PPh_3)_2$] (**12**). c) Crystal structure of [Pt(1,8-{$S(O)_2$}$_2$-nap)$(PMe_2Ph)_2$]·0.5 CH_2Cl_2 (**13**). The solvent molecule has been omitted for the sake of clarity.

Table 3. Bond lengths [Å] and angles [°] for complexes **2**, **4**, **10**, **11**, **12** and **13**, where E = Se for **2** and E = S for **4**, **10**, **11**, **12** and **13**.

	$\mathbf{2}_{\text{(molecule 1)}}$	$\mathbf{2}_{\text{(molecule 2)}}$	**4**	**10**	$\mathbf{11}_{\text{(molecule 1)}}$	$\mathbf{11}_{\text{(molecule 2)}}$	**12**	**13**
Pt(1)−E(1)	2.447(1)	2.4301(7)	2.320(1)	2.344(2)	2.310(5)	2.291(5)	2.306(2)	2.313(1)
Pt(1)−E(9)	2.436(1)	2.4595(7)	2.326(1)	2.338(2)	2.308(5)	2.332(5)	2.327(2)	2.288(1)
Pt(1)−P(1)	2.289(2)	2.292(2)	2.284(1)	2.308(2)	2.308(5)	2.295(5)	2.331(2)	2.336(1)
Pt(1)−P(2)	2.283(2)	2.287(2)	2.273(1)	2.316(2)	2.321(5)	2.337(5)	2.323(2)	2.327(1)
E(1)−C(1)	1.938(7)	1.940(6)	1.754(4)	1.829(8)	1.789(19)	1.806(18)	1.792(8)	1.835(4)
E(9)−C(9)	1.912(7)	1.915(7)	1.760(4)	1.767(10)	1.78(2)	1.791(17)	1.813(7)	1.770(5)
E(1)−E(1)	3.37(1)	3.36(1)	3.22(1)	2.94(1)	3.19(1)	3.17(1)	3.03(1)	3.14(1)
S(1)−O(1)	–	–	–	1.450(6)	1.436(14)	1.458(14)	1.452(5)	1.454(3)
S(1)−O(2)	–	–	–	–	1.455(13)	1.495(14)	1.466(5)	1.478(3)
S(9)−O(8)	–	–	–	–	–	–	–	1.469(3)
S(9)−O(9)	–	–	–	–	–	–	1.501(5)	1.437(3)
E(1)-Pt(1)-E(9)	87.36(2)	86.65(2)	87.62(4)	77.87(8)	87.25(18)	86.54(18)	81.69(6)	85.91(4)
P(1)-Pt(1)-P(2)	98.40(6)	98.84(6)	96.55(4)	97.86(6)	96.50(18)	96.53(18)	103.64(6)	98.12(4)
P(1)-Pt(1)-E(1)	87.50(5)	90.04(4)	85.88(4)	93.36(7)	90.45(18)	89.09(18)	90.01(6)	88.79(3)
P(2)-Pt(1)-E(9)	88.34(5)	85.11(5)	89.97(4)	91.14(7)	86.98(18)	88.58(17)	92.99(6)	90.36(4)
P(1)-Pt(1)-E(9)	169.80(5)	174.16(4)	173.45(4)	169.86(7)	171.95(18)	170.59(18)	152.29(6)	164.71(4)
P(2)-Pt(1)-E(1)	167.74(5)	168.47(5)	176.83(4)	168.56(7)	168.97(18)	172.61(19)	158.17(7)	165.56(3)
Pt(1)-E(1)-C(1)	109.2(2)	111.30(19)	113.24(14)	97.2(3)	110.3(6)	106.0(6)	103.0(2)	110.92(12)
E(1)-C(1)-C(10)	126.4(5)	129.0(5)	128.4(3)	126.3(7)	124.8(15)	122.3(14)	122.1(5)	127.9(3)
C(1)-C(10)-C(9)	126.4(6)	126.1(6)	125.8(3)	125.0(8)	126.9(16)	124.5(16)	127.0(6)	126.4(4)
C(10)-C(9)-E(9)	131.0(5)	124.9(5)	127.1(3)	122.5(7)	127.4(15)	131.8(15)	125.0(5)	120.1(3)
C(9)-E(9)-Pt(1)	110.81(19)	103.38(19)	110.28(14)	103.1(3)	114.7(7)	111.0(7)	106.3(2)	106.77(14)
Pt(1)-S(1)-O(1)	–	–	–	117.9(3)	115.1(6)	114.9(5)	113.3(2)	115.28(11)
Pt(1)-S(1)-O(2)	–	–	–	–	104.6(6)	109.6(6)	114.7(2)	107.84(10)
C(1)-S(1)-O(1)	–	–	–	106.0(4)	104.9(9)	105.8(9)	103.9(3)	107.02(15)
C(1)-S(1)-O(2)	–	–	–	–	104.7(9)	104.3(8)	106.0(3)	101.22(16)
O(1)-S(1)-O(2)	–	–	–	–	116.9(8)	115.1(8)	114.3(3)	113.66(15)
Pt(1)-S(9)-O(8)	–	–	–	–	–	–	–	108.64(13)
Pt(1)-S(9)-O(9)	-	-	-	-	-	-	115.64(19)	114.75(16)
C(9)-S(9)-O(8)	–	–	–	–	–	–	–	103.56(19)
C(9)-S(9)-O(9)	–	–	–	–	–	–	105.8(3)	107.4(2)
O(8)-S(9)-O(9)	–	–	–	–	–	–	–	114.78(19)
E(1)-C(1) ··· C(9)-E(9)	9	25	9	3	14	24	9	24
dihedral angles								
$(PtE_2)\cdots(E_2Nap)$	135	130	136	111	137	131	119	129
torsion angles of naphthalene ring								
C(4)-C(5)-C(10)-C(9)	178.9(6)	177.7(6)	174.7(4)	177.2(9)	178.8(17)	170.3(18)	175.5(7)	171.6(4)
C(6)-C(5)-C(10)-C(1)	177.6(6)	173.9(7)	179.1(4)	176.4(9)	179.0(18)	177.4(17)	179.3(6)	173.7(4)
C(4)-C(5)-C(10)-C(1)	1.7(9)	3.4(9)	3.5(6)	0.9(13)	1.0(3)	4.0(3)	2.3(10)	7.5(6)
C(6)-C(5)-C(10)-C(9)	1.7(9)	5.0(1)	2.7(6)	5.6(13)	3.0(3)	8.0(3)	2.9(10)	7.2(6)

2.287(2) Å) bond lengths of **2** closely resemble those of the related species *cis*-$[Pt(SePh)_2(PPh_3)_2]$ (2.290(6), 2.294(6) Å),[43] *cis*-$[Pt(Se_2CH_2)(PPh_3)_2]$ (2.274(2), 2.290(2) Å)[44] and the diselenooxalate complex *cis*-$[Pt(Se_2C_2O_2)(PPh_3)_2]$ (2.288(1), 2.303(1) Å).[45] The Pt(1)−Se(1) (2.447(1), 2.43(1) Å), and Pt(1)-Se(9) (2.436(1), 2.460(1) Å) distances of **2** can also be compared with the corresponding bonds in *cis*-$[Pt(SePh)_2(PPh_3)_2]$ (2.489(1), 2.451(1) Å)[43] and *cis*-$[Pt(Se_2C_2O_2)(PPh_3)_2]$ (2.446(1), 2.461(1) Å),[45] but are longer than those found in $[Pt(Se_2CH_2)(PPh_3)_2]$ (2.418(1), 2.435(1) Å);[44] this may be due to the fact that the latter complex bears an aliphatic rather than aromatic diselenolato ligand. The average distance between the two selenium atoms of **2** is 3.365(1) Å, which is 88 % of the van der Waals radii of selenium and implies that there is a significant interation between the two Se atoms. The nonbonded Se···Se moiety in **2** is over 1 Å larger then bonded Se−Se distance of naphtho[1,8-*cd*][1,2]diselenole[46] (2.357(1) Å) and is significantly larger than the nonbonded S···S distances of 3.22(1) (**4**), 2.94(1) (**10**), 3.17(1) and 3.19(1) (**11**), 3.03(1) (**12**) and 3.14(1) Å (**13**). The Pt−P (2.284(1), 2.273(1) Å) and Pt−S (2.320(1), 2.326(1) Å) bond lengths of $[Pt(1,8\text{-}S_2\text{-}nap)(PMe_3)_2]$ (**4**) are normal and bear direct comparison to the equivalent bonds in $[(PPh_3)_2Pt(ttn)Pt(PPh_3)_2]$: Pt−P = 2.293(3), 2.296(3) and Pt−S = 2.298(3), 2.315(3) Å.[3] An analysis of the Ni−S distances of a series of symmetrically derivatised complexes showed the following bond length trend Ni−S(O)R > Ni−SR and Ni−S(O)$_2$R. This was rationalized by invoking a combination of competing factors: the σ-donor ability, a contraction in the size of the sulfur atom with increasing oxidation state and destabilization of the M−S bond due to repulsion between the filled d orbitals of the metal and lone pairs on the ligand.[27] It has also been observed that the Pt−P bond length increases with the increasing *trans* influence of the co-ligand, the sulfenato −S(O)R ligand having a larger *trans* influence than the thiolato −SR ligand.[13–21] As there are no reported examples of platinum complexes with mixed phosphine–sulfinato ligand donor sets a comparison of the *trans* influence of sulfinato versus sulfenato versus thiolato ligands is not possible. Examination of the Pt–S bond lengths of the oxidized naphtha-1,8-dithiolate derivatives **10**, **11**, **12** and **13** shows no evident Pt–S bond length trend, the Pt–$S_{(thiolato)}$ distances of **10** and **11** are in the range 2.308(5)–2.338(2) Å; the Pt–$S_{(sulfenato)}$ bond lengths of **10** and **12** (2.338(2) and 2.332(5) Å, respectively) and the Pt–$S_{(sulfinato)}$ distance range of **11**, **12** and **13** (2.291(5)-2.313(1) Å) show considerable overlap. The *trans* influence of the sulfur ligand in relation to Pt–P bond length trend as discussed above is observed in complexes **10**, **11** and **12**: Pt–$P_{(trans\ \mathrm{to\ thiolato})}$ 2.308(2) (**10**), and 2.308(5) and 2.295(5) Å (**11**); Pt–$P_{(trans\ \mathrm{to\ sulfenato})}$ 2.316(2) (**10**), 2.337(5) Å (**12**). Additionally we find that the Pt–$P_{(trans\ \mathrm{to\ sulfinato})}$ distances of 2.321(5) and 2.337(5) in **11**, 3.323(2) in **12** and 2.336(1) and 2.327(1) Å in **13** are greater than the Pt–$P_{(trans\ \mathrm{to\ thiolato})}$ bond lengths; this implies that (-S(O)R) has a stronger *trans* influence than (-SR). However, there appears to be no significant difference in Pt–$P_{(trans\ \mathrm{to\ sulfenato})}$ versus Pt–$P_{(trans\ \mathrm{to\ sulfinato})}$ bond lengths. The S–O bond lengths appear to be independent of sulfur oxidation state and fall within a narrow range 1.436(14)–1.501(5) Å; previous studies of average S–O distances in –S(O)R and $-S(O)_2R$ complexes found that sulfinate S–O lengths were typically 0.1 Å shorter than those of sulfenate ligands.[27] The X-ray structures of **10**, **11** and **12** show that the oxygen atoms of the sulfenato groups in **10** and **12** and one oxygen atom of the sulfinato moieties of **11** and **12** lie approximately within the plane of the naphthalene ring. A similar situation is observed in the S(9) sulfinato group of complex **13**, in which O(9) and the naphthalene ring are co-planar, whereas the O(1) and O(2) oxygen atoms of the S(1) sulfinato group lie above and below the naphthalene ring plane, respectively; this may be a consequence of the distortion observed in the ligand (see below). The naphthalene–E_2 ligands are hinged with respect to the coordination plane and the angles defined by the Pt(1)-E(1)-E(9) and the E(1)-E(9)-naphthalene mean planes are variable and range from 111° in **10** to 137° in **11**; the most bent examples (those with a hinge angle closest to 90°) are molecules that contain a sulfenato –S(O)R moiety in **10** (111°) and **12** (119°). Another interesting feature of these complexes is observed in the naphthalene ring, which although planar when the dichalcogen bridge is intact[46] becomes twisted when incorporated in to a six-membered platinacycle. Upon coordination the naphthalene backbone of the ligand becomes "twisted"—the extent of the naphthalene ring distortion is variable (see dihedral S(1)-C(1)···C(9)-S(9) and naphthalene ring torsion angles in Table 3); the most planar example is $\mathbf{11}_{(\mathrm{molecule\ 1})}$ and the most twisted is **13**.

Conclusion

This paper reports the systematic synthesis of a series of bisphosphine platinum complexes of naphthalene-1,8-dichalcogenole and related ligands by metathetical and oxidative addition reactions. We have shown that novel compounds particularly those containing mixed thiolato/sulfenato, thiolato/sulfinato and sulenato/sulfinato donor sets are accessible through simple oxidative addition reactions between zero-valent platinum species and the appropriate E–E (E = S or Se) bridged precursor. Further investigations into the coordination chemistry of similar ligands, containing different aromatic hydrocarbon backbones, are currently underway.

Experimental

General: Unless otherwise stated, manipulations were performed under an oxygen-free nitrogen or argon atmosphere by using standard Schlenk techniques and glassware. Solvents were dried, purified and stored according to common procedures.[47] The ligands naphtho[1,8-*cd*][1,2]dithiole,[48] naphtho[1,8-*cd*][1,2]diselenole,[48] naphtho[1,8-*cd*][1,2]thiaselenole,[49] 5,6-dihydro-1,2-dithiacyclopent[*fg*]acenaphylene,[50] 4,5-dithiaacephenanthrylene,[51] 3-*tert*-butylnaptho[1,8-*cd*][1,2]dithiole,[52] naphtho[1,8-*cd*][1,2]dithiole 1-oxide,[53] naphtho[1,8-*cd*][1,2]dithiole 1,1-dioxide,[54,55] naphtho[1,8-*cd*][1,2]dithiole 1,1,2-trioxide,[56] disodium naphthalene-1,8-disulfinate,[56] $[Pt(PPh_3)_4]$[57] and sodium naphthalide ($NaC_{10}H_8$)[58] were prepared according to literature procedures and *cis*-$[PtCl_2(PMe_3)_2]$, *cis*-$[PtCl_2(PMe_2Ph)_2]$ and *cis*-$[PtCl_2(PPh_3)_2]$ were synthesised by the addition of two equivalents of the appropriate phosphine ligand to $[PtCl_2(cod)]$ (cod = 1,5-cyclooctadiene) in dichloromethane. All other reagents were obtained commercially.

Infrared spectra were recorded as KBr pellets in the range 4000–220 cm^{-1} on a Perkin–Elmer system 2000 Fourier transform spectrometer. $^{31}P\{^1H\}$ (109.4 MHz) and ^{195}Pt (58.1 MHz) NMR spectra were recorded on a Jeol DELTA GSX270 spectrometer with $\delta(P)$ referenced to external 85% H_3PO_4 and $\delta(Pt)$ to external H_2PtCl_6. ^{77}Se spectra were recorded either on a Bruker AM300 or a Jeol DELTA GSX270 operating at 57.2 and 51.5 MHz, respectively, with $\delta(Se)$ referenced to external H_2SeO_3 ($\delta(Se) = 1277$ ppm). Elemental analyses were performed by the St. Andrews University School of Chemistry Service and positive-ion FAB mass spectra were carried out by the EPSRC National Mass Spectrometry Service, Swansea.

Precious metal salts were provided on loan by Johnson Matthey plc.

The final product complexes are reasonably stable to atmospheric oxygen and moisture in the solid state, but were stored for longer periods under nitrogen.

$[Pt(1,8\text{-}S_2\text{-nap})(PPh_3)_2]$ (1)

Method A: $[Pt(PPh_3)_4]$ (0.433 g, 0.348 mmol) and naphtho[1,8-*cd*][1,2]dithiole (0.066 g, 0.347 mmol) were stirred in toluene (20 cm^3) for 2 h resulting in a dark yellow solution. The solution was filtered through a silica pad and further eluted with dichloromethane (100 cm^3). The filtrate was evaporated to dryness under reduced pressure, re-dissolved in the minimum amount of dichloromethane ca. 5 cm^3 and with stirring diethyl ether (25 cm^3) followed by hexane (50 cm^3) were slowly added to induce precipitation. The resulting bright yellow micro-crystalline solid was collected by suction filtration washed with diethyl ether (10 cm^3) and dried briefly in vacuo. Yield 0.293 g, 92%; FAB$^+$ MS: *m/z*: 910 $[M]^+$, 719/720 $[M-(S_2C_{10}H_6)]^{2+}$.

Method B: Super hydride ($LiBEt_3H$) (0.75 cm^3 of a 1.0 M solution in THF, 0.750 mmol) was added in one portion to a solution of naphtho[1,8-*cd*][1,2]dithiole (0.071 g, 0.373 mmol) in THF (10 cm^3). Upon addition an immediate colour change from bright red to very pale yellow was observed accompanied by the evolution of gas. The solution of $Li_2[1,8\text{-}S_2\text{-naphthalene}]$ was transferred by means of a stainless steel canula to a suspension of *cis*-$[PtCl_2(PPh_3)_2]$ (0.293 g, 0.371) in THF (10 cm^3) and the mixture was rapidly stirred for 2.5 h giving a dark yellow solution. Isolation of the product was identical to the procedure described for method A. Yield 0.288 g, 85%. The analytical and spectroscopic properties of this material were identical to those of material prepared by method A.

$[Pt(1,8\text{-}Se_2\text{-nap})(PPh_3)_2]$ (2): This was prepared by method A described for compound **1**, but with $[Pt(PPh_3)_4]$ (0.440 g, 0.354 mmol) and naphtho[1,8-*cd*][1,2]diselenole (0.101 g, 0.356 mmol). Upon evaporation of the filtrate to about 5 cm^3 a bright orange crystalline solid was deposited; this was collected by suction filtration, washed consecutively with toluene

(5 cm^3) and diethyl ether (2×10 cm^3), and dried in vacuo. Yield 0.299 g, 84%; FAB$^+$ MS: *m/z*: 1004 $[M]^+$, 719/720 $[M-(\mathrm{Se_2C_{10}H_6})]^{2+}$. This compound was also prepared by method B (described for compound **1**) with naphtho[1,8-*cd*][1,2]diselenole (0.080 g, 0.282 mmol), super hydride (0.56 cm^3 of a 1.0 M solution in THF, 0.56 mmol) and *cis*-$[\mathrm{PtCl_2(PPh_3)_2}]$ (0.223 g, 0.282 mmol). Isolation of the product was identical to the procedure described for method A. Yield 0.235 g, 83%. The analytical and spectroscopic properties of this material were identical to those of the material prepared by method A.

[Pt(1-S,8-Se-nap)(PPh$_3$)$_2$] (3): This was prepared by method A described for compound **1**, but with $[\mathrm{Pt(PPh_3)_4}]$ (0.390 g, 0.313 mmol) and naphtho[1,8-*cd*][1,2]selenathiole (0.074 g, 0.312 mmol) to give an orange solid. Yield 0.279 g, 95%; FAB$^+$ MS: *m/z*: 958 $[M+\mathrm{H}]^+$, 719/720 $[M-(\mathrm{SSeC_{10}H_6})]^{2+}$. This compound was also prepared by method B (described for compound **1**) with naphtho[1,8-*cd*][1,2]selenathiole (0.070 g, 0.295 mmol), super hydride (0.59 cm^3 of a 1.0 M solution in THF, 0.59 mmol) and *cis*-$[\mathrm{PtCl_2(PPh_3)_2}]$ (0.233 g, 0.295 mmol). Isolation of the product was identical to the procedure described for method A. Yield 0.206 g, 73%. The analytical and spectroscopic properties of this material were identical to those of material prepared by method A.

[Pt(1,8-S$_2$-nap)(PMe$_3$)$_2$] (4): *cis*-$[\mathrm{PtCl_2(PMe_3)_2}]$ (0.157 g, 0.375 mmol) was suspended in THF (30 cm^3) and ethene gas was bubbled through the suspension for 10 minutes. While ethene was passed over the suspension, sodium naphthalide (2.5 cm^3 of a 0.31 M THF solution, 0.775 mmol) was added dropwise over 45 mins resulting in a dirty yellow solution. Solid naphtho[1,8-*cd*][1,2]dithiole (0.071 g, 0.373 mmol) was added in one portion giving a bright yellow solution, which was stirred for 30 min and then evaporated to dryness under reduced pressure. The residue was taken up in dichloromethane (10 cm^3) and passed through a shallow plug of dry silica and washed through with more dichloromethane (100 cm^3). The filtrate and washings were combined and reduced in volume to about 5 cm^3; hexane (50 cm^3) was added with stirring followed by reducing the solvent volume to about 20 cm^3 to give a yellow solid. The precipitate was collected by suction filtration and dried in vacuo. Yield 0.152 g, 75%; FAB$^+$ MS: *m/z*: 539 $[M+\mathrm{H}]^+$, 347 $[M-(\mathrm{S_2C_{10}H_6})]^{2+}$. This compound was also prepared by method B (described for compound **1**) with naphtho[1,8-*cd*][1,2]dithiole (0.053 g, 0.279 mmol), super hydride (0.56 cm^3 of a 1.0 M solution in THF, 0.56 mmol) and *cis*-$[\mathrm{PtCl_2(PMe_3)_2}]$ (0.116 g, 0.277 mmol). Isolation of the product was identical to the procedure described above for **4**. Yield 0.104 g, 70%. The analytical and spectroscopic properties of this material were identical to those of material prepared by the first method described above.

[Pt(1,8-Se$_2$-nap)(PMe$_3$)$_2$] (5): A suspension of *cis*-$[\mathrm{PtCl_2(PMe_3)_2}]$ (0.153 g, 0.366 mmol) in THF (20 cm^3) was degassed for 20 min by bubbling ethane gas through the suspension. With continued ethane bubbling, super hydride (0.73 cm^3 of a 1.0 M solution in THF, 0.73 mmol) was added to the suspension dropwise over 30 mins (hydrogen evolution was observed) to give a pale yellow solution of $[\mathrm{Pt(C_2H_4)(PMe_3)_2}]$. Solid naphtho[1,8-*cd*][1,2]diselenole (0.104 g, 0.366 mmol) was added and the mixture was stirred for 1 h. The reaction solvent was removed under reduced pressure and the residue was taken up in dichloromethane (20 cm^3) and filtered through a shallow pad of silica; the product was further eluted with more dichloromethane (100 cm^3). The filtrate was evaporated under reduced pressure to about 5 cm^3 and the product was precipitated by the addition of hexane (50 cm^3) followed by reducing the solvent volume to about 20 cm^3 to give an orange solid. Yield 0.206 g, 89%; FAB$^+$ MS: *m/z*: 632 $[M+\mathrm{H}]^+$, 347 $[M-(\mathrm{Se_2C_{10}H_6})]^{2+}$. This compound was also prepared by method B (described for compound **1**) with naphtho[1,8-*cd*][1,2]diselenole (0.073 g, 0.257 mmol), super hydride (0.52 cm^3 of a 1.0 M solution in THF, 0.52 mmol) and *cis*-$[\mathrm{PtCl_2(PMe_3)_2}]$ (0.107 g, 0.256 mmol). Isolation of the product was identical to the procedure described above. Yield 0.121 g, 75%. The analytical and spectroscopic properties of this material were identical to those of the material prepared by the first method described above.

[Pt(1-S,8-Se-nap)(PMe$_3$)$_2$] (6): This was prepared by the method described for compound **5**, but with *cis*-$[\mathrm{PtCl_2(PMe_3)_2}]$ (0.138 g, 0.330 mmol), super hydride (0.66 cm^3 of a 1.0 M solution in THF, 0.66 mmol) and naphtho[1,8-*cd*][1,2]selenathiole (0.079 g, 0.333 mmol) to give an orange solid. The solid was recrystallised from a dichloromethane/hexane mixture by slow evaporation of the solvent over 4 days. Yield 0.163 g, 84%; FAB$^+$ MS: *m/z*: 586 $[M+\mathrm{H}]^+$, 347 $[M-(\mathrm{SSeC_{10}H_6})]^{2+}$. This compound was also prepared by method B (described for compound **1**) with naphtho[1,8-*cd*][1,2]selenathiole (0.065 g, 0.274 mmol), super hydride (0.55 cm^3 of a 1.0 M solution, 0.55 mmol) and *cis*-$[\mathrm{PtCl_2(PMe_3)_2}]$ (0.114 g, 0.273 mmol). Isolation of the product was identical to the procedure described above. Yield 0.122 g, 71%. The analytical and spectroscopic properties of this material were identical to those of the material prepared by the first method described above.

[Pt(1,2-S$_2$-acenap)(PPh$_3$)$_2$] (7): This was prepared by method A described for compound **1**, but with $[\mathrm{Pt(PPh_3)_4}]$ (0.350 g, 0.281 mmol) and 5,6-dihydro-1,2-dithiacyclopenta[*fg*]acenaphylene (0.061 g, 0.282 mmol) to give a bright orange crystalline solid. Yield 0.246 g, 94%; FAB$^+$ MS: *m/z*: 936 $[M]^+$, 719/720 $[M-(\mathrm{S_2C_{12}H_8})]^{2+}$.

[Pt(4,5-S$_2$-phenan)(PPh$_3$)$_2$] (8): This was prepared by method A described for compound **1**, but with $[\mathrm{Pt(PPh_3)_4}]$ (0.180 g, 0.145 mmol) and 4,5-dithia-acephenanthrylene (0.035 g, 0.146 mmol) to give a yellow solid. Yield 0.111 g, 80%; FAB$^+$ MS: *m/z*: 961 $[M+\mathrm{H}]^+$, 719/720 $[M-(\mathrm{S_2C_{14}H_8})]^{2+}$.

[Pt(1,8-S$_2$-2-*t*Bu-nap)(PPh$_3$)$_2$] (9): This was prepared by method A described for compound **1**, but with $[\mathrm{Pt(PPh_3)_4}]$ (0.290 g, 0.233 mmol) and 3-*tert*-butyl-naptho[1,8-*cd*][1,2]dithiole (0.058 g, 0.234 mmol). The resulting solution was stirred with heating (80 °C) for 30 min, upon which the solution turned red. The filtered reaction solution was evaporated to dryness and dissolved in dichloromethane (5 cm^3); hexane (30 cm^3) was then added. The solution was then reduced in volume to about 20 cm^3 and the yellow precipitate was collected by suction filtration, washed with hexane (2×10 cm^3) and dried in vacuo. Yield 0.172 g, 76%; FAB$^+$ MS: *m/z*: 967 $[M+\mathrm{H}]^+$, 719/720 $[M-(\mathrm{C_{14}H_{14}S_2})]^{2+}$.

[Pt(1-S,8-{S(O)}-nap)(PPh$_3$)$_2$] (10): This was prepared by method A described for compound **1**, but with $[\mathrm{Pt(PPh_3)}]$ (0.341 g, 0.274 mmol) and naphtho[1,8-*cd*][1,2]dithiole-1-oxide (0.057 g, 0.276 mmol). After stirring for 30 min a yellow precipitate started to separate and stirring was continued for a further 1.5 h. The precipitate was dissolved by the addition of dichloromethane (20 cm^3); the resulting solution was filtered through silica eluting first with dichloromethane (150 cm^3), which was discarded, and then with a 1:3 mixture of acetone/dichloromethane (150 cm^3). The filtrate was evaporated to dryness under reduced pressure and taken up in the minimum amount of toluene;diethyl ether (30 cm^3) then hexane (70 cm^3) were slowly added while stirring. The yellow/orange microcrystalline product was collected by suction filtration, washed with a 1:1 mixture of diethyl ether/hexane (2×10 cm^3) and dried in vacuo. Yield 0.214 g, 91%; FAB$^+$ MS: *m/z*: 927 $[M+\mathrm{H}]^+$, 719/720 $[M-(\mathrm{S_2OC_{10}H_6})]^{2+}$; IR (KBr): $\tilde{\nu} = 1095\ \mathrm{cm^{-1}}$ (s) (S=O).

[Pt(1-S,8-{S(O)$_2$}-nap)(PPh$_3$)$_2$] (11): This was prepared by method A described for compound **1**, but with $[\mathrm{Pt(PPh_3)}]$ (0.318 g, 0.256 mmol) and naphtho[1,8-*cd*][1,2]dithiole 1,1-dioxide (0.057 g, 0.256 mmol). A precipitate was deposited after 5 min and stirring was continued for a total of 30 min. The reaction mixture was poured on to a silica pad and eluted with dichloromethane (150 cm^3), which was discarded, followed by a 1:1 mixture of acetone/dichloromethane (150 cm^3). The acetone/dichloromethane filtrate was evaporated to dryness under reduced pressure and the residue was dissolved in a small amount of dichloromethane (ca. 5 cm^3). Hexane (50 cm^3) was slowly added to this solution while stirring. The bright yellow/orange microcrystalline solid was collected by suction filtration, washed with hexane (20 cm^3) and diethyl ether (20 cm^3) and dried in vacuo. Yield 0.230 g, 95%; FAB$^+$ MS: *m/z*: 943 $[M+\mathrm{H}]^+$, 719/720 $[M-(\mathrm{S_2O_2C_{10}H_6})]^{2+}$; IR (KBr): $\tilde{\nu} = 1185$ (s), $1063\ \mathrm{cm^{-1}}$ (s) (S(=O)$_2$).

[Pt(1-{S(O)},8-{S(O)$_2$}-nap)(PPh$_3$)$_2$] (12): This was prepared by method A described for compound **1**, but with $[\mathrm{Pt(PPh_3)}]$ (0.411 g, 0.330 mmol) and naphtho[1,8-*cd*][1,2]dithiole 1,1,2-trioxide (0.079 g, 0.332 mmol). After stirring for 17 h the yellow-orange microcrystalline precipitate was filtered off, washed with toluene (5 cm^3) and diethyl ether (2×10 cm^3) and dried in vacuo. Yield 0.302 g, 96%; FAB$^+$ MS: *m/z*: 959 $[M+\mathrm{H}]^+$, 719/720 $[M-(\mathrm{S_2O_3C_{10}H_6})]^{2+}$; IR (KBr): $\tilde{\nu} = 1101$ (s; S=O), 1212 (s; S(=O)$_2$), $1061\ \mathrm{cm^{-1}}$ (s; S(=O)$_2$).

[Pt(1,8-{S(O)$_2$}$_2$-nap)(PMe$_2$Ph)$_2$]·0.5 CH$_2$Cl$_2$ (13): A mixture of *cis*-$[\mathrm{PtCl_2(PMe_2Ph)_2}]$ (0.105 g, 0.194 mmol) and disodium naphthalene-1,8-disulfinic acid (0.072 g, 0.240 mmol) were stirred in methanol (20 cm^3) for 24 h. The resulting yellow solution was evaporated to dryness under reduced pressure and the residue was extracted with dichloromethane (3×15 cm^3) containing triethylamine, approximately 0.5% by volume. The

Table 4. Crystallographic data for complexes **2**, **4**, **10**, **11**, **12** and **13**.

	2	**4**	**10**	**11**	**12**	**13**
formula	$C_{46}H_{36}P_2PtSe_2$ $\cdot 0.25\,CH_2Cl_2$	$C_{16}H_{24}P_2PtS_2$	$C_{46}H_{36}OP_2PtS_2$	$C_{46}H_{36}O_2P_2PtS_2$ $\cdot 0.25\,CHCl_3$	$C_{46}H_{36}O_3P_2PtS_2$	$C_{26}H_{28}O_4P_2PtS_2$ $\cdot 0.5\,CH_2Cl_2$
M_r	1024.94	537.50	925.90	971.74	957.90	768.10
crystal system	triclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$C2/c$
a [Å]	11.9003(9)	12.8530(4)	10.6497(12)	11.855(2)	15.068(3)	18.865(4)
b [Å]	14.7985(11)	8.8142(3)	18.967(2)	14.613(3)	17.579(3)	15.201(3)
c [Å]	25.0528(18)	17.9522(6)	19.186(2)	24.799(5)	15.198(3)	19.066(5)
α [°]	74.2800(10)	90	90	74.707(4)	90	90
β [°]	86.6290(10)	109.4390(10)	95.726(2)	86.638(4)	103.771(3)	95.114(19)
γ [°]	76.4220(10)	90	90	74.177(4)	90	90
V [Å^3]	4128.2(5)	1917.85(11)	3856.0(8)	3996.7(13)	3909.8(11)	5446(2)
Z	4	4	4	4	4	8
ρ_{calcd} [g cm^{-3}]	1.649	1.862	1.595	1.615	1.627	1.874
μ [mm^{-1}]	5.303	7.693	3.866	3.784	3.819	5.555
reflections measured	20900	7981	19176	20280	19030	11506
independent reflections	11717	2722	5492	11375	5556	3884
final $R1$ [$I>2\sigma(I)$]	0.0346	0.0178	0.0343	0.0796	0.0406	0.0214
final $wR2$ [$I>2\sigma(I)$]	0.0895	0.0434	0.0749	0.1715	0.0896	0.0506

pale orange/yellow extracts were combined and filtered through a shallow Celite pad and evaporated to about 3 cm^3; the product was then precipitated by the addition of diethyl ether. The pale yellow solid was collected by suction filtration and briefly dried. The crude material was recrystallised by slow vapour diffusion of diethyl ether into a concentrated solution of **13** in dichloromethane/0.5 % triethylamine to give yellow crystals, which were collected by suction filtration and dried overnight in vacuo. Yield 0.109 g, 78 %; FAB$^+$ MS: *m/z*: 726/727 $[M+H]^+$, 471 $[M-(S_2O_4C_{10}H_6)]^{2+}$; IR (KBr): $\tilde{\nu}=1186$ (s), 1051 cm^{-1} (s) (S(=O)$_2$).

[Pt(1,8-{S(O)$_2$}$_2$-nap)(PPh$_3$)$_2$] (14): This was prepared by the method described for compound **13**, but with [PtCl$_2$(PPh$_3$)$_2$] (0.132 g, 0.167 mmol) and disodium naphthalene-1,8-disulfinic acid (0.067 g, 0.223 mmol) to give a yellow powder, which was collected by suction filtration and dried overnight in vacuo. Yield 0.117 g, 72 %; FAB$^+$ MS: *m/z*: 975 $[M+H]^+$, 719/720 $[M-(S_2O_4C_{10}H_6)]^{2+}$; IR (KBr): $\tilde{\nu}=1214$ (s), 1058 cm^{-1} (s) (S(=O)$_2$).

Crystal structure analysis: Details of the x-ray characterisation experiments are given in Table 4. Data for **2**, **4** and **10** were collected at 293 K and **11**, **12** and **13** at 125 K on a Bruker SMART CCD diffractometer equipped with an Oxford Instruments low-temperature attachment, with Mo$_{K\alpha}$ radiation ($\lambda=0.71073$ Å). In **11** the carbon atoms were refined isotropically, in all other structures all non-hydrogen atoms were refined anisotropically. All refinements were performed by using SHELXTL (Version 5.10, Bruker AXS, 1999). CCDC-215509 **2**, CCDC-215510 **4**, CCDC-215511 **10**, CCDC-215512 **11**, CCDC-215513 **12** and CCDC-215508 **13** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax (+ 44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.

Single crystals suitable for X-ray diffraction studies of compounds [Pt(1,8-Se$_2$-nap)(PPh$_3$)$_2$] (**2**), [Pt(1,8-S$_2$-nap)(PMe$_3$)$_2$] (**4**) and [Pt(1-{S(O)},8-{S(O)$_2$}-nap)(PPh$_3$)$_2$] (**12**) were obtained by layering a solution of each compound in CH$_2$Cl$_2$ with either diethyl ether or hexane. Single crystals of compound [Pt(1,8-{S(O)$_2$}$_2$-nap)(PMe$_2$Ph)$_2$]·0.5 CH$_2$Cl$_2$ (**13**) were acquired in a similar manner except that the solution of **13** in CH$_2$Cl$_2$ contained a small quantity of triethylamine to prevent acid formation and decomposition of the complex. Crystals of [Pt(1-S,8-{S(O)}-nap)(PPh$_3$)$_2$] (**10**) were obtained by the slow evaporation of a concentrated solution of the complex in CH$_2$Cl$_2$ and those of [Pt(1-S,8-{S(O)$_2$}-nap)(PPh$_3$)$_2$] (**11**) by layering a solution of **11** in CHCl$_3$ with diethyl ether.

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