Preparation of the First Complexes of Bidentate Sulfimides; the X-ray Crystal Structures of $[PdBr_2\{1,4\text{-}(PhS\{NH\})_2C_6H_4\}]_2$, $[PdCl_2\{1,2\text{-}(PhS\{NH\})(PhS)C_6H_4\}]$ and *trans*-$[PdCl_2\{1,2\text{-}(PhS\{NH\})(PhS)C_6H_4\}PPh_3]$

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Reaction of $[PPh_4]_2[Pd_2X_6]$ (where X = Cl, Br or I) with 1,4-$(PhS\{NH\})_2C_6H_4$ (**1**) in dichloromethane results in the formation of $[Pd\{1,4\text{-}(PhS\{NH\})_2C_6H_4\}X_2]_2$ (**2**). X-ray crystallography (performed using a synchrotron source) confirms that in the case where X = Br (**2a**) both the bis-sulfimides act as bridging ligands through N–Pd bonds producing an 18-membered ring system linking the four sulfur atoms into an almost perfect square. Changing the reaction solvent to methanol/dichloromethane results in the formation of a polymeric material. Reaction of $[PdCl_2(PhCN)_2]$ with 1,2-(PhS{NH})-(PhS)C_6H_4 (**3**) results in the formation of $[PdCl_2\{1,2\text{-}(PhS\{NH\})(PhS)C_6H_4\}]$ (**4**) in which **3** acts as a bidentate ligand, bound by N–Pd and S–Pd bonds to form a unique MSCCSN metallacycle. The Pd–S bond is broken upon reaction with one equivalent of PPh_3, generating *trans*-$[PdCl_2\{1,2\text{-}(PhS\{NH\})(PhS)C_6H_4\}PPh_3]$ (**5**); further reaction with PPh_3 results in complete removal of **3** from the system and formation of *trans*-$[PdCl_2(PPh_3)_2]$.

Introduction

Recent work within our group has demonstrated that the mononuclear sulfimide Ph_2SNH is an excellent ligand insofar as it readily forms N-bound complexes with a range of transition metal centres.[1] In addition, its importance as a ligand is enhanced by the fact that it is capable of stabilising unusual coordination geometries[2] and that significant hydrogen-bonding effects can be observed between the ligand and counterions.[3] In order to build upon these results, we have recently reported the preparation of a range of new sulfimide systems based upon polysulfide starting materials.[4] These include the bis-sulfimide 1,4-$(PhS\{NH\})_2C_6H_4$ (**1**) and the mixed sulfide/sulfimide 1,2-(PhS{NH})(PhS)C_6H_4 (**3**), both of which prove to have an interesting structure in their own right thanks to the appearance of hydrogen-bonding arrays generated by interactions between the sulfimide units and waters of crystallisation. They both also have clear potential as new ligands. Ligand **1** has the obvious potential to act as a bidentate bridge between two metal centres. Examples of such ligands are, of course, well-known and they can often act as the lynchpin for much important chemistry. By way of example, Godfrey et al. recently demonstrated the ability of 1,3-bis(diphenylphosphinoyl)propane to bridge manganese centres in binuclear complexes.[5] In this particular case the ligand is crucial to the product's ability to reversibly take up SO_2. Such properties highlight the need to investigate new ligand systems of this type, and here we demonstrate for the first time that **1** can act in this way and in doing so highlight the potential of an entirely new class of bidentate ligand. In the case of **3** the presence of both nitrogen and sulfur atoms capable of binding to metal centres provides the potential for the system to act as a bidentate chelating ligand. The use of ligands containing coordination sites of different binding strengths continues to be of importance (for example with the use of hemilabile ligands within catalytically important systems)[6] and here we show that **3** can indeed act as a bidentate ligand.

Results and Discussion

We have recently demonstrated that reaction of 1,4-$(PhS)_2C_6H_4$ with MSH (*O*-mesitylsulfonylhydroxylamine) results in the formation of a salt of the protonated bis-sulf-

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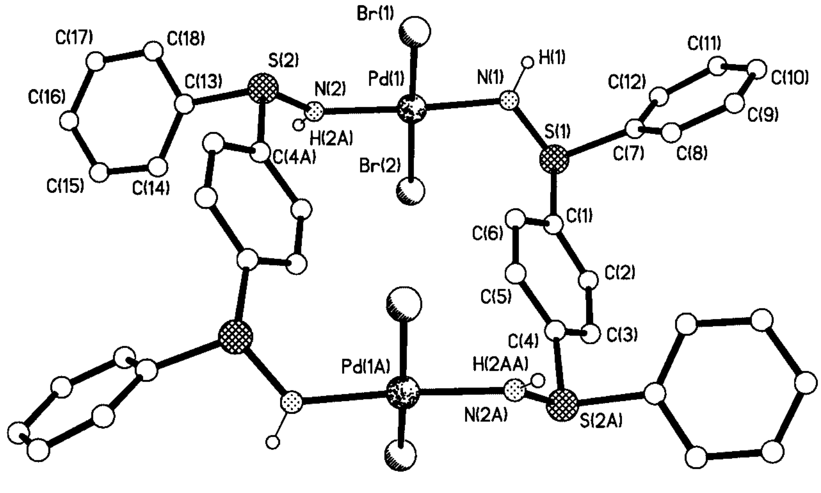


Figure 1. The X-ray crystal structure of one of the two unique molecules in the unit cell of **2a**; selected bond lengths (Å) and angles (°): Pd(1)−N(1) 2.020(5), Pd(1)−N(2) 2.025(5), Pd(1)−Br(1) 2.4411(9), Pd(1)−Br(2) 2.4227(9), N(1)−S(1) 1.622(5), N(2)−S(2) 1.618(5); Pd(1)−N(2)−S(2) 122.4(3), Pd(1)−N(1)−S(1) 122.2(3), Br(2)−Pd(1)−Br(1) 170.91(3), N(1)−Pd(1)−N(2) 174.7(2)

imide $[1,4\text{-}(PhS\{NH_2\})_2C_6H_4]^{2+}$ from which the free bis-sulfimide **1** may be generated by treatment with the base DBU. Compound **1** is an air-stable, colourless material which may be crystallised in hydrated or water-free forms, both of which have structures containing extended hydrogen-bonding arrays. In the light of the high affinity of the related monosulfimide Ph_2SNH for metal centres one might expect **1** to readily react with transition metal complexes and we have now found this to indeed be the case.

Reaction of a stirred suspension of **1** with $[PPh_4]_2[Pd_2Br_6]$ in CH_2Cl_2 results in the formation of an insoluble orange/red product **2a**. The IR spectrum of **2a** clearly indicates the presence of **1** as a ligand. We have previously shown that in complexes of Ph_2SNH the two key features which vary in the IR spectra are the SN and NH stretches, and in this case they are shifted from 928 and 3111 cm^{-1} respectively in the free ligand to 880 and 3260 cm^{-1} upon coordination. In addition, microanalysis confirms the formulation "$[PdBr_2\{1,4\text{-}(PhS\{NH\})_2C_6H_4\}]_n$", although, of course, it provides no information as to the value of *n*. Standard crystallisation techniques cannot be used upon **2a** as, once formed, it appears to be totally insoluble in a range of solvents. Small microcrystals of the product can, however, be obtained by changing the reaction conditions. If CH_2Cl_2 is added to a solid mixture of the two reagents without stirring, then a slow reaction occurs and **2a** forms as crystals large enough to be investigated by X-ray crystallography using a synchrotron source.

X-ray crystallography performed in this manner reveals that the structure of **2a** consists of two $PdBr_2$ units linked by two bis-sulfimide ligands, resulting in an overall binuclear 18-membered ring arrangement (Figure 1).

The resulting relative dispositions of the Pd−Br, P−N, S−N and bridging phenyl units are best illustrated by the side on view shown in Figure 2 (this illustrates the structure of one of the two independent molecules in the unit cell − see X-ray text below). The Pd−Br bonds are almost perpendicular to the Pd_2N_4 plane [N(2)−Pd(1)−Br(2) = 85.7°] while the S−N bonds of each of the ligands also project on either side of this plane (in what has been referred to as a "sofa-bed" arrangement).[7] The linking phenyl units of each ligand are parallel to each other and inclined at an angle of 52.8° to the Pd_2N_4 plane. Perhaps the most intriguing thing about the structure is that the positions of the sulfur atoms are such that they define an almost perfect square, with S(2)−S(1) = 6.325 Å, S(2)−S(1A) = 6.326 Å and S(1)−S(2)−S(1A) = 91.5°. As Figure 2 shows, the fact that the bridging phenyls are offset relative to each other precludes any π-π interactions. Unlike many of the complexes of Ph_2SNH we have previously investigated there appear to be no significant interactions between the N−H groups of the ligands and halide ligands of adjacent molecules.

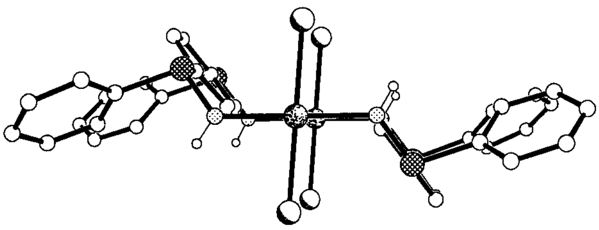
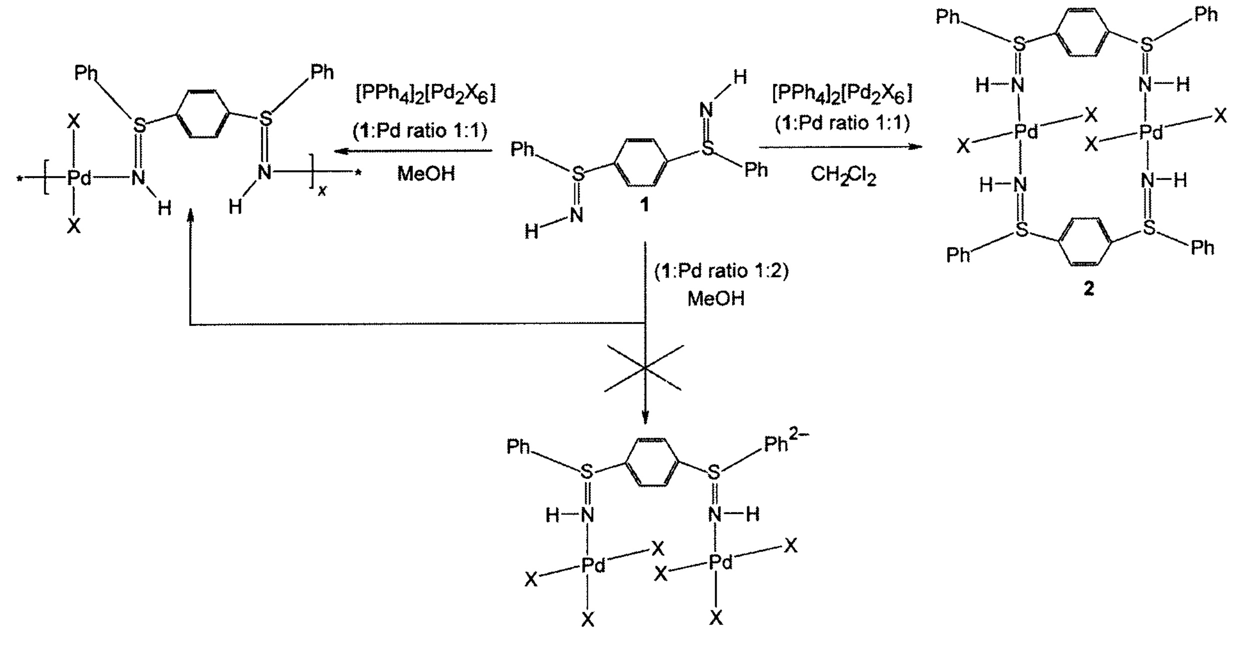


Figure 2. The X-ray crystal structure of **2a** viewed side-on, illustrating the relative disposition of the sulfimide groups and the bridging phenyls

Complex **2a** appears to be the only isolable material from this reaction. The initial yield equates to 67% based upon palladium and more of the same material is obtained when the reaction filtrate is treated with Et_2O. The latter procedure generates **2a** as an orange solid which does not then redissolve back into the CH_2Cl_2. From this observation we can conclude that a small amount of another, soluble, complex of **1** is present in the initial filtrate; however, all attempts to isolate this result in formation of **2a** and so it is difficult to speculate as to its nature. The reaction of $[PPh_4]_2[Pd_2I_6]$ with **1** appears to proceed in an identical manner to that of its bromo counterpart (Scheme 1). Again, the product is an insoluble orange/red material whose IR spectrum is extremely similar to that of **2a**. Taken together with microanalysis this allows us to formulate it as $[PdI_2\{1,4\text{-}(PhS\{NH\})_2C_6H_4\}]_2$ (**2b**) with confidence. Although we have yet to produce crystals suitable for X-ray crystallographic confirmation, we have every reason to believe that **2b** has the same kind of binuclear structure as **2a**. Likewise $[PdCl_2\{1,4\text{-}(PhS\{NH\})_2C_6H_4\}]_2$ (**2c**) forms in the analogous reaction with $[PPh_4]_2[Pd_2Cl_6]$; in this case microanalysis results indicate that the dichloromethane solvate forms. The IR spectrum of this material is, however, very similar to that of **2a** and **2b** and in this case Pd−Cl stretches at 346 and 304 cm^{-1} consistent with the *trans*-halides are observed.

The reaction time needed for the formation of compounds **2** is long (typically three days), a fact dictated by the insolubility of **1** in CH_2Cl_2. Although this would appear inefficient, in fact it is key to the formation of the binuclear product; changing the solvent system has a dramatic effect upon the course of the reaction (Scheme 1). Compound **1** is actually soluble in methanol and so addition of a solution of the ligand in this solvent to a solution of $[PPh_4]_2[Pd_2Br_6]$ in CH_2Cl_2 results in an immediate reaction. Again, an insoluble product is generated (with just $[PPh_4]Br$ left in solution, as shown by IR spectroscopy) but in this case rather than the bright orange red colour of **2a** the product is a pale brown colour. IR spectroscopy reveals the presence of bands due to **1** but the key stretches, ν[N−H] and ν[N−S], are both stronger and broader than those in **2a** and are shifted to 3220 and 897 cm^{-1}, respectively. Microanalysis supports the formulation $[PdBr_2\{1,4\text{-}(PhS\{NH\})_2C_6H_4\}]$ but unlike **2a** (which shows the peaks which may be predicted from the aforementioned single crystal data) the X-ray powder pattern of this product shows no discernible peaks. This leads us to believe that this product is an amorphous polymeric material rather than the binuclear structure of **2a**. Interestingly, it forms even when only one equivalent of **1** is used in the reaction. In this case the expected $[PPh_4]_2[(PdBr_3)_2\{1,4\text{-}(PhS\{NH\})_2C_6H_4\}]$ (in which the bis-sulfimide would link two $[PdBr_3]^-$ units) does not form. Rather, the polymeric material is generated, while the reaction filtrate contains just $[PPh_4]Br$ and unchanged $[PPh_4]_2[Pd_2Br_6]$ (as shown by IR spectroscopy). Given that it is reasonable to assume this reaction proceeds via a transient intermediate of the form $[PdBr_3\mathbf{1}]^-$ in which one of the nitrogen atoms of the ligand is bound to palladium, it would appear that the halide *trans* to N in this case is activated towards displacement by another nitrogen. Similar results are observed for reactions involving $[Pd_2Cl_2]^{2-}$ and $[Pd_2I_2]^{2-}$, generating insoluble polymeric products which are very pale brown and dark brown, respectively. The IR spectra of both products are analogous to that of the bromide product with broad ν[N−H] (3211 and 3217 cm^{-1} for chloride and iodide, respectively) and very broad ν[N−S] peaks (centred on 897 cm^{-1} in both cases).

It would appear, therefore, that only when the reaction of **1** with $[Pd_2X_6]^{2-}$ is slowed down by the use of CH_2Cl_2 as solvent is a molecular product seen; the use of methanol



Scheme 1

encourages the fast formation of a polymeric material. It should be noted, though, that in some solvents the reaction does not proceed at all. For example, if the reactions are attempted in MeCN then after three days of stirring the mixture simply consists of a suspension of unchanged **1** in the solution of the palladium starting material. As for the structure of the polymeric complexes we can only speculate that they possess a linear polymeric arrangement made up of alternating PdX_2**1** units. Of course other structural motifs could be envisaged and it may even be that the material contains a mixture of different oligomers (although we can be sure that none of the binuclear complex is present thanks to the IR and powder X-ray results); only single crystal X-ray crystallography would provide an unequivocal answer and we have yet to obtain crystalline samples. Once formed the material is totally insoluble in all solvents and techniques used to obtain single crystals of **2a** are not amenable in this case due to the fast reaction time.

Reaction of $[PdCl_2(PhCN)_2]$ with 1,2-(PhS{NH})(PhS)C_6H_4 (**3**; molar ratio 1:1) in CH_2Cl_2 results in the formation of an orange solution from which a mass of dark orange/red crystals appears upon standing overnight. X-ray crystallography reveals that this product is $[PdCl_2\{1,2\text{-}(PhS\{NH\})(PhS)C_6H_4\}]$ (**4**) in which **3** acts as a bidentate ligand bound to the palladium through the sulfimide nitrogen and the thioether sulfur (Figure 3) (Scheme 2).

The resulting metallacycle, which shows significant deviation from planarity (thus, for example, the two sulfurs ap-

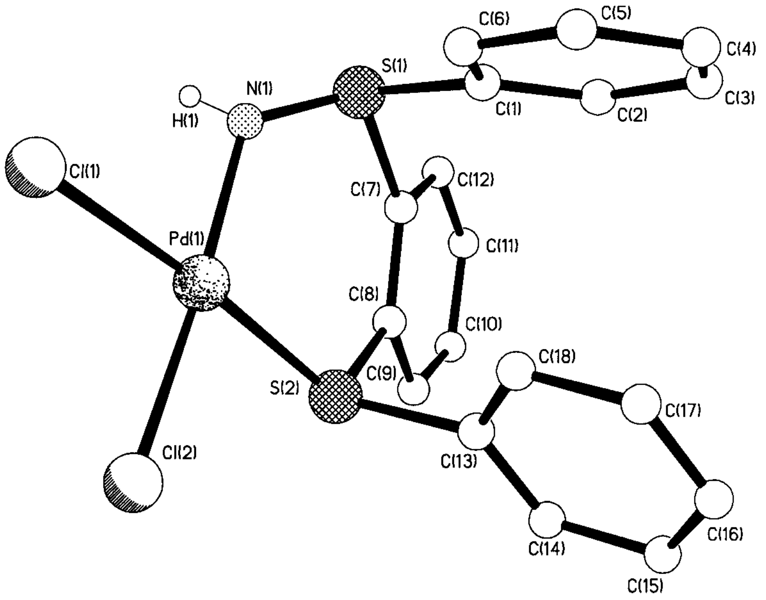
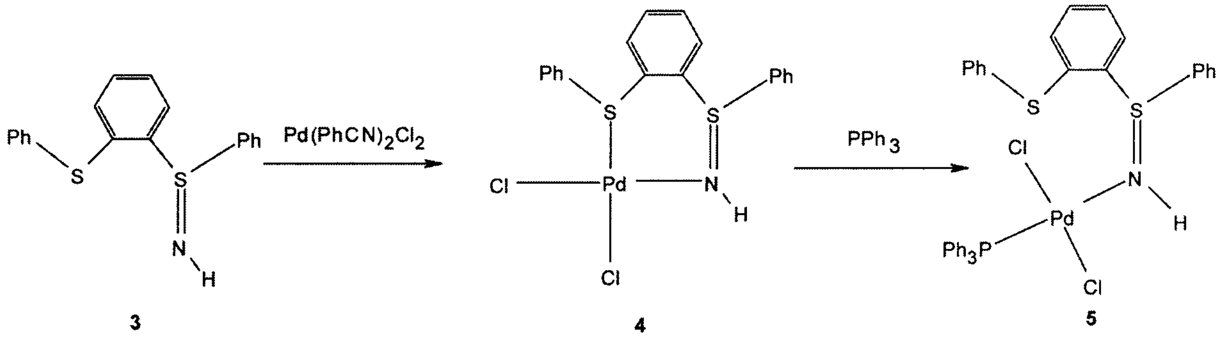


Figure 3. The X-ray crystal structure of **4**; selected bond lengths (Å) and angles (°): Pd(1)−N(1) 2.0203(19), N(1)−S(1) 1.5971(19), S(1)−C(7) 1.7969(2), C(7)−C(8) 1.396(3), C(8)−S(2) 1.791(2), S(2)−Pd(1) 2.2771(6), Pd(1)−Cl(1) 2.3056(6), Pd(1)−Cl(2) 2.3271(6); Pd(1)−N(1)−S(1) 128.28(11), N(1)−S(1)−C(7) 113.75(10), S(1)−C(7)−C(8)125.82(17), C(7)−C(8)−S(2) 126.45(17), C(8)−S(2)−Pd(1) 114.14(8), Cl(1)−Pd(1)−N(1) 85.58(6), Cl(2)−Pd(1)−S(2) 84.25(2)



Scheme 2

pear 0.2821 Å (S1) and 0.2162 Å (S2) above the mean plane of the six atoms in the metallacycle), constitutes a rare example of an XNSCCS ring. A search of the Cambridge Structural Database[8] reveals only eight examples within which such an arrangement is observed. As Figure 4 shows, the only examples (**a** and **b**) in which atom X is a metal contain a tridentate ligand.[9] The rest consist of the two examples shown wherein X is a nitrogen atom (**c** and **d**) together with four examples in which this atom is carbon (including the one shown, **e**).[10a−10f]

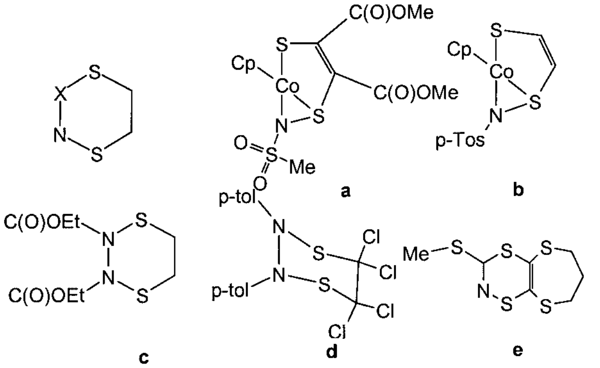


Figure 4. Previous examples of species exhibiting the XSCCSN cyclic unit observed in **4**

Perhaps the most intriguing feature of the structure of **4** is the fact that the molecules arrange themselves into dimers (Figure 5). These units are held together by hydrogen bonding between the N−H groups and chlorides of opposite molecules. The contact between molecules is close, with a Pd−Pd distance of 3.512 Å. Interestingly, this value is almost exactly the same as the closest Pd−Pd interactions in [Pd(S_2N_2H)(PMe_2Ph)$_2$][BF_4] which also has Pd attached to a sulfur and to an N−H unit on an S−N bond.[11] In that case a 1-D structure was formed by an infinite array of the cations; in the case of **4** this cannot take place as the orientation of the non-bridging phenyl groups — both to one side of the plane of each metallacycle — precludes the close approach of further molecules.

That the thioether group of **3** should coordinate to a metal centre is of no great surprise given that the coordination chemistry of such units is extensive. In general, however, such ligands are relatively weakly bound and, indeed, can often act as easily substituted leaving groups. Of the two coordination sites in **4** one would thus expect the Pd−S bond to be broken by an incoming ligand and this can be demonstrated by the reaction of **4** with triphenylphosphane. Slow addition of the solid phosphane to a stirred solution of **4** in CH_2Cl_2 results in lightening of the colour of the solution; removal of the solvent in vacuo followed by trituration with petroleum ether results in a yellow solid **5** (Scheme 2) The ^{31}P NMR spectrum of this solid ($CDCl_3$) consists of a singlet at $\delta = 27.7$ ppm while the IR spectrum confirms the presence of bands typically associated with both sulfimide units (911 cm^{-1}) and with phosphanes (1096 cm^{-1}). Slow diffusion of diethyl ether into a CH_2Cl_2 solution of the product results in the formation of orange crystals for which X-ray crystallography reveals the structure shown in Figure 6. As Figure 6 shows, **5** consists of a palladium centre coordinated to a PPh_3 ligand and to **3** (acting in this case as a monodentate N-bound ligand) bound in a *trans* fashion. Two *trans*-chloride ligands make up the rest of the coordination sphere.

The course of the reaction of **4** with PPh_3 thus involves two steps: substitution of the Pd−S bond by the phosphane, followed by isomerisation to the observed *trans* arrangement. Presumably the latter effect is brought about by the significant steric interactions that would be present between the six phenyl groups in the initially formed *cis*

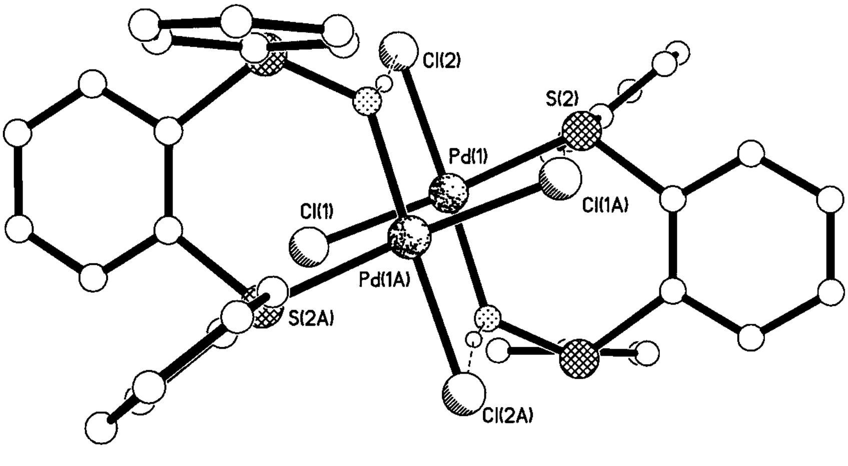


Figure 5. The formation of dimers within the overall structure of **4**; intra-dimer distances (Å) and angles (°): Pd(1)−Pd(1A) 3.512, S(2)−Cl(1A) 3.428, N(1)−Cl(2A) 3.469(2), N(1)−H(1)−Cl(2A) 165(3)

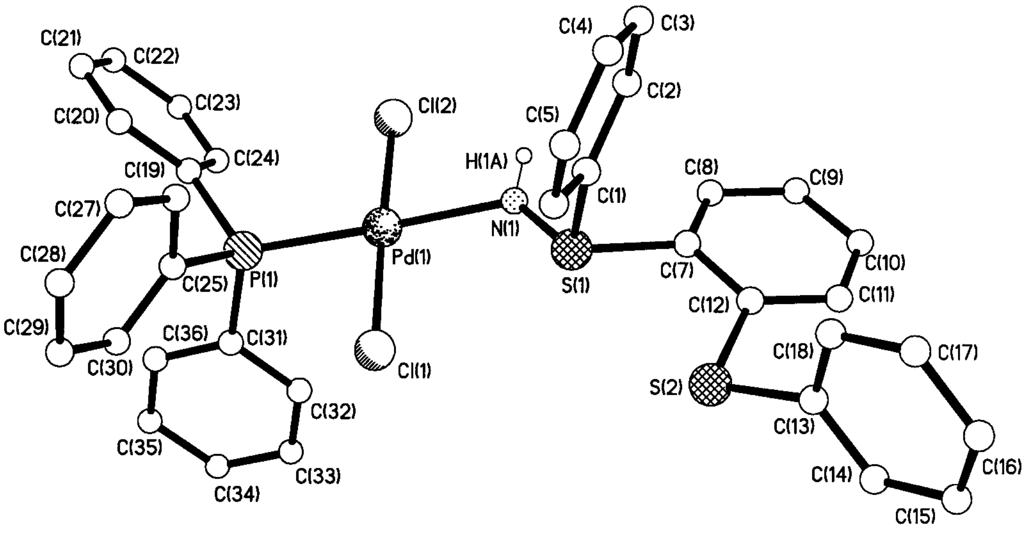


Figure 6. The X-ray crystal structure of **5**; selected bond lengths (Å) and angles (°): Pd(1)−N(1) 2.094(6), N(1)−S(1) 1.603(6), S(1)−C(7) 1.823(7), C(7)−C(12) 1.382(9), C(12)−S(2) 1.798(8), S(2)−C(13) 1.773(7), Pd(1)−Cl(1) 2.2873(18), Pd(1)−Cl(2) 2.3010(17), Pd(1)−P(1) 2.2331(14); Pd(1)−N(1)−S(1) 121.6(3), N(1)−S(1)−C(7) 106.0(3), S(1)−C(7)−C(12)115.9(6), C(12)−S(2)−C(13) 102.8(3), Cl(1)−Pd(1)−N(1) 94.79(18), Cl(2)−Pd(1)−N(1) 84.47(18)

intermediate. The ^{31}P chemical shift of the phosphane group is consistent with it being *trans* to an N−H unit.

Addition of the phosphane to **4** has to be very slow in order to obtain pure **5**. If this is not carefully observed then variable amounts of a yellow, far less soluble product are obtained. Microanalysis indicates that this product is $[PdCl_2(PPh_3)_2]$ and in such cases it appears in the ^{31}P NMR spectrum of the product as a peak at $\delta = 23.4$ ppm. The ability of PPh_3 to break the Pd−N bond as well as the Pd−S bond of the starting material can be confirmed by addition of one molar equivalent of the phosphane to **5**. This results in the immediate precipitation of the sparingly soluble $[PdCl_2(PPh_3)_2]$.

Conclusion

The isolation and full characterisation of **2a** (together with **2b** and **2c**) constitutes the first successful use of a bis-sulfimide system as a ligand. It is, therefore, the first example of the use of an entirely new class of bidentate ligand and this observation strongly suggests that many more examples of complexes of **1** should be isolable (although the observed polymer formation upon using methanol as solvent does highlight a problem which may need to be resolved in other systems). Such results also indicate that the coordination chemistry of other examples of bis-sulfimides should be extensive. Although (as shown in previous work) the *ortho*-isomer 1,2-$(PhS\{NH\})_2C_6H_4$ cannot be formed in the same manner as **1**, the mixed sulfimide/sulfide 1,2-$(PhS\{NH\})(PhS)C_6H_4$ **(3)** is known and the isolation of complex **4** confirms its potential as a chelating ligand. The isolation of **5** also confirms that the Pd−S bond within this molecule is significantly weaker than the Pd−N bond.

Experimental Section

Compounds **1** and **3** were prepared by the reaction of MSH with appropriate thioether starting materials.[4] Salts of the type $[PPh_4]_2[Pd_2X_6]$ were prepared from $PdCl_2$ (X = Cl or Br) as reported previously[12] or, in the case of X = I, by addition of a hot solution of NaI (20 mmol) and PdI_2 (2.2 mmol) in EtOH (100 mL) to a hot solution of $[PPh_4]I$ (2.2 mmol) in the same solvent (100 mL) followed by filtration. $[PdCl_2(PhCN)_2]$ was prepared by the dissolution of $PdCl_2$ into hot benzonitrile followed by precipitation with 60:80 petroleum ether. Microanalysis was performed by the Loughborough Departmental service. ^{31}P NMR spectra were recorded on a Jeol FX90Q spectrometer operating at 36.21 MHz. IR spectra were run on a Perkin Elmer PE2000 spectrometer.

$[PdBr_2\{1,4\text{-}(PhS\{NH\})_2C_6H_4\}]_2$ (2a): A solution of $[PPh_4]_2[Pd_2Br_6]$ (0.102 g, 0.074 mmol) in CH_2Cl_2 (20 mL) was treated with **1** (0.05 g, 0.15 mmol) added in one portion with stirring. The resulting mixture was then stirred for three days during which time a red/orange precipitate formed. The latter was filtered from the solution, washed with CH_2Cl_2 (50 mL), Et_2O (20 mL) and then dried in vacuo yielding 60 mg of red/orange solid. A further 10 mg was obtained when the filtrate was treated with Et_2O. Total yield 70 mg, 79%. $C_{36}H_{32}Br_4N_4S_4Pd_2$ (1181.3): calcd. C 36.8, H 2.7, N 4.8; found C 36.3, H 2.6, N 4.4. IR (KBr): $\tilde{\nu} = 3260$ cm^{-1} (ν N−H), 880 (ν N−S).

Microcrystalline material of sufficient size for use in synchrotron X-ray crystallography was generated by a variation on the above procedure wherein the starting materials were mixed (in the same amounts as above) as solids and then the CH_2Cl_2 added without stirring. After one week the solution was decanted from the resulting crystalline mass which was then washed with CH_2Cl_2. The IR spectrum of the material prepared this way was identical to that prepared above.

$[PdI_2\{1,4\text{-}(PhS\{NH\})_2C_6H_4\}]_2$ (2b): This was prepared as a red/orange solid by reaction of $[PPh_4]_2[Pd_2I_6]$ (0.202 g, 0.122 mmol) with **1** (0.079 g, 0.244 mmol) in exactly the same way as for **3**. Yield 105 mg, 63%. $C_{36}H_{32}I_4N_4Pd_2S_4$ (1369.3): calcd. C 31.6, H 2.4, N 4.1; found C 31.9, H 2.4, N 4.1. IR (KBr): $\tilde{\nu}$ = 3260 cm^{-1} (ν N−H), 880 (ν N−S).

$[PdCl_2\{1,4\text{-}(PhS\{NH\})_2C_6H_4\}]_2\cdot CH_2Cl_2$ (2c): This was prepared as a red/orange solid by reaction of $[PPh_4]_2[Pd_2Cl_6]$ (0.082 g, 0.077 mmol) with **1** (0.050 g, 0.154 mmol) in exactly the same way as for **3**. Yield 45 mg, 61%. $C_{37}H_{34}Cl_6N_4Pd_2S_4$ (1088.5): calcd. C 40.8, H 3.1, N 5.1; found C 40.3, H 3.1, N 4.8. IR (KBr): $\tilde{\nu}$ = 3260 cm^{-1} (ν N−H), 898 (ν N−S).

$[PdCl_2\{1,2\text{-}(PhS\{NH\})(PhS)C_6H_4\}]$ (4): A solution of $[PdCl_2(PhCN)_2]$ (0.176 g, 0.460 mmol) in dichloromethane (10 mL) was treated with a solution of 1,2-(PhS{NH})(PhS)C_6H_4 (0.142 g, 0.460 mmol) in an equal volume of the same solvent added dropwise with stirring. After addition of the ligand a precipitate was present which then redissolved after a minute of stirring. The solution was then left to stand for 48 hours and the resulting orange/red or brown crystals were collected. Yield: 0.165 g (86%). $C_{18}H_{15}Cl_2NPdS_2$ (486.7): calcd. C 44.4, H 3.1, N 2.9; found C 44.4, H 3.0, N 2.8. IR (KBr): $\tilde{\nu}$ = 3215, 3053, 944 cm^{-1}.

***trans*-$[PdCl_2\{1,2\text{-}(PhS\{NH\})(PhS)C_6H_4\}PPh_3]$ (5):** A solution of **4** (0.039 g, 0.08 mmol) in dichloromethane (10 mL) was treated with solid PPh_3 (21 mg, 0.08 mmol) added slowly in small portions with vigorous stirring. After complete addition of the PPh_3 the clear solution was reduced in volume and petroleum ether 40:60 (50 mL) was added. The resulting solid was then recrystallised from dichloromethane/Et_2O giving orange crystals. Yield: 0.036 g (61%). $C_{36}H_{30}Cl_2NPPdS_2$ (749.0): calcd. C 57.2, H 3.9, N 1.7; found C 57.7, H 4.0, N 1.9. ^{31}P NMR ($CDCl_3$): δ = 27.7 ppm. IR (KBr): $\tilde{\nu}$ = 3294, 3048, 1096, 911 cm^{-1}.

X-ray Crystallographic Study: Data (Table 1) for **2a** were collected at 150 K on a Bruker AXS SMART 1 K CCD area-detector diffractometer using synchrotron radiation (λ = 0.6879 Å) at Daresbury SRS Station 9.8.[13,14] Absorption correction was applied semi-empirically from equivalent and repeated data. The structure was solved by direct methods and refined by full-matrix least-squares on F^2. The asymmetric unit comprises two half molecules on centres of symmetry. Some disorder is present within one of the molecules with alternative positions for the sulfimide SNH unit with 90.4:9.6 (4)% refined occupancies. Hydrogen atoms were placed in geometrical positions and allowed to ride on their attached atom with U_{iso}(H) set to be 1.2 times U_{eq} of the carrier atom.

Data for **4** and **5** were collected at 150 K with a Bruker AXS SMART 1000 CCD diffractometer using Mo-K_α radiation (λ = 0.71073 Å). Both structures were solved by Patterson synthesis and refined by full-matrix least-squares methods on F^2. NH hydrogens were located from the difference map and their coordinates were freely refined. All other hydrogens were placed in geometrical positions using a riding model as described above. Some disorder is present in **5** with alternative positions for the sulfur and nitrogen atoms with refined occupancies of 84.0:16.0 (5)%.

The programs used were Bruker SMART,[15a] SAINT,[15a] SHELXTL[15b] and local programs.

CCDC-176115 (**2a**), -186575 (**4**) and -186576 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html

Table 1. Crystallographic data of **2a**, **4**, **5**

Compound	**2a**	**4**	**5**
Formula	$C_{36}H_{32}Br_4N_4Pd_2S_4$	$C_{18}H_{15}Cl_2NPdS_2$	$C_{36}H_{30}Cl_2NPPdS_2$
Mol. wt.	1181.34	486.73	749.00
Crystal dimensions	0.070 × 0.020 × 0.005	0.19 × 0.11 × 0.08	0.33 × 0.15 × 0.05
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	8.4402(15)	9.5236(8)	9.5178(7)
b (Å)	11.044(2)	10.7767(9)	9.9441(7)
c (Å)	22.519(4)	11.1578(9)	17.7459(13)
α (°)	94.962(3)	61.497(2)	90.768(2)
β (°)	98.383(3)	66.767(2)	99.786(2)
γ (°)	101.418(2)	67.985(2)	96.508(2)
V (Å^3)	2021.2(6)	899.72(13)	1643.6(2)
Z	2	2	2
Absorption coefficient, μ (mm^{-1})	5.082	1.560	0.930
Min. and max. transmission	0.717 and 0.975	0.756 and 0.885	0.749 and 0.955
θ range (°)	1.83 to 25.46	2.15 to 28.89	2.06 to 25.00
Wavelength (Å)	0.6877	0.71073	0.71073
Decay	20%	0%	0%
Measured reflections	16679	7941	12081
Independent reflections	8215	4144	5772
Observed reflections [$F^2 > 2\sigma(F^2)$]	5244	3678	4576
R_{int}	0.0430	0.0142	0.0276
R [$F^2 > 2\sigma(F^2)$][a]	0.0453	0.0236	0.0553
$wR2$ [all data][b]	0.0991	0.0622	0.1313
Largest difference map features (e·Å^{-3})	0.942 and −1.144	0.953 and −0.698	2.943 and −1.503

[a] $R = \|F_o\| - |F_c\|/|F_o|$. [b] $wR2 = \{[w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]\}^{1/2}$.

[or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] P. F. Kelly, A. C. Macklin, A. M. Z. Slawin, K. W. Waring, *Polyhedron* **2000**, *19*, 2077−2081 and references therein.

[2] P. F. Kelly, A. M. Z. Slawin, K. W. Waring, *J. Chem. Soc., Dalton Trans.* **1997**, 2583−2584.

[3] P. F. Kelly, A. M. Z. Slawin, K. W. Waring, *Inorg. Chem. Commun.* **1998**, *1*, 249−250.

[4] M. R. J. Elsegood, K. E. Holmes, P. F. Kelly, J. Parr, J. M. Stonehouse, *New. J. Chem.* **2002**, *26*, 202−206.

[5] W. I. Cross, S. M. Godfrey, C. A. McAuliffe, R. G. Pritchard, *Chem. Commun.* **2001**, 1764−1765.

[6] See, for example: A. Bader, E. Lindner, *Coord. Chem. Rev.* **1991**, *108*, 27−110.

[7] A. G. Constable, W. S. McDonald, B. L. Shaw, *J. Chem. Soc., Dalton Trans.* **1979**, 1109−1111.

[8] F. H. Allen, O. Kennard, *Chem. Des. Autom. News* **1993**, *8*, 1; F. H. Allen, O. Kennard, *Chem. Des. Autom. News* **1993**, *8*, 31−37.

[9] M. Nomura, T. Yagisawa, C. Takayama, T. Sugiyama, Y. Yokaguma, K. Shimizu, A. Sugimori, M. Kajitani, *J. Organomet. Chem.* **2000**, *611*, 376−385.

[10] [10a] V. A. Starodub, *J. Struct. Chem.* **1998**, *39*, 88−92. [10b] M. R. Bryce, G. R. Davison, A. S. Batsanov, J. A. K. Howard, *J. Chem. Soc., Perkin Trans. 1* **1992**, 2295−2302. [10c] M. R. Bryce, S. Yoshida, A. S. Batsanov, J. A. K. Howard, *J. Chem. Soc., Perkin Trans. 1.* **1997**, 1157−1161. [10d] M. R. Bryce, G. R. Davison, A. S. Batsanov, J. A. K. Howard, *J. Chem. Soc., Chem. Commun.* **1992**, 478−480. [10e] K. T. Potts, J. S. Baum, *J. Heterocycl. Chem.* **1991**, *28*, 1637−1639. [10f] K.-H. Linke, H. G. Kalker, *Z. Anorg. Allg. Chem.* **1977**, *434*, 157−164.

[11] R. Jones, P. F. Kelly, D. J. Williams, J. D. Woollins, *J. Chem. Soc., Dalton Trans.* **1988**, 803−807.

[12] P. F. Kelly, A. M. Z. Slawin, A. Soriano-Rama, *J. Chem. Soc., Dalton Trans.* **1996**, 53−59.

[13] R. J. Cernik, W. Clegg, C. R. A. Catlow, G. Bushnell-Wye, J. V. Flaherty, G. N. Greaves, I. Burrows, D. J. Taylor, S. J. Teat, M. Hamichi, *J. Synchrotron Rad.* **1997**, *4*, 279−286.

[14] W. Clegg, M. R. J. Elsegood, S. J. Teat, C. Redshaw, V. C. Gibson, *J. Chem. Soc., Dalton Trans.* **1998**, 3037−3039.

[15] [15a] SMART and SAINT software for CCD diffractometers, Bruker AXS Inc, Madison, WI, **1994**. [15b] G. M. Sheldrick. *SHELXTL user manual*, version 5, Bruker AXS Inc., Madison, WI, **1994**.

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