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Reactions of mono- and bis-*N*-bromosulfimides with thio-ether crowns, phosphines and selenides

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The brominated sulfimide Ph_2SNBr reacts with diphosphines 1,2-$(PPh_2)_2C_2H_4$ and 1,4-$(Ph_2P)_2(C_6H_4)$ to give the bis-*N*-phosphoniosulfimidium cations [1,2-$(Ph_2PNSPh_2)_2C_2H_4]^{2+}$ and [1,4-$(Ph_2PNSPh_2)_2(C_6H_4)]^{2+}$, respectively. Treatment of the bis-sulfimide 1,4-$[PhSNH]_2C_6H_4$ with *N*-bromosuccinimide results in 1,4-$[PhSNBr]_2C_6H_4$, which in turn reacts with triphenylphosphine to generate [1,4-$(PhS\{NSPPh_3\})_2C_6H_4]Br_2$. Both Ph_2SNBr and 1,4-$[PhSNBr]_2C_6H_4$ react with the thio-ether crown [9-ane]S_3, giving [9[ane]S_3NSPh_2]Br and [1,4-{[9-ane]$S_2S(NSPh)_2C_6H_4]Br_2$, respectively. The first examples of seleniosulfimidium salts have been isolated from the reactions of Ph_2SNBr and 1,4$(PhS\{NBr\})_2C_6H_4$ with Ph_2Se and the structures of the $[Ph_2SNSePh_2]^+$ and [1,4-$(PhSNSePh_2)_2C_6H_4]^{2+}$ cations confirmed by X-ray crystallography. Reaction of 1,2-$PhS(NH)C_6H_4SPh$ with one equivalent of *N*-bromosuccinimide followed by addition of $Na[BPh_4]$ results in [1,2-$(PhS)_2(\mu\text{-}N)C_6H_4][BPh_4]$ in which a CCSNS ring is observed; two forms of this material may be isolated upon crystallisation—X-ray crystallography reveals them to differ by the relative orientations of the phenyl rings.

Introduction

In the course of recent work we have been able to demonstrate that the sulfimide Ph_2SNH can act as an excellent ligand towards a range of metal centres.[1] Particular interest in the results stems not only from the ability of the ligand to stabilise unusual combinations of coordination geometries but also from the extensive hydrogen-bonding effects seen in the resulting complexes. An obvious strategy for building upon such results comes in the form of the preparation of structural variations upon the original ligand and we have gone some way towards this by looking at the chemistry of bis-sulfimides and mixed sulfide/sulfimides.[2] The first examples of both such species were reported in this journal[3] and subsequently shown to act as effective ligands.[2] Similarly, we have been able to isolate the first examples of complexes of the substituted sulfimide $Ph_2SN(CH_2)_2CN$.[4] In order to pave the way for investigations into more substantial variations upon the original ligand, we have now begun to investigate reactions of *N*-halosulfimides with a variety of species. Only a few reports currently exist on the synthesis, properties and reactions of these compounds.[5]

N-Halosulfimides, usually prepared by the reaction of an *N*-unsubstituted sulfimide and *N*-bromo- or *N*-chlorosuccimide in an inert solvent, are known to react with a variety of sulfides, phosphines and tertiary amines to form *N*-substituted sulfimidium salts according to eqn. (1):

$$R_2SNX + ER'_n \rightarrow [R_2SNER'_n]^+ X^-, \quad (E = S,\ P \text{ or } N \text{ and } X = \text{halide}) \quad (1)$$

There is, however, little structural information available on the products of such reactions. One example of a fully elucidated system comes in the form of the $[Ph_2SNSPhMe]^+$ cation, generated in the reaction of *N*-bromodiphenylsulfimide with methylphenylsulfide. For the X-ray study the resulting bromide salt was converted to the perchlorate and crystallography revealed an S–N–S angle of 109.6(5)°, suggesting a tetrahedral conformation around the nitrogen atom, with S–N distances of 1.60(1) (N–SPh_2) and 1.67(1) Å.[6] Similarly, the symmetric $[Me_2SNSMe_2]^+$ cation has been structurally characterised and exhibits an S–N–S angle 110.8° and S–N bond lengths almost symmetrical at 1.63 and 1.64 Å.[7] The only other structurally characterised compound of this type is the *N*-phosphoniosulfimide $[Ph_3PNSPh_2][SbCl_6]$,[8] formed by the reaction of *N*-chlorodiphenylsulfimide and triphenylphosphine, which has S–N and P–N distances of 1.60(1) Å and an S–N–P angle of 123.6(8)°.

In order to increase the amount of structural data available for such compounds and to increase the diversity of systems of this type, we have now undertaken a variety of novel reactions within this area. Specifically we have aimed to:

(i) Determine the ability of bis-phosphines to undertake such reactions.

(ii) Determine the ability of our recently reported example of a bis-sulfimide, 1,4-$[PhSNH]_2C_6H_4$, to act as source of the corresponding brominated sulfimide and then to undergo reactions analogous to those noted above.

(iii) Undertake the first investigation of the reactivity of a thio-crown system towards halosulfimides.

(iv) Investigate the possibility of generating S–N–Se systems *via* reaction with a selenide.

(v) Determine the ability of the mixed sulfide/sulfimide system 1,2-$(PhS\{NH\})(PhS)C_6H_4$ to undergo intramolecular ring closure reactions *via* halosulfimide formation.

Results and discussion

Preparation of new *N*-phosphoniosulfimidium salts

A specific aim of this area of the work was to generate systems in which more than one cationic PNS unit is present. There are two approaches that may be taken to the formation of such

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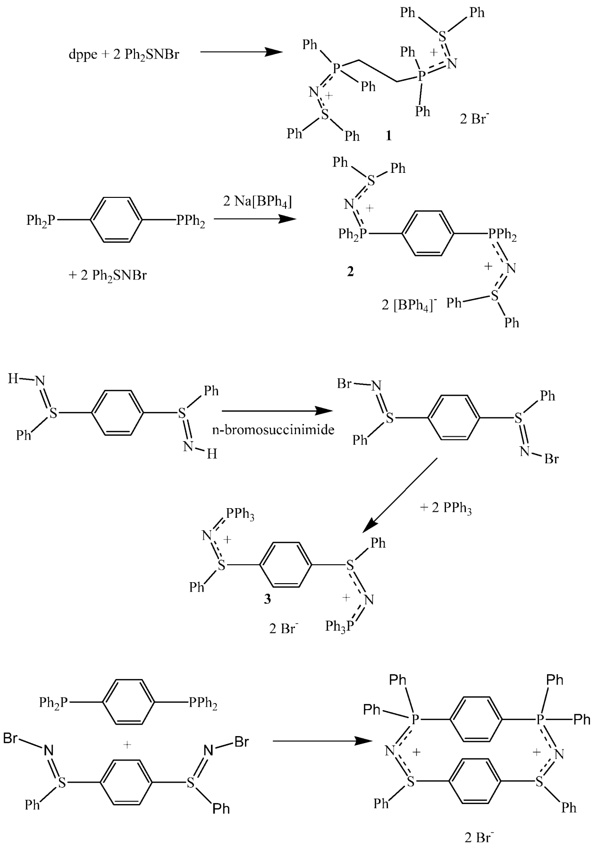
systems, namely reaction of Ph_2SNBr with bis-phosphines or, alternatively, the reaction of monophosphines with bis-bromosulfimides. Here we present examples of both classes of reaction.

Reaction of 2 equiv of Ph_2SNBr with $1,2\text{-}(PPh_2)_2C_2H_4$ (Scheme 1) results in the formation of colourless $[1,2\text{-}(Ph_2PNSPh_2)_2C_2H_4]Br_2$ (**1**), which may be crystallised by slow diffusion of Et_2O into a CH_2Cl_2 solution. X-Ray crystallography confirms (Fig. 1) that the cation contains two $PNSPh_2$ units, within which S–N and P–N distances of 1.6224(14) and 1.6101(14) Å, respectively, are observed.

One of the most striking features of the structure of **1** is the fact that the $PNSPh_2$ units take up positions on opposite sides of the central axis defined by the ethyl backbone. This presumably reduces steric interactions, which would be significant if both units were aligned on the same side of the backbone; this effect does, however, also manifest itself in the structure of the $[1,4\text{-}(Ph_2PNSPh_2)_2(C_6H_4)]^{2+}$ cation (Fig. 2), in which the $PNSPh_2$ units are separated by the intervening phenyl group.

This cation is made in the same manner as **1**, by reaction of $1,4\text{-}(Ph_2P)_2(C_6H_4)$ with 2 equiv of Ph_2SNBr; in this case subsequent reaction with $Na[BPh_4]$ allows isolation of $[1,4\text{-}(Ph_2PNSPh_2)_2(C_6H_4)][BPh_4]_2$, **2**, which is more readily crystallised than the bromide salt (an effect which will be noted for many of the systems within this study). In the case of **2** the S–N bonds are seen to be parallel to each other and at 26° to the central phenyl; the P–N bonds point in the opposite direction relative to the phenyl bridge, at an angle of 39°. A comparison of bond distances to those in **1** reveals the S–N distance to be significantly shorter in **2** at 1.605(6) Å; both this and the P–N distance [1.603(6) Å)] are consistent with substantial double bond character of both bonds and delocalisation of the positive charge across the SNP unit.

Interestingly, if such reactions are performed in an equimolar ratio, the addition of the Ph_2SN unit to one phosphine appears to activate the other to oxidation. Thus, in the 1:1 reaction of Ph_2SNBr with dppe the principal product appears to be the oxide $[1,2\text{-}(Ph_2PNSPh_2)(Ph_2PO)C_2H_4]^+$ unless the reaction is performed under rigorously anaerobic conditions.



Scheme 1

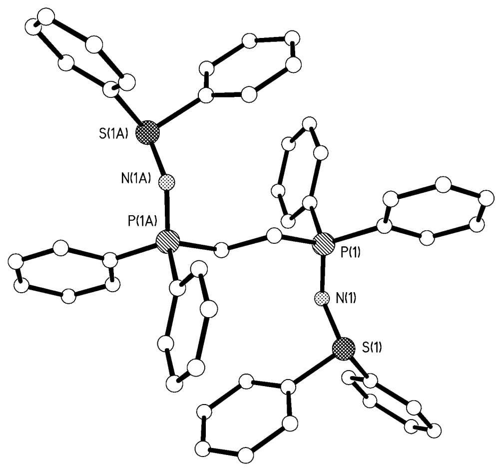


Fig. 1 The crystal structure of the cation in **1**. Selected bond lengths and angles (see text also): N(1)–S(1) 1.6224(14), N(1)–P(1) 1.6101(14) Å; S(1)–N(1)–P(1) 120.68(8)°.

In previous work we reported the isolation of the first example of a bis-sulfimide, namely $1,4\text{-}[PhSNH]_2C_6H_4$. Reaction of this compound with *N*-bromosuccinimide proceeds in an entirely analogous manner to that of monosulfimides and $1,4\text{-}[PhSNBr]_2C_6H_4$ may be isolated as a yellow solid. The reactivity of this mirrors that of Ph_2SNBr in that treatment with PPh_3 generates $[1,4\text{-}(PhS\{NSPPh_3\})_2C_6H_4]Br_2$ (**3**). The X-ray crystal structure of **3** (Fig. 3) confirms the presence of the two cationic SNP units; unlike in the structure of **2** the N–S and P–N bonds are much closer to being in the same plane as the central phenyl unit.

The results thus show that brominated monosulfimides react with diphosphines and that brominated bis-sulfimides react with monophosphines. This raises the possibility of combining the two reaction strategies and generating cyclic structures by reaction of a brominated bis-sulfimide with a diphosphine. The reaction chosen was that of $1,4\text{-}(PhSNBr)_2C_6H_4$ with $1,4\text{-}(Ph_2P)_2(C_6H_4)$ in the hope of generating the structure shown in Scheme 1. The reaction was performed using high dilution conditions in order to suppress the formation of polymeric species. After removal of the solvent, a sticky solid resulted for which ^{31}P NMR revealed a mixture with a strong peak at 36.6 ppm, a shift similar to those found in the other S–N–P compounds. Although this species could still be construed as polymeric, the high solubility and mass spectrometry of this

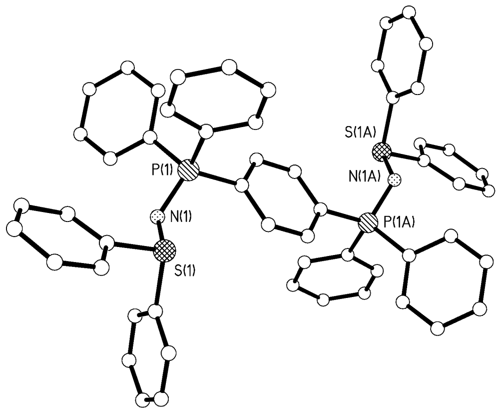


Fig. 2 The cation in **2**. Selected bond lengths and angles (see text also): N(1)–S(1) 1.605(6), N(1)–P(1) 1.603(6) Å; S(1)–N(1)–P(1) 125.2(4)°.

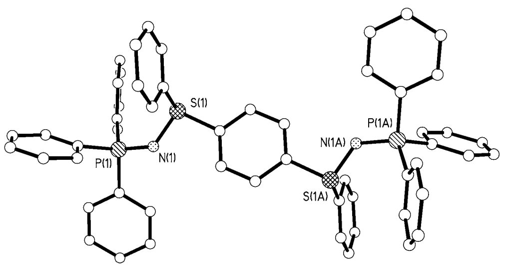


Fig. 3 The crystal structure of the cation in **3**. Selected bond lengths and angles (see text also): N(1)–S(1) 1.599(3), N(1)–P(1) 1.599(3) Å; S(1)–N(1)–P(1) 125.84(18)°.

product suggested otherwise, the latter revealing the highest peak at m/z 770, consistent with the tentative formulation. Microanalysis of this product was, however, unsatisfactory, thus conversion to the BPh_4^- salt was attempted and treatment of the solid with $Na[BPh_4]$ in MeOH resulted in a solid that can tentatively be formulated as cyclo-$[(Ph)SNP(Ph)_2C_6H_4P(Ph)_2NS(Ph)C_6H_4][BPh_4]_2$, exhibiting only a single peak in the ^{31}P NMR at 35.6 ppm as well as a peak for the molecular ion in electrospray mass spectrometry. Unfortunately, despite repeated attempts we have thus far been unable to grow single crystals of this material and so ultimate confirmation of the structure remains elusive.

Preparation of new *N*-sulfoniosulfimidium salts and the first examples of *N*-seleniosulfimidium salts

While Ph_2SNBr has been shown to react with simple organo monosulfides, the analogous reactivity towards polysulfide systems has not been reported. Here we have gone some way towards addressing this by investigating the ability of the bromosulfimide to react with the thio-crown $[9\text{-ane}]S_3$ (Scheme 2). In part this was prompted by the fact that previous work in this group resulted in a series of azasulfonium salts generated by the reaction of $[9\text{-ane}]S_3$ with the aminating agent *O*-mesitylsulfonylhydroxylamine (MSH).[9] In the course of such reactions one or more of the sulfur atoms of the crown were converted through to $S{=}NH_2^+$ groups, indicating that this crown is susceptible to sulfimidation.

Reaction of $9[\text{ane}]S_3$ with 1 equiv of Ph_2SNBr in CH_2Cl_2 results in the formation of an oily solid after removal of the solvent. Washing of the solid with ether eventually leaves a white solid that analyses (CHN) as the desired product, namely $[9[\text{ane}]S_3NSPh_2]Br$. Attempts to crystallise this product have so far proved unsuccessful; upon conversion to the $[BPh_4]^-$ salt (by addition of $Na[BPh_4]$), however, the product **4** can be readily crystallised. The X-ray crystal structure of this material reveals (Fig. 4) the desired mono-substituted thioether crown, with the sulfoniosulfimidium unit exhibiting an S–N–S angle of 108.55(10)° and S–N distances of 1.6433(17) Å and N–S(crown) 1.6559(17) Å. Interestingly, the latter distance is almost identical to the S–N distance in the cation $\{[9\text{-ane}]S_3(NH_2)\}^+$ ([1.642(2) Å].[9]

The ^1H NMR of **4** shows the thia-crown protons as three pairs of signals in an AB pattern each consisting of eight-line multiplets. Three signals are observed in the aliphatic region of the ^{13}C NMR spectrum, consistent with the solid-state structure not being retained in solution. A similar effect was noted in the case of $\{[9\text{-ane}]S_2SNH_2\}^+$.

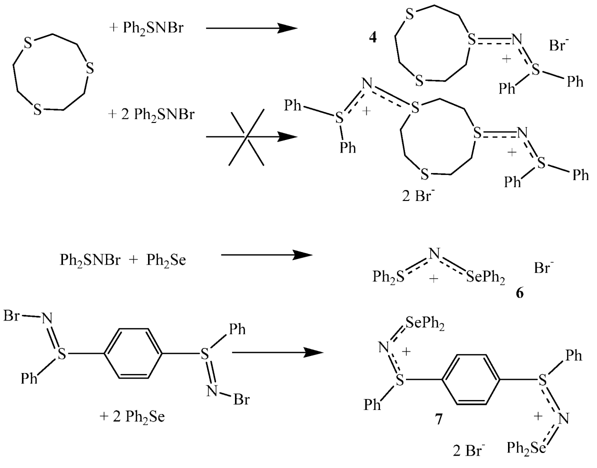
Addition of further Ph_2SNBr does not appear to result in the addition of more Ph_2SN units to the structure. This contrasts to the reaction of the crown with MSH during which addition of two sulfimidium units was shown to be possible. Presumably in this case the steric bulk of the phenyl groups on the incoming units mitigates against addition of more than one.

As noted above, $1,4\text{-}[PhSNBr]_2C_6H_4$ is readily prepared from the corresponding free bis-sulfimide and just as this compound reacts analogously to Ph_2SNBr when treated with phosphines, it also reacts with $[9\text{-ane}]S_3$. Reaction of 2 equiv of the crown with 1 equiv of the bis-sulfimide results in the formation of $[1,4\text{-}\{[9\text{-ane}]S_2S(NSPh)\}_2C_6H_4]Br_2$, **5**, in which a crown unit is added to both sulfimide units of the starting material. Unfortunately, even after conversion to the $[BPh_4]^-$ salt we have been unable to crystallise this material and obtain structural confirmation *via* X-ray crystallography.

Although a number of previous reports exist of reactions between *N*-halosulfimides with sulfides, phosphines and tertiary amines, there is, to the best of our knowledge, no report of a reaction with selenides. In order to address this omission, we investigated the reactivity of both Ph_2SNBr and $1,4\text{-}[PhSNBr]_2C_6H_4$ towards Ph_2Se.

Reaction of Ph_2SNBr with Ph_2Se in CH_2Cl_2 results in the formation of the *N*-seleniosulfimidium salt $[Ph_2SNSePh_2]Br$, **6**, isolated as a colourless solid after removal of the solvent and trituration with ether. It is noteworthy that this reaction is significantly faster and more efficient than the corresponding reaction with Ph_2S (which is reported to occur at high temperatures, though in our hands we have found even then that the yield is low; this is one reaction that appears to be more efficient using Ph_2SNCl).

The X-ray crystal structure of **6** (Fig. 5) reveals the $[Ph_2SNSePh_2]^+$ cation is disordered with the S and Se sites partially occupied by both elements. This disorder, which results from the symmetric nature of the molecule, has been refined to give the relative occupancies of $[Ph_2SNSePh_2]^+$: $[Ph_2SeNSPh_2]^+$ as 83.2:16.8(2)%. This disorder makes it rather difficult to compare the S–N and Se–N bond lengths as each



Scheme 2

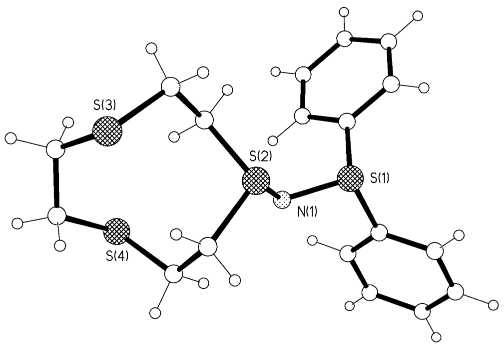


Fig. 4 The crystal structure of the cation of **4**. Selected bond angles (see text also): C(18)–S(2)–C(13) 105.94(9)°, C(14)–S(3)–C(15) 103.43(11)°, C(16)–S(4)–C(17) 105.03(11)°.

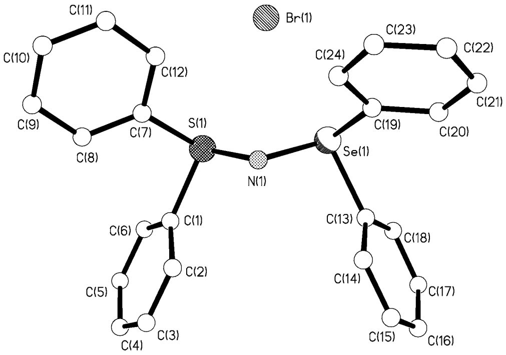


Fig. 5 The crystal structure of **6**.

will have some character of the minor component. If we consider the Se–N bond length, for example, the true value for this bond will be longer than that observed as the partial sulfur character will act to shorten the bond. The opposite is true for the corresponding S–N bond length. Although the bond lengths obtained from the crystal structure cannot be quoted reliably, relative effects can be observed. The Se–N bond length within **6** is observed to be 1.832(3) Å with the S–N bond at 1.678(3) Å and an S–N–Se angle of 107.61(15)°. The sulfur character means that the true Se–N bond is longer than this value. Recent work by Chivers and Laitinen *et al.* revealed Se–N single bonds of 1.844(3) Å within $(Me_3SiNSN)_2Se$,[10] while single bond lengths of 1.827(5) and 1.869(2) Å have been also been noted in OSN–Se–NSO[11] and $(Me_3Si)_2N$–Se–$N(SiMe_3)_2$,[12] respectively. The Se–N distance observed in **6** is thus within this single bond range, even after the shortening effect of the sulfur character. Thus, within the SNSe unit we see a significant degree of multiple bonding character for the S–N bond but little for Se–N.

The ^1H NMR spectrum of **6** in $CDCl_3$ reveals a multiplet in the aromatic region. Included in this are two distinct doublets of doublets, most likely corresponding to the hydrogens in the 4-position from the sulfur and selenium. The ^{13}C NMR spectrum reveals the expected eight different carbon environments, corresponding to the four positions of the carbon atoms in the phenyl rings attached to the sulfur and selenium.

In the analogous reaction of 1,4-$(PhSNBr)_2C_6H_4$ with 2 equiv of Ph_2Se, the expected bis-*N*-seleniosulfimide [1,4-$(PhSNSePh_2)_2C_6H_4]Br_2$ is isolated; subsequent conversion to the $[BPh_4]^-$ salt [1,4-$(PhSNSePh_2)_2C_6H_4][BPh_4]_2$ (**7**) allows crystallisation. X-Ray crystallography reveals the structure shown in Fig. 6 and confirms that both sulfimide units have indeed reacted with the incoming selenides. In **7** there is no disorder of the sulfur and selenium sites so the value of the Se–N bond length of 1.814(2) Å is a true representation of the bonding within these units.

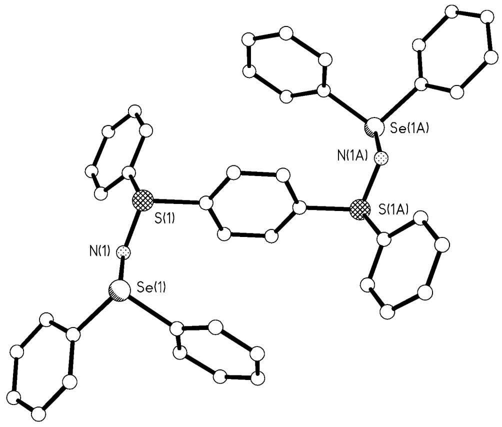


Fig. 6 The crystal structure of the cation in **7**. Selected bond lengths and angles; N(1)–S(1) 1.637(2), N(1)–Se(1) 1.814(2) Å; S(1)–N(1)–Se(1) 109.35(11)°.

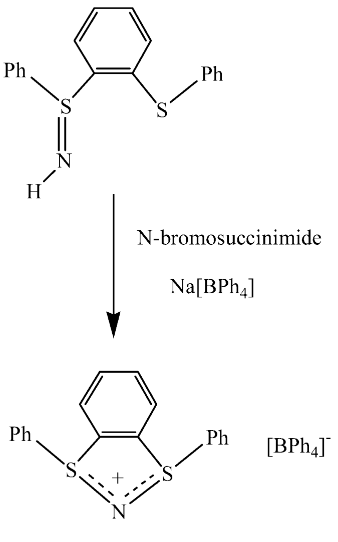
The ^{77}Se chemical shifts of compounds **6** and **7** are very similar (694 and 696 ppm, respectively), highlighting the similarity in chemical environment in the two cases. It is worth noting that unlike a number of other Se–N systems such as $(Me_3SiNSN)_2Se$ and $(Me_3Si)_2N$–Se–$N(SiMe_3)_2$, neither **6** nor **7** appear to be significantly sensitive to air. Thus, samples of **6**, for example, have been kept sealed (in air) in sample vials for many months without significant discolouration.

Cyclisation reactions of 1,2-PhS(NH)C_6H_4SPh

Reaction of the monosulfimide 1,2-PhS(NH)C_6H_4SPh with one equivalent of *N*-bromosuccinimide (Scheme 3) results in the generation of a yellow solution analogous to that of Ph_2SNBr formed from Ph_2SNH. This solution does decolourise with time, indicative of intramolecular attack from the *N*-bromosulfimide group on the sulfide unit. However, there are two problems with the reaction as it stands: firstly, the time taken for completion of the decolourisation appears very variable, suggesting that factors not yet determined have a big influence on this reaction time. Secondly, the bromide salt produced tends to form as an oil and while we have had some success at growing single crystals, the yield of the latter is very low, though X-ray crystallography (which we are not presenting formally here) does confirm the connectivity of the resulting ring system.

A far more satisfactory situation prevails if $Na[BPh_4]$ is added to the reaction mixture in methanol. Now the decolourisation is instantaneous and the product, [1,2-$(PhS)_2(\mu$-N)-$C_6H_4][BPh_4]$, **8**, precipitates. Crystallisation of this product by ether vapour diffusion into CH_2Cl_2 solutions results in the formation of two crystal types: colourless needles (**8a**) and colourless plates (**8b**). X-Ray crystallography confirms that in both cases the desired intramolecular cyclisation has taken place, but they differ by the relative disposition of the phenyl groups.

The asymmetric unit of **8a** contains 3 [1,2-$(PhS)_2(\mu$–N)-$C_6H_4]^+$ cations, all of which contain the phenyl rings in an "anti" arrangement as shown in Fig. 7. The cations form dimers by a close N···S approach of 3.100, 3.141 and 3.181 Å, giving a four-membered ring with an angle of approximately 104° at the nitrogen and approximately 75° at the sulfur



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Scheme 3 The cyclisation reaction of 1,2-PhS(NH)C_6H_4SPh with *N*-bromosuccinimide.

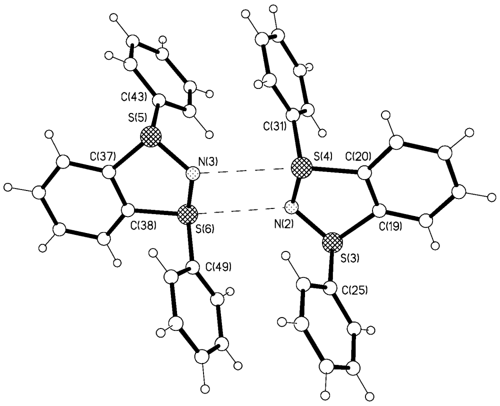

Fig. 7 One of the two unique dimers formed by the cations in **8a**. Selected bond lengths and angles (see text also): N(2)–S(3) 1.618(3), N(2)–S(4) 1.669(3), N(3)–S(5) 1.609(3), N(3)–S(6) 1.677(3) Å; S(3)–N(2)–S(4) 113.35(14)°, S(5)–N(3)–S(6) 113.25(14)°. For the other cation: N(1)–S(1) 1.617(3), N(1)–S(2) 1.663(3) Å, S(1)–N(1)–S(2) 114.36(16)°.

[the cations containing N(1) dimerise with themselves and those containing N(2) and N(3) interact with each other].

The asymmetric unit of **8b** contains a single $[1,2\text{-}(PhS)_2(\mu\text{–}N)C_6H_4]^+$ cation and one $[BPh_4]^-$ anion. In contrast to **8a**, the phenyl rings are arranged in a ”syn” position as shown in Fig. 8(a). There are no significant N···S interactions but there is a weak C–H···N hydrogen bond (C···N distance of 3.298 Å, C–H···N angle of 144.8°) to a phenyl hydrogen. This interaction links the cations into a 1-D chain as shown in Fig. 8(b). [If the cations are viewed along an S–C bond (a C of the terminal phenyl rings) the other ring is at 180° in **8a** and 0° in **8b**, hence the "anti" and "syn" terminology.]

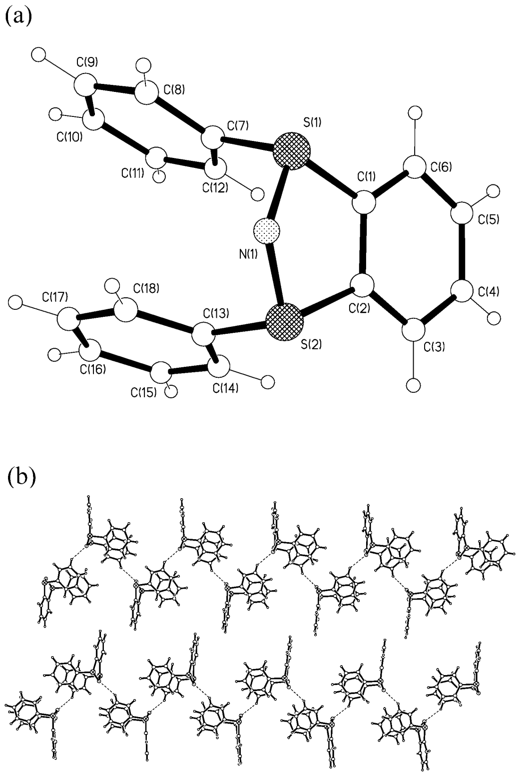

Fig. 8 (a) The structure of the cation in **8b** showing the syn arrangement of the phenyl rings. (b) The extended 1-D chain formed *via* a weak C–H···N hydrogen bond. Selected bond lengths and angles (see text also): N(1)–S(1) 1.6494(17), N(1)–S(2) 1.6501(19) Å; S(1)–N(1)–S(2) 111.84(10)°.

Conclusion

The isolation of compounds **1**–**3** confirms that the basic reaction of phosphines with bromosulfimides can be extended to diphosphines and bis-sulfimides; the results also indicate that such reactions may be adapted to generate new cyclic species of which cyclo-$[(Ph)SNP(Ph)_2C_6H_4P(Ph)_2NS(Ph)C_6H_4][BPh_4]_2$ is the first example. As noted in the text we have yet to confirm the cyclic structure of this material by X-ray crystallography, though work towards solving this problem is under way. The suggested structure (Scheme 1), if ultimately confirmed, will raise the possibility of isolation of a series of variations upon this structure, including a range of variations in ring size and of substituents.

The isolation of **4** and **5** constitutes a rare example of post ring-closure derivatisation of a thio-ether crown system and raises the possibility of using such reactions either as linking mechanisms or as a means of introducing pendant arm coordinating groups into the system. The latter would require the preparation of derivatised versions of Ph_2SNBr containing potentially coordinating groups; we have already gone some way to addressing this by formation of hydroxy substituted sulfimides and many more examples should be possible.

The isolation of **6** and **7** represents a simple route into a new class of Se–N species; in this context it is also important to note that unlike many other Se–N compounds the products are neither explosive nor air-sensitive. Finally, the isolation of the cyclic product **8** illustrates a new route to SN heterocycles. Again, the potential for derivatisation to this structure should mean that this intramolecular ring closure technique should provide a route to many more interesting structures.

Experimental

General

Ph_2SNBr,[5] $1,4\text{-}\{PhS(NH)\}_2C_6H_4$,[3] $1,2\text{-}C_6H_4(PhS)(PhSNH)\cdot H_2O$,[3] $1,4\text{-}(PPh_2)_2C_6H_4$[13] and *O*-mesitylenehydroxlyamine (MSH)[3] were prepared according to the literature methods. Diethyl ether was dried over sodium/benzophenone and dichloromethane over CaH_2.

Microanalyses were performed by the Loughborough Departmental Service, IR spectra recorded on a Perkin–Elmer 2000 spectrometer and NMR on a Bruker AC250 spectrometer. FAB mass spectra were recorded on a JEOL JMS SX102 (positive ion mode) and ES-MS were performed by the EPSRC Mass Spectrometry Service, University Of Wales, Swansea.

Syntheses

$[1,2\text{-}(Ph_2PNSPh_2)_2C_2H_4]Br_2$ (1). A solution of Ph_2SNBr (873 mg, 3.11 mmol) in toluene (5 ml) was treated with dppe (621 mg, 1.56 mmol) in an equal volume of the same solvent, added with stirring. A white precipitate appeared immediately; this was filtered and washed with diethyl ether (4 × 5 ml). The resulting white solid was recrystallised from CH_2Cl_2–Et_2O. Yield 1.24 g, 76%. CHN: Found C 62.3, H 4.2 N 2.6%; Calcd for $C_{50}H_{44}N_2Br_2P_2S_2$: C 62.8, H 4.6, N 2.9%. IR (cm^{-1}) 1119, 1091 ν(P–N). FAB-MS m/z 798 $(M-2Br)^+$. ^1H NMR ($CDCl_3$) δ 7.43–7.79 (20H, m), 3.13 (4H, m).^{13}C NMR ($CDCl_3$) δ 137.3, 134.4, 132.4, 132.2, 130.4, 130.0, 126.9, 123.7, 122.7, 21.1. ^{31}P NMR ($CDCl_3$) δ 40.4 (s).

$[1,4\text{-}(Ph_2PNSPh_2)_2(C_6H_4)][Br]_2$ (2). A solution of Ph_2SNBr (178 mg, 0.64 mmol) in toluene (15 ml) was treated with $1,4\text{-}(Ph_2P)_2(C_6H_4)$ (142 mg, 0.32 mmol) in the same solvent

(10 ml). After stirring overnight, an off-white solid had precipitated which was filtered, washed with toluene (10 ml) and diethyl ether (2 × 10 ml) and then recrystallised from CH_2Cl_2–ether. Yield 308 mg, 96%. CHN Calcd for $C_{54}H_{44}N_2Br_2P_2S_2 \cdot 1.5CH_2Cl_2$: C 58.8, H 4.2, N 2.5%; Found C 59.0, H 4.7 N 2.1%. IR (cm^{-1}) 843m ν(S–N), 1112s, 1064s ν(P–N). FAB-MS *m*/*z* 927 $(M - Br)^+$. ^1H NMR ($CDCl_3$) δ 7.44–7.95 (40H, m). Dichloromethane is also evident in the ^1H NMR spectra of **2** at 5.27 ppm and integrates to approximately 3 protons. ^{13}C NMR ($CDCl_3$) δ 136.8, 134.7, 133.6, 133.4, 132.8, 130.6, 130.1, 129.3, 126.7, 124.1, 123.1. ^{31}P NMR ($CDCl_3$) δ 33.2 (s).

This material was converted to the analogous $[BPh_4]^-$ salt by treating the material (151 mg, 0.15 mmol) dissolved in MeOH (10 ml) with $Na[BPh_4]$ (107 mg, 0.31 mmol) in MeOH (5 ml). A colourless solid precipitated immediately. Stirring was continued for a further 15 min. The solid was collected by filtration, washed with MeOH (10 ml) and then Et_2O (10 ml) and dried under vacuum. Yield 202 mg, 91%. CHN Calcd for $C_{102}H_{84}B_2N_2P_2S_2$: C 82.5, H 5.7, N 1.9%; Found C 82.3, H 5.3 N 1.9%. X-Ray quality crystals of this material were obtained by recrystallisation from acetonitrile–diethyl ether.

$[1,4\text{-}(PhS\{NSPPh_3\})_2C_6H_4]Br_2$ (3). 1,4-$\{PhS(NH)\}_2C_6H_4$ (425 mg, 1.31 mmol) was dissolved in degassed MeOH (15 ml) and cooled in ice. *N*-Bromosuccinimide (487 mg, 2.74 mmol) was dissolved in degassed acetone (10 ml) and added to the MeOH solution. The resulting yellow precipitate of 1,4-$[PhSNBr]_2C_6H_4$ was collected by filtration, washed with MeOH, then acetone and dried *in vacuo*. Yield 573 mg, 90%. CHN Calcd for $C_{18}H_{15}Br_2N_2S_2$: C 44.8, H 2.9, N 5.8%; Found C 44.8, H 3.3 N 5.6%. IR (cm^{-1}) 867br ν(S–N).

A suspension of this material (178 mg, 0.29 mmol) in degassed CH_2Cl_2 (15 ml) was treated with PPh_3 (154 mg, 0.59 mmol) added as a solid with stirring in a single portion. After 5 min of stirring the initial suspension had completely dissolved, giving a colourless solution that was stirred overnight. The resulting slightly cloudy solution was filtered through Celite and the volume of the filtrate was reduced to *ca.* 3 ml. The addition of diethyl ether (40 ml) with stirring gave a colourless solid. After filtration the material was washed with Et_2O, leaving a slightly off-white solid. Yield 267 mg, 93%. CHN Calcd. for $C_{54}H_{44}N_2Br_2P_2S_2$: C 64.5, H 4.4, N 2.8%; Found C 64.4, H 4.0, N 2.6%. IR (cm^{-1}) 844m ν(S–N), 1113s, 1088s ν(P–N). FAB-MS *m*/*z* 927 $(M - Br)^+$. ^1H NMR ($CDCl_3$) δ 7.98–8.02 (6H, m), 7.48–7.62 (48H m). ^{13}C NMR ($CDCl_3$) δ 141.7, 136.9, 134.3, 1133.3, 132.6, 130.6, 129.9, 128.6, 127.0, 125.0, 124.4. ^{31}P NMR ($CDCl_3$) δ 34.8 (s).

Reaction of $1,4\text{-}(PhSNBr)_2C_6H_4$ with $1,4\text{-}(Ph_2P)_2(C_6H_4)$. A solution of 1,4-$(PPh_2)_2C_6H_4$ (11 mg, 0.025 mmol) in dry CH_2Cl_2 (60 ml) was added dropwise with into dry CH_2Cl_2 (250 ml) containing 1,4-$[PhSNBr]_2C_6H_4$ (12 mg, 0.025 mmol, prepared as above). After stirring for 12 h, more 1,4-$[PhSNBr]_2C_6H_4$ (12 mg, 0.025 mmol) was added to the reaction mixture. Another solution of the diphosphine was added dropwise to the reaction and stirred for a further 12 h. This was repeated twice more. The solvent was then removed under reduced pressure, leaving a white residue that was extracted with MeOH (3 × 10 ml), the combined extracts filtered and then treated with $Na[BPh_4]$ (70 mg, 0.2 mmol) in MeOH (5 ml). A white precipitate immediately formed and after 1 h stirring this was filtered and washed with MeOH, CH_2Cl_2 and Et_2O (10 ml of each) and dried. Yield 28 mg, 20%. CHN: Found C 79.6, H 5.4, N 2.1%; Calcd For $C_{96}H_{78}N_2B_2P_2S_2 \cdot 0.5CH_2Cl_2$: C 80.0, H 5.5, N 1.9%. IR (cm^{-1}) 916w ν(S–N), 1069s, 1118s ν(P–N). ES-MS (CH_3CN) *m*/*z* 1088 $(M - BPh_4)^+$, 770 $(M - 2BPh_4 + 2H)^+$, 384 $(M - 2BPh_4)^{2+}$. ^{31}P NMR (CD_3CN) δ 35.6.

$[9[ane]S_3NSPh_2][BPh_4]$ (4). A solution of $9[ane]S_3$ (31 mg, 0.17 mmol) in toluene (5 ml) was added to Ph_2SNBr (48 mg, 0.17 mmol) dissolved in an equal volume of the same solvent. After stirring overnight, the solvent was removed under reduced pressure to give a yellow oil, which was triturated with Et_2O (20 ml). A white precipitate formed that was filtered and washed with Et_2O, leaving $[9[ane]S_3NSPh_2]Br$ as an off-white solid after drying. Yield 55 mg, 70%. CHN Calcd for $C_{18}H_{22}NBrS_4$: C 46.9, H 4.8, N 3.0%; Found C 46.4, H 4.7 N 3.3%. IR (cm^{-1}) 920br ν(S–N). FAB-MS *m*/*z* 380 $(M - Br)^+$. ^1H NMR ($CDCl_3$) δ 7.53–7.69 (10H, m), 4.27 (2H, m), 3.64 (2H, m), 3.27 (2H, m), 3.03 (2H, m), 2.91 (2H, m), 2.80 (2H, m). ^{13}C NMR ($CDCl_3$) δ 136.3, 131.7, 129.2, 126.6, 51.4, 34.0, 26.3.

This material was converted to the analogous $[BPh_4]^-$salt by treating the material (80 mg, 0.17 mmol) dissolved in MeOH (5 ml) with $Na[BPh_4]$ (60 mg, 0.18 mmol) in MeOH (5 ml). A white solid precipitated immediately, which was filtered, washed with MeOH and Et_2O (10 ml of both), then recrystallised from acetonitrile–diethyl ether to produce crystals of X-ray quality. Yield 56 mg, 45%. CHN Calcd for $C_{42}H_{42}NBS_4 \cdot MeCN$: C 71.4, H 6.0, N 3.8%; Found C 71.4, H 6.0 N 3.8%. IR (cm^{-1}) 927br ν(S–N). ES-MS (acetone) *m*/*z* 380 $(M - BPh_4)^+$. ^1H NMR ($CDCl_3$) δ 7.76 (4H, m), 7.64 (6H, m) 7.30 (8H, m) 7.02 (8H, m), 6.87 (4H, m), 4.35 (2H, m), 3.70 (2H, m), 3.33 (2H, m), 3.10 (2H, m), 3.00 (2H, m), 2.85 ppm (2H, m). ^{13}C NMR ($CDCl_3$) δ 136.8, 135.4, 132.7, 130.0, 126.6, 125.3, 121.4, 117.0, 52.1, 34.6, 26.7.

$[1,4\text{-}\{[9\text{-}ane]S_2S(NSPh)\}_2C_6H_4][BPh_4]_2$ (5). 1,4-$\{PhS(NBr)\}_2$-C_6H_4 (101 mg, 0.21 mmol) was suspended in dry methanol and $9[ane]S_3$ (77 mg, 0.43 mmol) was added as a solid in a single portion. The suspended mixture was stirred overnight (16 h) giving a very pale yellow, clear solution. To this was added solid $Na[BPh_4]$ (147 mg, 0.43 mmol) and the mixture was stirred for 20 min. The resulting precipitate was collected by filtration, washed with MeOH (3 × 5 ml) and Et_2O (3 × 10 ml), then dried *in vacuo* overnight. Yield 181 mg, 65%. CHN Calcd for $C_{78}H_{78}B_2N_2S_8$: C 70.9, H 5.9, N 2.1%; Found C 70.4, H 5.8 N 2.2%. IR (cm^{-1}) 915w ν(S–N). ES-MS (MeCN) *m*/*z* 1001 $(M - BPh_4)^+$, 341 $(M - 2BPh_4)^{2+}$. ^1H NMR (CD_2Cl_2) δ 7.41–7.19 (28H, m), 6.87 (18H, m) 6.77 (8H, m), 3.87 (2H, m), 3.78 (2H, m), 3.23 (4H, m), 2.93–2.43 (16H, m). ^{13}C NMR (CD_2Cl_2) δ 136.3, 136.0, 134.6, 131.5, 131.4, 129.9, 128.9, 128.4, 126.4, 126.3, 122.5, 52.9, 52.1, 36.1, 35.9, 28.0, 27.9.

Unfortunately, unlike other instances where the $[BPh_4]^-$ salt was prepared, the introduction of the anion did not increase the ease of crystallisation and no crystals of X-ray quality could be generated.

$[Ph_2SNSePh_2]Br$ (6). A solution of Ph_2SNBr (850 mg, 3 mmol) in CH_2Cl_2 (5 ml) was treated with a solution of Ph_2Se (710 mg, 3 mmol) in CH_2Cl_2 (5 ml), added dropwise with stirring. The resulting mixture was allowed to stir overnight after which time the solvent was removed *in vacuo*. After washing with Et_2O (2 × 20 ml) and drying in vacuo, **6** was obtained as a white solid. Yield 1.39 g, 89%. CHN Calcd for $C_{24}H_{20}NBrSSe$: C 56.1, H 3.9, N 2.7%; Found C 55.2, H 3.7 N 2.7%. IR (cm^{-1}) 871s ν(S–N), 643m ν(Se–N). FAB-MS *m*/*z* 434 $(M - Br)^+$. ^1H NMR ($CDCl_3$) δ 7.35–7.50 (m, 12H) 7.61–7.65 (m, 4H) 7.87–7.89 ppm (m, 4H). ^{13}C NMR ($CDCl_3$) δ 127.9, 129.6, 130.3, 130.4, 132.4, 132.8, 137.5, 138.87. ^{77}Se NMR ($CDCl_3$) δ 677.9 (s).

Table 1 X-Ray crystallographic data

	1	**2**	**3**	**4**	**6**	**7**	**8a**	**8b**
Formula	$C_{50}H_{44}Br_2N_2P_2S_2 \cdot 2CH_2Cl_2$	$C_{102}H_{84}B_2N_2P_2S_2$	$C_{54}H_{44}Br_2N_2P_2S_2 \cdot 2CH_3OH$	$C_{42}H_{42}BNS_4 \cdot CH_3CN$	$C_{24}H_{20}BrNSSe$	$C_{90}H_{74}B_2N_2S_2Se_2$	$C_{126}H_{102}B_3N_3S_6 \cdot C_4H_{10}O \cdot 0.5CH_2Cl_2$	$C_{42}H_{34}BNS_2 \cdot 0.5CH_2Cl_2$
M	1128.60	1485.39	1070.88	740.87	513.34	1427.17	1999.48	670.10
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a/Å	14.1746(7)	9.984(2)	9.4252(5)	10.0080(17)	8.0966(5)	11.4390(7)	15.4453(9)	10.1131(7)
b/Å	14.7287(7)	28.483(6)	14.7382(8)	10.0428(17)	15.4700(9)	16.4905(10)	17.0255(10)	10.9151(8)
c/Å	12.9914(6)	13.850(3)	18.3414(10)	20.281(3)	16.7219(10)	19.0299(11)	20.8544(12)	31.609(2)
α/°	90	90	90	103.872(3)	90	90	91.183(2)	90
β/°	107.527(2)	92.243(2)	95.367(2)	96.430(3)	97.160(2)	102.904(2)	103.617(2)	96.854(2)
γ/°	90	90	90	95.884(3)	90	90	93.015(2)	90
U/Å^3	2586.3(2)	3935.8(14)	2536.6(2)	1948.7(6)	2078.2(2)	3499.0(4)	5319.3(5)	3464.2(4)
Z	2	2	2	2	4	2	2	4
μ/mm^{-1}	1.954	0.161	1.787	0.278	3.840	1.167	1.248	0.263
Measured reflections	22509	22487	21995	17238	17434	30423	38966	17069
Indep. reflections	6250	5141	6139	8974	4939	8465	18627	6085
Obs. reflections $[F^2 > 2\sigma(F^2)]$	5433	2358	4279	6057	4473	5680	10122	4271
R_{int}	0.0205	0.1715	0.0396	0.0304	0.0328	0.0329	0.0460	0.0354
R $[F^2 > 2\sigma(F^2)]$	0.0269	0.0854	0.0507	0.0452	0.0380	0.0389	0.0548	0.0409
$wR2$ (all data)	0.0784	0.2870	0.1455	0.1119	0.0871	0.1046	0.1340	0.0999

[1,4-(PhSNSePh$_2$)$_2$C$_6$H$_4$][BPh$_4$]$_2$ (7). A solution of 1,4-[PhSNBr]$_2$C$_6$H$_4$ (50 mg, 0.1 mmol) in CH_2Cl_2 (10 ml) was treated with a solution of Ph_2Se (55 mg, 0.24 mmol) in CH_2Cl_2 (10 ml) added slowly, with stirring. After stirring for a further 5 days, the CH_2Cl_2 was removed under reduced pressure and the residue stirred overnight with Et_2O (10 ml). After filtration the resulting solid was extracted into MeOH (10 ml), the solution filtered and then treated with a solution of Na[BPh$_4$](70 mg, 0.22 mmol) in MeOH (5 ml) with stirring. The resulting white precipitate was filtered, washed with MeOH and Et_2O (10 ml of each) and then dried *in vacuo*, to give **7** as a white solid. Yield 71 mg, 50%. CHN Calcd for $C_{90}H_{74}N_2B_2S_2Se_2$: C 75.7, H 5.2, N 2.0%; Found C 76.0, H 5.1 N 2.0%. IR (cm^{-1}) 878m ν(S–N), 643m ν(Se–N). ES-MS (acetone) m/z 1107 $(M-BPh_4)^+$, 395 $(M-2BPh_4)^{2+}$. ^{77}Se NMR (d_6-DMSO) δ 695.5.

[1,2-(PhS)$_2$(μ-N)C$_6$H$_4$][BPh$_4$] (8). A solution of 1,2-PhS(NH)C$_6$H$_4$SPh·H$_2$O (0.25 g, 0.76 mmol) in MeOH (15 ml) was treated with *N*-bromosuccinimide (0.136 g, 0.76 mmol) added as a solid with stirring. The resulting yellow solution was stirred for 10 min after which time solid Na[BPh$_4$] (0.261 g, 0.76 mmol) was added with vigorous stirring, immediately generating a white precipitate. After further stirring for 10 min the solid was filtered and washed with cold MeOH (5 ml) and then Et_2O (20 ml) before drying *in vacuo*. Yield 0.326 g, 86%. CHN Calcd for $C_{42}H_{34}BNS_2$: C 80.4, H 5.4, N 2.2%; Found C 80.3, H 5.3, N 2.1%. IR (cm^{-1}) 908w ν(S–N). ES-MS (MeOH) m/z 308 $(M-BPh_4)$. ^{1}H NMR (CDCl$_3$) δ 9.10 (dd, 1H), 8.64 (dd, 1H), 8.01 (dd, 1H), 7.92 (d, 2H), 7.73 (dd, 1H), 7.50 (m, 4H), 7.13 (d, 2H), 7.06 (t, 2H). ^{13}C NMR (CDCl$_3$) δ 137.4, 137.1, 136.7, 134.5, 134.4, 134.1, 130.7, 129.7, 129.6, 128.2, 127.8, 127.5.

Crystallography

Data for all complexes was collected at 150 K with a Bruker SMART AXS 1000 CCD diffractometer and Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å). All structures were solved by direct methods and were refined by full-matrix least-squares methods on F^2. All hydrogens were placed in geometrical positions using a riding model. Programs used were Bruker SMART,[14a] SAINT,[14a] SHELXTL[14b] and local programs. Any unusual structural aspects of these complexes are described below and the crystal structure data is presented in Table 1.†

6. The [Ph$_2$SNSePh$_2$]$^+$ cation is disordered with the S and Se sites partially occupied by both elements. This disorder has been refined to give the relative occupancies of [Ph$_2$SNSePh$_2$]$^+$: [Ph$_2$SeNSPh$_2$]$^+$ of 83.2:16.8(2)%.

7. The asymmetric unit contains half a [1,4-(PhSNSePh$_2$)$_2$-C$_6$H$_4$]$^+$ cation and a [BPh$_4$]$^-$ anion. The cation is disordered with alternative positions for the S and Se atoms [refined occupancies of 91.61:8.39(17)%]. This disorder has been modelled with geometric and displacement parameter restraints applied. It is clear that the minor disorder extends throughout the S–N–Se section of the molecule and probably also includes the phenyl and C$_6$H$_4$ rings. However, due to the low occupancy, only the S and Se sites were modelled as disordered.

8. Both **8a** and **8b** contain diffuse solvent molecules that could not be modelled using a point atom model. The PLATON squeeze program[15] was used to model this as half a CH_2Cl_2 molecule per asymmetric unit for each structure.

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