Synthesis and structural study of (8-phenylsulfanylnaphth-1-yl)diphenylphosphine metal complexes

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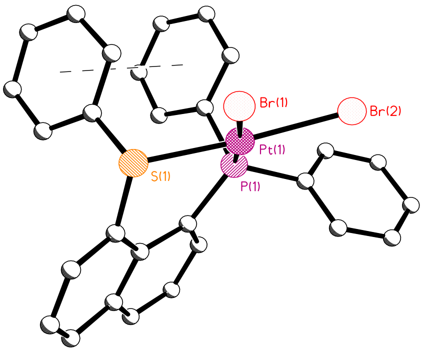
INDEX ENTRY: The hemilabile ligand Nap(SPh)(PPh_2) undergoes more distortion on coordination to platinum than when coordinated to ruthenium.



Abstract

A series of three platinum(II) halide complexes **2-4** $[Pt(X)_2\{Nap(PPh_2)(SPh)\}]$ (Nap = naphthalene-1,8-diyl; X = Cl, Br, I) and a ruthenium(II) *p*-cymene complex **5** $[Ru(\eta^6\text{-}MeC_6H_4{}^iPr)(Cl)\{Nap(PPh_2)(SPh)\}]^+Cl^-$ of the sterically crowded *peri*-substituted naphthalene phosphine **1** have been prepared. The compounds were fully characterised by multinuclear NMR, IR and MS and X-ray data for **1-5** are compared. Molecular structures are analysed by naphthalene ring torsions, *peri*-atom displacement, splay angle magnitude, P···S interactions, aromatic ring orientations and geometry around the metal centre. Platinum adopts a strictly square planar geometry which increases the distortion of the naphthalene skeleton in **2-4**. Conversely, the classical-piano stool conformation of **5** results in a pseudo octahedral conformation around the ruthenium atom which influences the naphthalene geometry to a much lesser extent with distortion of a similar magnitude to the free ligand **1**.

Introduction

The theory of hemilability was introduced in the late 1970s[1] and since then there has been great interest in mixed ligands containing different donor atoms[2] and their uses associated with coordination chemistry and homogenous catalysis. The difference in electronic properties of the two donor atoms ensures they have distinctive interactions with the metal centre. One site offers a ‘soft’ donor atom which binds strongly to a ‘soft’ transition metal atom such as Rh(I), Pt(II) or Ru(II), whilst a ‘hard’ donor atom is less strongly bound and is thus coordinatively labile. The significance of hemilabile ligands in homogeneous catalysis lies in the susceptibility of the weak donor atom to dissociate from the metal, forming a free coordination site for the incoming substrate, and the increased stability of the catalyst precursor due to the chelating ability of these bidentate ligands.[3]

The ever-increasing demand for novel catalytic systems has focused attention on preparing low-valent transition-metal complexes containing mixed bidentate ligands with a significant contrast between the properties of coordinating groups.[4] Ligands possessing one strong and one weak donor atom such as P,O-[5] and P,N-donor[6] ligands have been extensively applied in catalysis and there is a growing interest with respect to potential applications of P,S-ligands.[7] Additionally, the electronic differences of the P and S donors of the chelate ligand might control reaction selectivities via operation of the *trans* effect. In this context, (8-phenylsulfanylnaphth-1-yl)diphenylphosphine **1**[8,9] is a suitable candidate because it is an asymmetric chelating ligand with substantial electronic and steric differences between the two donor atoms.

The work presented in this paper builds on our earlier studies of sterically crowded 1,8-disubstituted naphthalenes[8,9,10] and complements the work on copper(I) dimers previously undertaken.[9] Herein we report on the synthesis and structural study of a complete series of platinum(II) halide complexes of **1** (**2-4**) along with a ruthenium(II) *p*-cymene complex **5**.

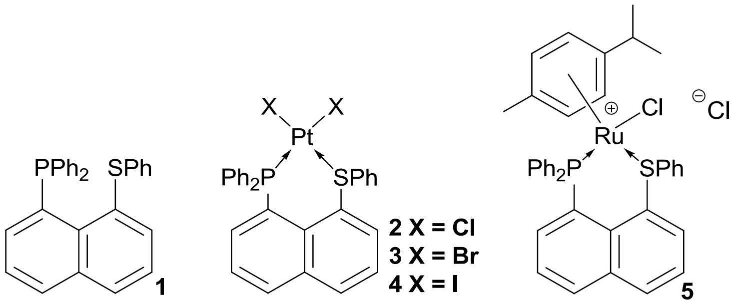
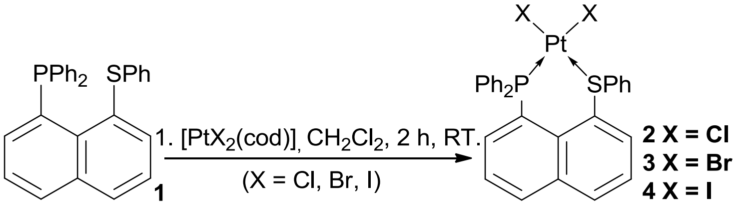


Fig. 1 *Platinum (II)* **2-4** *and ruthenium (II)* **5** *complexes of the peri-substituted naphthalene phosphine* **1**.

Results and Discussion

Ligand **1** reacts with the well known precursors [PtX_2(cod)] (cod = cyclooctadiene; X = Cl, Br, I) to afford a series of platinum(II) dihalide complexes, **2**, **3** and **4** (Scheme 1).[11,12] Following the displacement of the cyclooctadiene component, the square-planar platinum atom coordinates to two halogen atoms and to the bidentate ligand **1** via sulfur and phosphorus forming a six-membered ring **2-4** [$Pt(X)_2\{Nap(PPh_2)(SPh)\}$] (Nap = naphthalene-1,8-diyl; X = Cl, Br, I). All four complexes were characterised by multinuclear NMR and IR spectroscopy, mass spectrometry and microanalysis. ^{31}P NMR spectroscopy data is displayed in Table 1.



Scheme 1 *Reaction scheme for the preparation of the (8-phenylsulfanylnaphth-1-yl)diphenylphosphine platinum (II) dihalides* **2**, **3**, **4**.

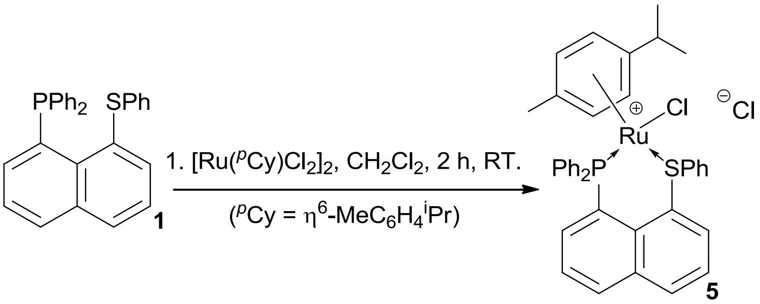
Table 1 Phosphorus-31 spectroscopic data for **1-5** [δ (ppm), *J* (Hz)]

Compound	δ_P	$^{1}J\{^{31}P\text{-}^{195}Pt\}$
1	-5.30	n/a
2	1.37	3521
3	0.98	3408
4	0.34	3263
5	37.99	n/a

The phosphorus-31 NMR spectra for the platinum complexes display an [AX]-pattern (A = P^{III}, X = Pt) with large values for $^{1}J\{^{31}P\text{-}^{195}Pt\}$, indicative of direct coordination of one phosphorus atom to the platinum centre. Signals for all three complexes occur upfield compared with ligand **1** and a move to lower chemical shifts is observed with the decreasing electronegativity of the halogen from chlorine to iodine. A decrease in the coupling constants of the platinum satellites is also observed [**2 Cl** $\delta = 1.37$ ppm, $^{1}J\{^{31}P\text{-}^{195}Pt\} = 3521$ Hz, **3 Br** $\delta = 0.98$ ppm, $^{1}J\{^{31}P\text{-}^{195}Pt\} = 3408$ Hz, **4 I** $\delta = 0.343$ ppm, $^{1}J\{^{31}P\text{-}^{195}Pt\} = 3263$ Hz]. The values for the chloride coupling constant lie between the values for Pt(dppe)Cl$_2$ ($^{1}J\{^{31}\mathrm{P}\text{-}^{195}\mathrm{Pt}\}$ = 3620 Hz)[13] and Pt(dppp)Cl$_2$ ($^{1}J\{^{31}\mathrm{P}\text{-}^{195}\mathrm{Pt}\}$ = 3406 Hz)[14] and are in the range for similar sulfur/phosphorus platinum dihalide complexes in the literature.[15]

The decrease in the coupling constants from the dichloride complex to the diiodide species is fully consistent with the larger *trans* influence of iodine relative to chlorine. [16]-[18] The variation in *J*(Pt-P) is not reflected in the P-Pt bond lengths of the three complexes [**2 Cl** 2.232(3)Å, **3 Br** 2.2326(15)Å, **4 I** 2.319(2)Å].

When ligand **1** was treated with an equimolar amount of [Ru(η^6-MeC$_6$H$_4$^{i}Pr)Cl$_2$]$_2$ dimer in dichloromethane at room temperature, the complex [Ru(η^6-MeC$_6$H$_4$^{i}Pr)(Cl){Nap(PPh$_2$)(SPh)}]$^+$Cl$^-$ **5** was obtained as an air-stable red solid (Scheme 2). The ^{31}P NMR spectrum displays a down field shift [37.99 ppm] compared with **1** with a chemical shift in accord with similar compounds from the literature (Table 1).[19]



Scheme 2 *The reaction scheme for the preparation of [Nap(PPh$_2$)(SPh)Ru(Cl)(η^6-MeC$_6$H$_4$^{i}Pr)]$^+$Cl$^-$* **5**.

A loss of the twofold symmetry of the *p*-cymene ligand is observed in the ^{1}H NMR spectrum, similar to other reported *p*-cymene complexes.[20] Coordination of ruthenium to four unrelated ligands makes the central metal stereogenic. The methyl protons of the isopropyl group and the aromatic protons of the *p*-cymene ligand are diastereotopic and thus inequivalent in the ^{1}H NMR spectrum altering the pattern of resonances compared with the initial dimer.[21] The four aromatic hydrogen atoms of the *p*-cymene ligand appear as four sets of doublets at *ca* δ = 5.5-4.9 ppm instead of two doublets as in the starting complex and the two isopropyl methyls of the *p*-cymene appear as two doublets at δ = 0.93 and 0.69 ppm instead of one doublet.

Table 2 Selected interatomic distances [Å] and angles [°] for **1-5**

Compound	**1**[8,9]	**2**	**3**	**4**	**5**
Peri-region distances and sub-van der Waals contacts					
P(1)···S(1)	**3.0330(7)**	**3.182(6)**	**3.191(3)**	**3.203(2)**	**3.013(3)**
Σr_{vdW} - P···S; % ΣrvdW[a]	0.567; 84	0.418; 88	0.409; 89	0.397; 89	0.587; 84
P(1)-C(1)	1.8548(19)	1.80(2)	1.807(13)	1.837(6)	1.816(10)
S(1)-C(9)	1.785(2)	1.76(2)	1.763(13)	1.770(7)	1.829(10)
Naphthalene bond lengths					
C(1)-C(2)	1.376(3)	1.40(2)	1.366(17)	1.395(9)	1.385(14)
C(2)-C(3)	1.404(3)	1.40(3)	1.409(18)	1.398(10)	1.399(14)
C(3)-C(4)	1.353(3)	1.35(2)	1.339(17)	1.369(9)	1.381(15)
C(4)-C(5)	1.415(3)	1.44(2)	1.415(17)	1.411(10)	1.396(14)
C(5)-C(10)	1.442(3)	1.41(3)	1.428(18)	1.456(9)	1.444(14)
C(5)-C(6)	1.420(3)	1.44(3)	1.426(17)	1.404(9)	1.425(14)
C(6)-C(7)	1.358(3)	1.39(3)	1.350(18)	1.341(10)	1.348(15)
C(7)-C(8)	1.399(3)	1.38(3)	1.386(17)	1.401(12)	1.384(15)
C(8)-C(9)	1.377(3)	1.38(2)	1.377(16)	1.383(9)	1.394(13)
C(9)-C(10)	1.437(3)	1.46(2)	1.444(16)	1.434(9)	1.414(14)
C(10)-C(1)	1.448(3)	1.45(2)	1.465(16)	1.437(8)	1.434(13)
Peri-region bond angles					
P(1)-C(1)-C(10)	124.07(13)	128.7(14)	126.9(8)	125.9(4)	124.9(7)
C(1)-C(10)-C(9)	126.90(17)	125.0(18)	125.6(11)	127.8(6)	127.7(9)
S(1)-C(9)-C(10)	123.11(13)	124.4(14)	125.8(8)	126.2(4)	121.3(7)
Σ of bay angles	**Σ = 374.1(3)**	**Σ = 378.1(32)**	**Σ = 378.3(19)**	**Σ = 379.9(10)**	**Σ = 373.9(16)**
Splay angle[b]	14.1	18.1	18.3	19.9	13.9
C(4)-C(5)-C(6)	118.60(18)	117(2)	120.0(12)	119.7(6)	118.2(9)
Out-of-plane displacement					
P(1)	0.007(1)	0.212(23)	0.303(135)	-0.003(8)	-0.096(10)
S(1)	0.127(1)	-0.294(22)	-0.299(13)	-0.074(9)	0.217(10)
Central naphthalene ring torsion angles					
C:(6)-(5)-(10)-(1)	178.49(16)	175.9(16)	170.8(10)	-178.2(7)	176.9(7)
C:(4)-(5)-(10)-(9)	-179.5(2)	176.9(16)	174.7(10)	-177.2(7)	177.5(7)
Metal geometry - bond lengths[c]					
P(1)-M(1)	-	2.221(4)	2.232(3)	2.2326(15)	2.319(2)
S(1)-M(1)	-	2.261(4)	2.256(3)	2.2752(16)	2.356(2)
M(1)-L(1)	-	2.376(4)	2.4817(14)	2.6553(4)	2.396(2)
M(1)-L(2)	-	2.300(5)	2.4244(15)	2.6052(4)	1.744(1)[d]
Metal geometry - bond angles					
P(1)-M(1)-S(1)	-	90.46(17)	90.61(11)	90.56(5)	80.22(8)
P(1)-M(1)-L(1)	-	176.70(18)	175.93(8)	176.21(4)	89.03(9)
P(1)-M(1)-L(2)	-	92.55(17)	92.92(8)	92.43(4)	-
S(1)-M(1)-L(1)	-	87.77(16)	86.26(8)	87.42(4)	89.61(8)
S(1)-M(1)-L(2)	-	175.35(18)	175.58(8)	168.80(5)	-
L(1)-M(1)-L(2)	-	89.39(17)	90.09(4)	90.163(15)	-

[a] van der Waals radii used for calculations: r_{vdW}(P) 1.80 Å, r_{vdW}(S) 1.80 Å;[22] [b]**Splay angle:** Σ of the three bay region angles – 360; [c]**L(1):** X(1) for **2-4**, Cl(1) for **5**, **L(2):** X(2) for **2-4**, ^{p}Cy for **5**; [d]**M(1)-L(2):** Ru···centroid distance.

X-ray investigations

Single crystals were obtained for **2-5** by diffusion of pentane into saturated solutions of the individual compound in dichloromethane. The molecular structures were analysed; each complex crystallises with one molecule in the asymmetric unit. Selected interatomic distances, angles and torsion angles are listed in Table 2. Further crystallographic information can be found in Table 4 and the Supporting Information.

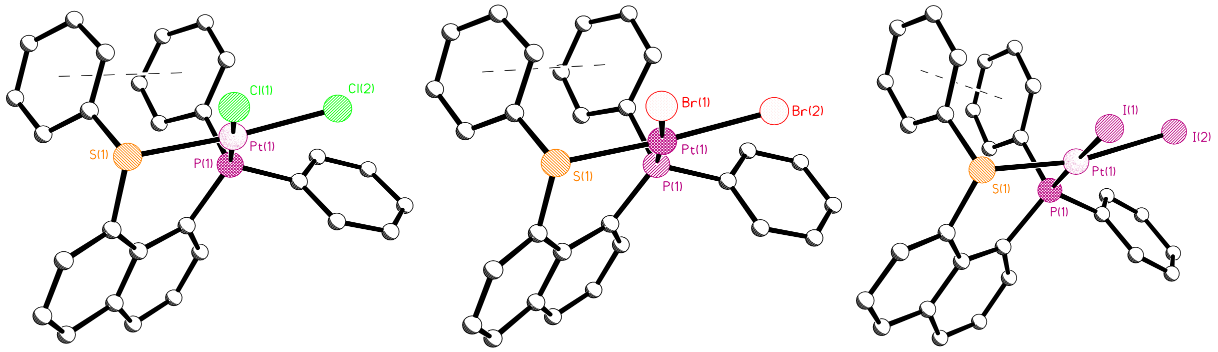


Fig. 2 *Crystal structures of the platinum halide complexes* **2**, **3** *and* **4** *illustrating the centroid-centroid distance resulting in π-π stacking*. The full numbering of the naphthalene ligand is illustrated in Figire 4

The molecular structures of **2-4** are shown in Figure 2. The three monomeric chelated metal complexes have similar structures with a typical square planar metal environment. In each case, the unsymmetrical phosphino-sulfanyl ligand **1** acts as a bidentate ligand coordinating via the phosphorus(III) and the sulfur atom to form a six-membered chelate ring. As a consequence of the geometry of the ligand, the halogen atoms in the three complexes arrange in a *cis*-orientation. Square planar geometry around the central metal is consistent throughout the series with angles around the platinum atom varying only slightly from 90° (Table 2, Figure 3).

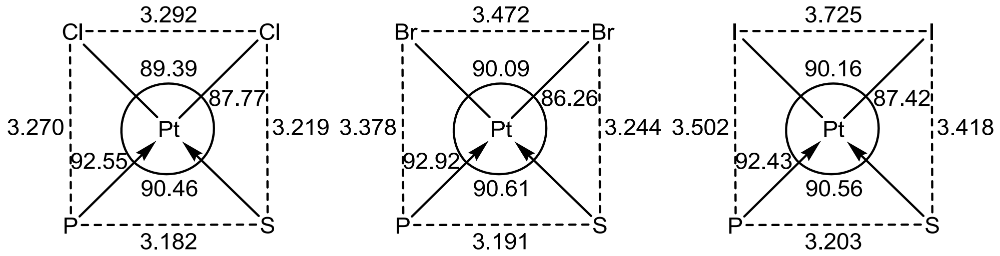


Fig. 3 *The angles [°] and distances [Å] associated with the square planar geometry of the platinum metal in the dihalide complexes* **2**, **3** *and* **4**.

The Pt-X(1) bond *trans* to P(1) is longer in all three species compared to the Pt-X(2) bond *trans* to S(1), which is consistent with the greater *trans* influence of phosphorus compared to sulfur.[18] As expected, Pt-X bonds lengthen with increasing size of the halogen atom and non-bonded intramolecular halogen-halogen distances increase to accommodate the larger atoms. The remaining non-bonded intramolecular distances around the platinum core also increase to maintain the square planar geometry (Figure 3). Pt-S and Pt-P bond distances are within the usual ranges.[15]

The PtSPC$_3$ six-membered rings in **2-4** are hinged about the P···S vector and can be described as a twisted envelope type conformation; P(1), S(1), C(1), C(10) and C(9) are approximately coplanar with the platinum atom sitting in the *peri*-gap above this plane. The displacement of Pt(1) from the C(1)–C(10)–C(9)–P(1)–S(1) plane is comparable in all three compounds [**2** 1.05(1) Å, **3** 1.00(1) Å, **4** 1.00(1) Å] with the angle inclined by the Pt(1)–P(1)–S(1) plane being similar [**2** 42.0(4)°, **3** 39.4(4) °, **4** 38.9(5)°].

The square planar conformation of ligand atoms around the central platinum metal together with the increasing size of the halogen atoms dictates the geometry of the naphthalene scaffold and the *peri*-substituents in **2-4**. This is contrary to the effects of copper coordination we observed in our previous paper.[9] As expected, the non-bonded intramolecular halogen-halogen distance lengthens when larger halogen atoms are present. To maintain the square planar geometry around platinum, the *peri*-atoms are forced further apart and non-covalent intramolecular P···S separations are elongated [**2** 3.182(6) Å, **3** 3.191(3) Å, **4** 3.203(2) Å]. The *peri*-distance in all three complexes is significantly longer than phosphine **1** [3.0330(7) Å] and is an indication of the enhanced steric interactions and extra naphthalene distortion taking place compared to the free ligand. Nonetheless, the *peri*-distance in all three complexes is shorter than the sum of van der Waals radii for phosphorus and sulfur by 11-12 %.

The increase in the P···S separation is accompanied by a widening of the bay region; P-C and S-C bonds are tilted in opposite directions and there is a notable increase in the positive splay angle [**2** 18.1°, **3** 18.3°, **4** 19.9°] compared with phosphine **1** [14.1°]. A similar displacement of the *peri*-atoms to either side of the naphthalene least-squares plane is observed in chloride **2** and bromide **3** [0.2-0.3 Å], but only a minor out-of-plane distortion is displayed by iodide **4** whose *peri*-atoms essentially lie on the naphthyl plane [0.003(8) Å, -0.074(9) Å].

The general distortion of the naphthalene skeleton is observed in all three complexes with stretching of C-C bonds and C-C-C angles. Bond lengths around C10, closer to the repulsive interactions, are on average longer than those around C5 [average 1.45 Å and 1.42 Å respectively] and C(1)-C(10)-C(9) bond angles splay to a mean 126°, away from the 'ideal' geometry as observed for C(4)-C(5)-C(6) (average 119°).[23] Further deformation of the naphthalene geometry is observed with a buckling of the usually rigid backbone. Maximum C-C-C-C torsion angles are in the range 2-4° for **2** and **4** but the deviation from planarity is more pronounced in bromide **3** [*ca* 5-9°].

Table 3 Torsion angles [°] categorising the naphthyl and phenyl ring conformations in **2**, **3, 4** and **5**

Naphthalene ring conformations

Compound	**C(10)-C(1)-P(1)-C(11)**	**C(10)-C(1)-P(1)-C(17)**	**C(10)-C(9)-S(1)-C(23)**
2	θ_1 -146.2(1); twist	θ_2 -103.8(1); axial	θ_3 69.7(1); axial
3	θ_1 142.2(1); twist	θ_2 -105.4(1); axial	θ_3 72.4(1); axial
4	θ_1 155.0(1); equatorial	θ_2 -94.6(1); axial	θ_3 86.6(1); axial
5	θ_1 -92.6(1); axial	θ_2 155.4(1); equatorial	θ_3 164.6(1); equatorial

Phenyl ring conformations

Compound	**C(1)-P(1)-C(11)-C(12)**	**C(1)-P(1)-C(17)-C(18)**	**C(9)-S(1)-C(23)-C(24)**
2	γ_1 -72.5(1); axial	γ_2 -0.30(1); equatorial	γ_3 23.0; equatorial
3	γ_1 -65.6(1); axial	γ_2 177.4(1); equatorial	γ_3 162.2(1); equatorial
4	γ_1 -70.3(1); axial	γ_2 -32.4(1); equatorial	γ_3 -8.4(1); equatorial

5	γ_1 -161.6(1); equatorial	γ_2 103.0(1); axial	γ_3 -112.8(1); axial

The geometrical arrangement of the free ligand, [Nap(PPh$_2$)(SPh)] **1**, in the platinum(II) halides **2-4** can be described by the conformation and arrangement of the naphthyl and phenyl rings, relative to the C(ar)-P(1)-C(ar) and C(ar)-S(1)-C(R) planes. When θ and γ approach 90° the orientation is denoted axial and when the angles indicate a quasi-planar arrangement (close to 180°), they are termed equatorial (see Table 3).[24] When angle θ is axial, the respective P-C$_{Ph}$/S-C$_{Ph}$ bond lies perpendicular to the naphthyl plane whilst an equatorial conformation aligns the bond on or close to the plane. Axial conformations of angle θ correspond to a type A structure and equatorial to type B.[24,25] From previously reported nomenclature,[25] the structural arrangement ligand **1** adopts in complexes **2-4** can thus be described as type BA-A-*c* (*c*-cis orientation of phenyl groups with respect to the naphthyl plane).[25]

Torsion angles (γ) show that the two phenyl rings arranged *cis* to the naphthyl plane adopt equatorial conformations in all three complexes and thus overlap in a slipped packing arrangement; **2** [γ_2 -0.30(1)°, γ_3 23.0(1)°], **3** [γ_2 177.4(1)°, γ_3 162.1(1)°], **4** [γ_2 -32.4(1)°, γ_3 -8.4(1)°].[26] The distance between the two interacting centroids increases with the increasing size of the halogen atoms but in all cases this distance is within the known range for typical centroid-centroid π-stacking [3.3-3.8 Å][26] so possible π-π stacking is envisaged [Cg(17-22)···Cg(23-28): **2** 3.536(1) Å, **3** 3.574(1) Å, **4** 3.598(1) Å].

The molecular structure of **5** is shown in Figure 4 and 5. The metal centre adopts a classical piano-stool geometry with coordination by the aromatic *p*-cymene ligand, a terminal chlorine ligand and the unsymmetrical phosphino-sulfanyl ligand **1**. The chlorine atom and the *peri*-atoms of **1** act as the legs of the piano stool and point away from the *p*-cymene ligand to avoid steric overcrowding resulting in a pseudo octahedral ruthenium(II) metal centre.

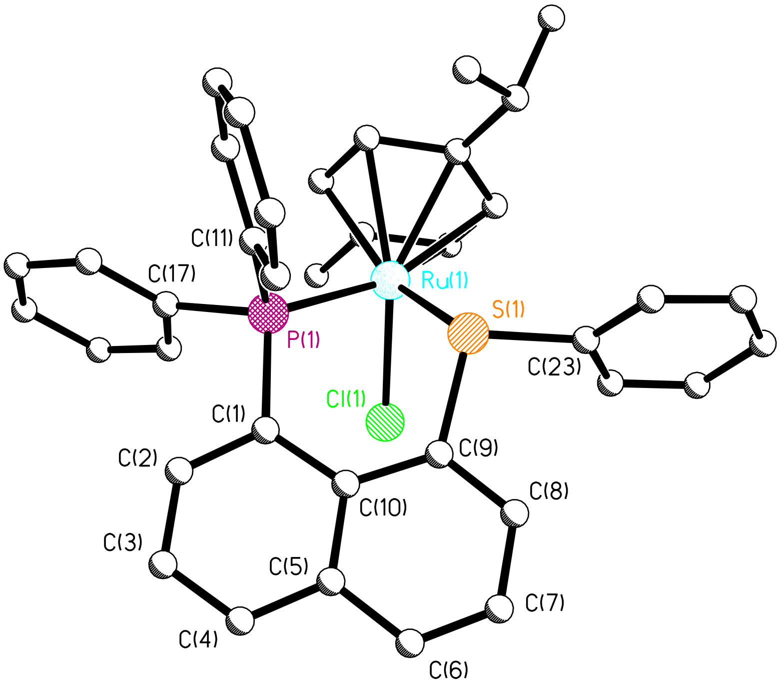


Fig. 4 *The crystal structure of [Nap(PPh$_2$)(SPh)Ru(Cl)(η^6-MeC$_6$H$_4{}^i$Pr)]$^+$Cl$^-$* **5**,*(counteranion Cl$^-$ omitted for clarity).*

Like the platinum halides **2-4**, **1** acts as a bidentate ligand coordinating via phosphorus(III) and sulfur forming a six-membered chelate ring (Figure 4). A twisted envelope type conformation of the RuSPC$_3$ six-membered ring is displayed with a hinge about the P···S vector; P(1), S(1), C(1), C(10) and C(9) are approximately coplanar with the ruthenium atom sitting in the *peri*-gap but 1.39(1) Å above this plane and the Pt(1)–P(1)–S(1) plane is inclined by 51.2(4)°.

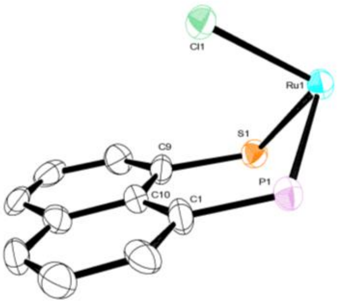


Fig. 5 *Core in the crystal structure of complex* **5** *illustrating the geometry around the six-membered RuPSC$_3$ ring.*

The ruthenium metal centre in **5** influences the molecular distortion of the naphthalene scaffold to a much lesser extent compared with the rigid square planar geometry in the platinum complexes. The degree of steric strain occurring in the naphthalene moiety in **5** is comparable to that of the free ligand **1**. The non-bonded intramolecular *peri*-distance [3.013(3) Å] is notably shorter than the separation found in the platinum complexes and similar to that of the free ligand [3.0330(7) Å **1**]. Corresponding splay angles 14.1° **1** and 13.9° **5** are also noticeably more acute compared with the platinum species [18.1-19.9°] implying P-C and S-C bonds are tilted away from each other to a lesser extent due to the reduced steric repulsion acting in the bay region. The displacement of the phosphorus and sulfur atoms from the best naphthalene plane in the ruthenium complex is minimal but slightly more pronounced compared with the free ligand [0.007(1) Å & 0.127(1) Å **1**; -0.10(1) Å & 0.22(1) Å **5**]. No major distortion of the naphthalene skeleton is observed in **5** with the maximum C-C-C-C torsion angle 3.1° for C(6)-C(5)-C(10)-C(1).

Torsion angles θ (Table 3) indicates the naphthalene unit in **5** displays an equatorial-axial-equatorial conformation with respect to the C(ar)-P(1)-C(ar) and C(ar)-S(1)-C(R) planes. This arrangement corresponds to a BA-B type arrangement.[24,25] Only one phenyl ring lies perpendicular to the naphthalene plane so no overlap of axial centroids and therefore no π-π stacking is observed.[26]

Table 4 Crystallographic data for compounds **2-5**

Compound	**2**.CH_2Cl_2	**3**. CH_2Cl_2	**4**. CH_2Cl_2	**5**.$(CH_3)_2CO$
Empirical Formula	$C_{29}H_{22}Cl_5PPtS$	$C_{29}H_{23}Br_2PPtSCl_2$	$C_{29}H_{23}I_2PPtSCl_2$	$C_{41}H_{41}Cl_2OPRuS$
Formula Weight	805.88	860.34	954.34	784.78
Temperature (°C)	-148(1)	-148(1)	-148(1)	-148(1)
Crystal Colour, Habit	colourless, prism	colourless, platelet	yellow, prism	orange, block
Crystal Dimensions (mm^3)	0.10 X 0.05 X 0.03	0.12 X 0.12 X 0.03	0.21 X 0.21 X 0.03	0.21 X 0.09 X 0.03
Crystal System	monoclinic	monoclinic	monoclinic	monoclinic
Lattice Parameters	a = 13.524(6) Å	a = 12.8977(13) Å	a = 15.053(4) Å	a = 9.829(3) Å
	b = 15.311(7) Å	b = 15.5520(14) Å	b = 11.559(3) Å	b = 22.199(6) Å
	c = 14.029(6) Å	c = 14.5122(15) Å	c = 17.567(4) Å	c = 17.506(5) Å
	-	-	-	-
	β = 102.103(9)°	β = 103.571(3)°	β = 108.385(5)°	β = 106.021(6)°
	-	-	-	-
Volume (Å^3)	V = 2840(2)	V = 2829.7(5)	V = 2900.7(12)	V = 3671.4(18)
Space Group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/n$
Z value	4	4	4	4
Dcalc (g/cm^3)	1.884	2.019	2.185	1.42
F000	1560	1640	1784	1616
m(MoKa) (cm^{-1})	55.392	81.09	72.769	7.045
No. of Reflections Measured	22810	15702	18781	16039
Rint	0.087	0.069	0.042	0.083
Min and Max Transmissions	0.570 - 0.847	0.493 - 0.784	0.475 - 0.804	0.861 - 0.979
Independent Reflections	4928	5127	5877	6381
Observed Reflection (No. Variables)	4650(335)	4639(326)	5732(326)	5505(430)
Reflection/Parameter Ratio	14.71	15.73	18.03	14.84
Residuals: R_1 (I>2.00s(I))	0.0987	0.0677	0.0394	0.1126
Residuals: R (All reflections)	0.1044	0.0774	0.041	0.1311
Residuals: wR_2 (All reflections)	0.2505	0.1637	0.1146	0.1848
Goodness of Fit Indicator	1.169	1.255	1.223	1.3
Maximum peak in Final Diff. Map	5.58 e /Å^3	1.10 e /Å^3	2.32 e /Å^3	0.93 e /Å^3
Minimum peak in Final Diff. Map	-2.23 e /Å^3	-1.61 e /Å^3	-2.25 e /Å^3	-0.57 e /Å^3

Conclusion

The design and synthesis of novel phosphorus ligands is of great importance to chemists and is an area which has seen great development. The work presented in this paper describes the metal coordination of our previously reported ligand (8-phenylsulfanylnaphth-1-yl)diphenylphosphine **1**[8,9] and complements the preliminary work undertaken by us on a series of copper(I) dimers.[9]

The unsymmetrical phosphino-sulfanyl ligand **1** has been shown to act as a bidentate ligand which can coordinate via both phosphorus(III) and the sulfur atom to form six-membered chelate rings.[9] Upon treatment with the known precursors [PtX_2(cod)] (X = Cl, Br, I), the naphthalene units of the complexes formed are forced into greater distortion to maintain the strictly square planar geometry required by the central platinum atom. Non-bonded *peri*-distances are noticeably longer and increase with the increasing size of the halogen atoms. Likewise there is an increase in the positive splay angles in the bay region in the platinum species and the *peri*-atoms are displaced to greater distances from the mean naphthalene plane. This is contrary to the effects of the tetrahedral environment of the copper atom when coordinated to **1** we observed in our previous paper, which showed no influence on the naphthalene structure.[9] Coordination of **1** with the precursor [Ru(η^6-Me$C_6H_4{}^{i}$Pr)Cl_2]$_2$ dimer afforded a classical-piano stool structure with a pseudo octahedral coordination of the ruthenium atom. The degree of steric strain operating in the naphthalene unit was observed to be of a similar magnitude to that occurring in the free ligand and the copper dimers previously reported, with corresponding values for the displacement of *peri*-atoms within and out of the plane and consequently the non-covalent *peri*-distance.

Experimental Section

All experiments were carried out under an oxygen- and moisture-free nitrogen atmosphere using standard Schlenk techniques and glassware. Reagents were obtained from commercial sources and used as received. Dry solvents were collected from a MBraun solvent system. (8-phenylsulfanylnaphth-1-yl)diphenylphosphine **1** was prepared in house.[8,9] Elemental analyses were performed by the University of St. Andrews School of Chemistry Microanalysis Service. Infra-red spectra were recorded as KBr discs in the range 4000-300 cm^{-1} on a Perkin-Elmer System 2000 Fourier transform spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Jeol GSX 270 MHz spectrometer with δ(H) and δ(C) referenced to external tetramethylsilane. ^{31}P NMR spectra were recorded on a Jeol GSX 270 MHz spectrometer with δ(P) referenced to external phosphoric acid. Assignments of ^{13}C and ^{1}H NMR spectra were made with the help of H-H COSY and HSQC experiments. All measurements were performed at 25 °C. All values reported for NMR spectroscopy are in parts per million (ppm). Coupling constants (*J*) are given in Hertz (Hz). Mass spectrometry was performed by the University of St. Andrews Mass Spectrometry Service. Electron impact mass spectrometry (EIMS) and Chemical Ionisation Mass Spectrometry (CIMS) was carried out on a Micromass GCT orthogonal acceleration time of flight mass spectrometer. Electrospray Mass Spectrometry (ESMS) was carried out on a Micromass LCT orthogonal accelerator time of flight mass spectrometer.

Platinum halide complexes of ligand 1 [Pt(X)$_2${Nap(PPh_2)(SPh)}]: To a schlenk tube containing ligand **1** (8-phenylsulfanylnaphth-1-yl)diphenylphosphine (1 molar equivalent) and Pt(cod)X_2 (1 molar equivalent) was added dichloromethane (5 mL). The reaction was stirred for 1 h and the solvent removed to near dryness. Suitable crystals were obtained by diffusion of pentane into saturated solution of the individual compound in dichloromethane.

(8-phenylsulfanylnaphth-1-yl)diphenylphosphine platinum dichloride [Pt(Cl)$_2${Nap(PPh_2)(SPh)}] 2: (0.08 g, 98 %); (Found: C, 48.6; H, 3.4. Calc. for $C_{28}H_{21}PSPtCl_2$: C, 49.1; H, 3.1 %); $^{v}{}_{\mathrm{max}}$(KBr tablet)/cm^{-1}: 3430br, 3054s, 2919s, 1964w, 1577s, 1478s, 1434s, 1321s, 1258w, 1154s, 1096vs, 1204s, 994s, 941s, 885s, 830vs, 765vs, 736vs, 687vs, 584vs, 526vs, 505vs, 418vs, 330vs, 294s; δ_H(270 MHz, $CDCl_3$) 8.31-8.26 (1 H, m, nap 5-H), 8.26-8.21 (2 H, m, nap 4,7-H), 7.70-7.64 (1 H, m, nap 6-H), 7.53-7.42 (3 H, m, nap 3-H, 2 x P*Ph*$_2$ 4-H), 7.42-6.94 (12 H, m, nap 2-H, 2 x P*Ph*$_2$ 2,3,5,6-H), 6.85-6.76 (1 H, m, S*Ph* 4-H), 6.73-6.63 (4 H, m, S*Ph* 2,3,5,6-H); δ_C(67.9 MHz, $CDCl_3$) 139.3(d, *J* 4.2 Hz), 137.6(s), 135.2(s), 134.8(s), 133.7(s), 131.2(s), 128.8(d, *J* 6.2 Hz), 128.3(s), 128.1(d, *J* 5.1 Hz), 127.7(s), 126.6(s), 126.3(d, *J* 10.4 Hz); δ_P(109 MHZ, $CDCl_3$) 1.37 ($J_{P\text{-}Pt}$ 3521.2 Hz); *m/z* (ES^+) 651.10, ($[M\text{-}Cl]^+$, 60 %), 614.13 ($[M\text{-}Cl_2]^+$, 100 %).

(8-phenylsulfanylnaphth-1-yl)diphenylphosphine platinum dibromide $[Pt(Br)_2\{Nap(PPh_2)(SPh)\}]$ 3: (0.2 g, 98 %); (Found: C, 43.0; H, 2.6. Calc. for $C_{28}H_{21}PSPtBr_2$: C, 43.5; H, 2.7 %); $^{v}_{max}$(KBr tablet)/cm^{-1}: 3047s, 1578w, 1477s, 1434vs, 1339s, 1269s, 1181s, 1154s, 1095vs, 996s, 887s, 827s, 766vs, 735vs, 585s, 569s, 525vs, 503vs; δ_H(270 MHz, $CDCl_3$) 8.30-8.26 (2 H, m, nap 5,7-H), 8.26-8.22 (1 H, m, nap 4-H), 7.69-7.64 (1 H, m, nap 6-H), 7.53-7.46 (2 H, m, nap 2,3-H), 7.46-6.96 (10 H, m, 2 x P*Ph*$_2$ 2-6-H), 6.84-6.78 (1 H, m, S*Ph* 4-H), 6.74-6.62 (4 H, m, S*Ph* 2,3,5,6-H); δ_C(67.9 MHz, $CDCl_3$) 139.6(d, *J* 4.2 Hz), 137.5(s), 135.2(s), 134.7(s), 133.8(br s), 131.1(s), 128.8(s), 128.6(s), 128.2(br s), 127.7(s), 126.6(s), 126.2(d, *J* 9.3 Hz); δ_P(109 MHz, $CDCl_3$) 0.98 ($J_{P\text{-}Pt}$ 3408.6 Hz); *m/z* (ES^+) 695.05 ($[M\text{-}Br]^+$, 100 %), 614.13 ($[M\text{-}Br_2]^+$, 22 %).

(8-phenylsulfanylnaphth-1-yl)diphenylphosphine platinum diiodide $[Pt(I)_2\{Nap(PPh_2)(SPh)\}]$ 4: (0.1 g, 99 %); (Found: C, 36.1; H, 2.2. Calc. for $C_{28}H_{21}PSPtI_2$: C, 36.5; H, 2.4 %); $^{v}_{max}$(KBr tablet)/cm^{-1}: 3050w, 2962w, 2221w, 1573w, 1476s, 1434s, 1335w, 1260s, 1151w, 1095vs, 1021vs, 907s, 882s, 800vs, 764s, 727vs, 690vs, 581s, 564s, 522s, 502s, 476w, 450w; δ_H(270 MHz, $CDCl_3$) 8.33-8.27 (2 H, m, nap 5,7-H), 8.27-8.20 (1 H, m, nap 4-H), 7.70-7.62 (1 H, m, nap 6-H), 7.57-7.43 (2 H, m, nap 2,3-H), 7.43-6.95 (10 H, m, 2 x P*Ph*$_2$ 2-6-H), 6.83-6.75 (1 H, m, S*Ph* 4-H), 6.75-6.68 (2 H, m, S*Ph* 2,6-H), 6.68-6.59 (2 H, m, S*Ph* 3,5-H); δ_C(67.9 MHz, $CDCl_3$) 139.7(d, *J* 3.4 Hz), 137.3(s), 134.9(s), 134.4(d, *J* 2.9 Hz), 130.9(s), 128.7(s), 128.3(s), 127.7(s), 126.5(s), 126.1(d, *J* 10.5 Hz); δ_P(109 MHz, $CDCl_3$) 0.34 ($J_{P\text{-}Pt}$ 3263.1 Hz); *m/z* (ES^+) 742.06 ($[M\text{-}I]^+$, 100 %).

(8-phenylsulfanylnaphth-1-yl)diphenylphosphine ruthenium *p*-cymene chloride $[Ru(\eta^6\text{-}MeC_6H_4{}^iPr)(Cl)\{Nap(PPh_2)(SPh)\}]$ 5: To a schlenk tube containing ligand (8-phenylsulfanylnaphth-1-yl)diphenylphosphine (0.12 g, 0.29 mmol) and $[Ru(^pCy)Cl_2]_2$ (0.18 g, 0.29 mmol) was added dichloromethane (5 mL). The reaction was stirred for 2 h and the filtered. Removal of the solvent and recrystallisation of the red solid from dichloromethane/pentane gave orange crystals (0.1 g, 92 %); $^{v}_{max}$(KBr tablet)/cm^{-1}: 3397br, 3053vs, 2961vs, 2272w, 1656vs, 1467s, 1436vs, 1387vs, 1319s, 1278w, 1198w, 1157w, 1113s, 1093s, 1055s, 1030s, 997w, 875s, 821w, 758s, 693vs, 560s, 519s, 498s, 448vs, 294s; δ_H(270 MHz, $CDCl_3$) 8.03 (1 H, d, *J* 7.2 Hz, S*Ph* 4-H), 7.99-7.87 (3 H, m, nap 4-H, S*Ph* 2,6-H), 7.83 (1 H, d, *J* 8.0 Hz, nap 5-H), 7.65-7.35 (12 H, m, S*Ph* 3,5-H, 2 x P*Ph*$_2$ 2-6-H), 7.35-7.16 (3 H, m, nap 2,3,6-H), 7.03 (1 H, d, *J* 6.9 Hz, nap 7-H), 5.47 (1 H, d, *J* 6.4 Hz, Ar-*H*), 5.40 (1 H, d, *J* 5.9 Hz, Ar-*H*), 5.27 (1 H, d, *J* 5.9 Hz, Ar-*H*), 4.98 (1 H, d, *J* 6.4 Hz, Ar-*H*), 2.30-2.10 (1 H, m, Ar-C*H*$(CH_3)_2$), 1.89 (3 H, s, Ar-C*H*$_3$), 0.93 (3 H, d, *J* 6.9 Hz, Ar-CH(C*H*$_3$)$_2$), 0.69 (3 H, d, *J* 6.9 Hz, Ar-CH(C*H*$_3$)$_2$); δ_C(67.9 MHz, $CDCl_3$) 134.6(d, *J* 2.1 Hz), 134.0(d, *J* 4.1 Hz), 133.9(d, *J* 3.1 Hz), 133.3(s), 132.5(s), 132.4(s), 131.8(d, *J* 2.0 Hz), 131.7(s), 131.5(s), 130.8(s), 129.8(d, *J* 10.4 Hz), 129.4(d, *J* 10.4 Hz), 125.7(s), 125.5(d, *J* 9.4 Hz), 96.0(s), 95.9(s), 81.3(s), 80.6(s), 30.7(s), 22.8(s), 20.6(s), 18.4(s); δ_P (109 MHz, $CDCl_3$) 37.99; *m/z* (ES^+) 691.12 ($[M]^+$, 100 %).

Crystal structure analyses

X-ray crystal structures were determined for compounds **2-5** at -148(1) °C on a Rigaku ACTOR-SM, Saturn 724 CCD area detector with SHINE optic using Mo-Kα radiation (λ = 0.71073 Å). The data were corrected for Lorentz, polarisation and absorption. The data for the complexes analysed was collected and processed using CrystalClear

(Rigaku).[27] The structures were solved by direct methods[28] and expanded using Fourier techniques.[29] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure[30] and SHELXL-97.[31] Although several attempts were made the crystal quality for **2** was poor; the high residual peak cited is very close to the platinum centre.

Appendix A Supplementary Data

CCDC 766927-766930 contain the supplementary crystallographic data for <yyy>. These data can be obtained free of charge via http://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; or e-mail: deposit@ccdc.cam.ac.uk.

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Supporting Information Available

X-ray crystallographic files for **2-5**.

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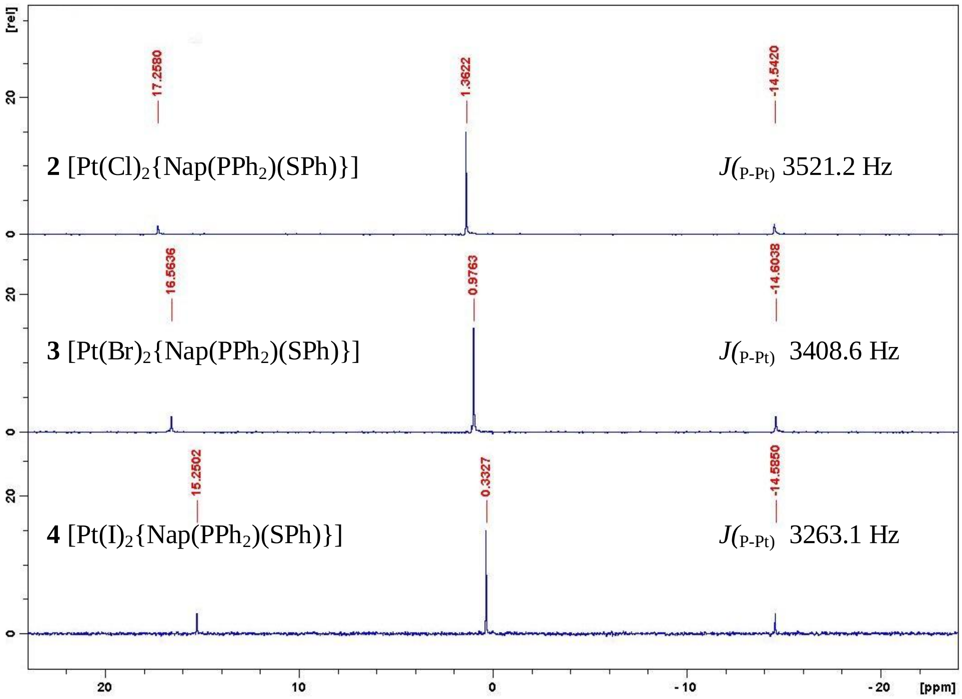

Fig. *^{31}P-{^{1}H} NMR spectra for the platinum halide complexes of* **1**, *showing the upfield shift with decreasing electronegativity of the halogen and decrease in the platinum-phosphorus coupling constant.*