The first use of the free selenimide $Ph_2Se{=}NH$ as a synthon; the synthesis and X-ray crystal structure of $[Ph_2SeNSePh_2][BPh_4]$†

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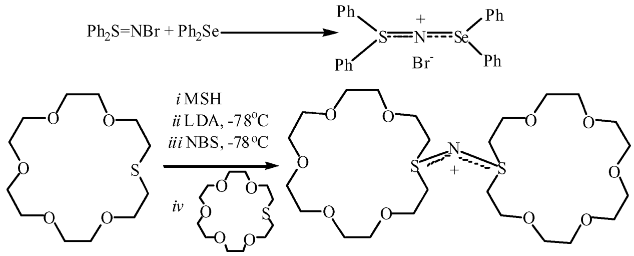
Reaction of *o*-mesitylsulfonylhydroxylamine (MSH) with Ph_2Se results in the $[Ph_2SeNH_2]^+$ cation; low temperature deprotonation (LDA), bromination (NBS) and then treatment with Ph_2Se–$Na[BPh_4]$ generates $[Ph_2SeNSePh_2][BPh_4]$, *via* the selenimides $Ph_2Se{=}NH$ and $Ph_2Se{=}NBr$.

Sulfimides (also previously referred to as sulfilimines), ylides of the general formula $RR'S{=}NX$, have been known for many years and have been the subject of much interest.[1] Within such work, the most intense scrutiny has been reserved for free sulfimides, *i.e.* those in which X = H; within this group of compounds, diphenylsulfimide, $Ph_2S{=}NH$, has undoubtedly received most attention, with its ability to act as a source of the NH unit in aziridination reactions one of the key attractions.[2] Derivatisation to halosulfimides of the type $Ph_2S{=}NX$ has also been much studied; the chloro and bromo species have been the subjects of the bulk of the work, and while $Ph_2S{=}NCl$ is the more reactive of the two, it has been reported to explode on storage.[3] Thus, although $Ph_2S{=}NBr$ (prepared by the reaction of $Ph_2S{=}NH$ with *N*-bromosuccinimide, NBS) is somewhat less reactive, its stability makes it a more amenable reagent.

Early synthetic applications of $Ph_2S{=}NBr$ included the formation of cations of the type $[Ph_2SNPR_3]^+$ by reaction with phosphines.[4] We have built upon such work by showing that it can react with selenides, diphosphines, thio-crowns[5] and with elemental selenium (to generate Se_4N_4).[6] In an extension to the latter work we recently demonstrated that oxo-crown ethers bearing one sulfur atom can react with the aminating agent *o*-mesitylsulfonylhydroxylamine (MSH) to generate sulfimidium salts.[7] Although free dialkyl sulfimides are markedly less stable than their diaryl counterparts,[8] it was shown that low temperature deprotonation of such salts generated the corresponding free sulfimides of the crowns. The latter (undoubtedly very unstable) compounds were not isolated; rather, their presence *in situ* was inferred from the fact that treatment with NBS, and then with a further equivalent of the parent crown, generated the linked crown system shown in Scheme 1. The fact that this "one-pot" reaction clearly generated—and then utilised—the unstable free and bromo sulfimides raises the question of its applicability to selenimide systems.



Scheme 1 Two previous examples of the use of bromosulfimides, in the formation of a mixed sulfur–selenium system (top) and in the one-pot preparation of linked crowns *via* formation unstable sulfimide intermediates (bottom).

In contrast to the sulfimides, relatively little work has been performed on their selenium analogues. By analogy with sulfimide preparations, reaction of Chloramine-T with Ph_2Se leads to the *p*-toluenesulfonyl derivative $Ph_2Se{=}NR$ (R = *p*-$MeC_6H_4SO_2$),[9] though this cannot act as a source of the free selenimide, $Ph_2Se{=}NH$, by acidolysis. More recently, studies have been performed on optically active tosyl derivatives of selenimides.[10] Although computational investigations into inversion in the free selenimide $Ph_2Se{=}NH$ have been undertaken,[11] the material itself remains elusive. In 1966 Appel and Büchler showed that reaction of Ph_2SeCl_2 with ammonia resulted in $[Ph_2SeNSePh_2]Cl$ and postulated the uncharacterised selenimidium salt $[Ph_2Se{=}NH_2]Cl$ as an intermediate.[12a] No definitive evidence was presented for the formation of $Ph_2Se{=}NH$, while the $[Ph_2SeNSePh_2]^+$ cation was subsequently prepared by reaction of Ph_2SeCl_2 with $(Me_3Si)_2NH$, though the product was not fully characterised by X-ray crystallography.[12b] Here we present evidence for the formation of $Ph_2Se{=}NH$ and $Ph_2Se{=}NBr$ as reactive intermediates.

The ability of the aminating agent MSH to generate sulfimidium salts *via* reaction with sulfides is well documented; thus addition of the solid reagent to a stirred ethereal solution of Ph_2S results in formation of a precipitate of $[Ph_2S{=}NH_2][mesSO_3]$. We have now found that the analogous reaction with Ph_2Se is equally effective. The resulting off-white solid can be characterised as $[Ph_2Se{=}NH_2][mesSO_3]$ **1** through a combination of microanalysis, IR and NMR spectroscopy; it is, however, very air sensitive—especially in solution—and thus far, attempts to crystallise the material have failed. The solid material also appears to be somewhat light sensitive and darkening (due to elemental selenium formation) of samples occurs over a number of days even when samples are kept in darkened anaerobic conditions. If used soon after formation however, **1** can act as a source of the free selenimide. Thus if a suspension of the material is treated with the base LDA at low temperature (−50 °C), complete dissolution occurs. Treatment of this mixture with NBS followed by Ph_2Se leads to the formation of the $[Ph_2SeNSePh_2]^+$ cation (Scheme 2),

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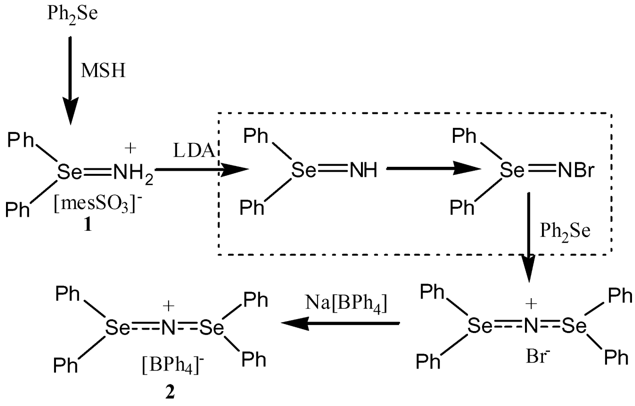

Scheme 2 The formation of **2** from **1**; note neither species within the dotted box are isolated.

which can be precipitated as $[Ph_2SeNSePh_2][BPh_4]$ **2** by metathesis with $Na[BPh_4]$.

Within the structure shown in Fig. 1, the most pertinent features are the Se–N distances (N(1)–Se(1) 1.8020(16) Å, N(1)–Se(2) 1.8141(16) Å) and the Se(1)–N(1)–Se(2) angle (109.63(8)°); note that parameters for the other independent molecule within the unit cell are extremely similar. All these values are effectively identical to those within the analogous salt of the mixed chalcogen cation $[Ph_2SeNSPh_2]^+$.[13] The Se–N distances are shorter than those of typical Se–N single bonds, indicating some degree of multiple bonding, as expected. There is a marked asymmetry within the cation in terms of the Se–N distances, and inspection of the cation–anion disposition reveals that close contacts exists between one of the two selenium atoms and the π system of one of the phenyl rings of the $[BPh_4]^-$ counterion. This effect is seen in both independent molecules, with chalcogen–phenyl centroid distances of 3.450 and 3.437 Å for Se(1) and Se(3) respectively. A similar effect was seen in the case of $[Ph_2SeNSPh_2][BPh_4]$, wherein analogous contacts were observed between the selenium and atom and a phenyl ring, together with a hydrogen bonding interaction from a phenyl C–H to the sulfur. The latter effect is not apparent in **2**. It would appear, therefore, that this Se···π interaction is strong; however, geometrical constraints will stop such interactions occurring at both selenium atoms, hence the asymmetry with the Se–N bond distances (interestingly, the selenium atom undertaking this interaction is the one exhibiting the shorter Se–N bond distance).

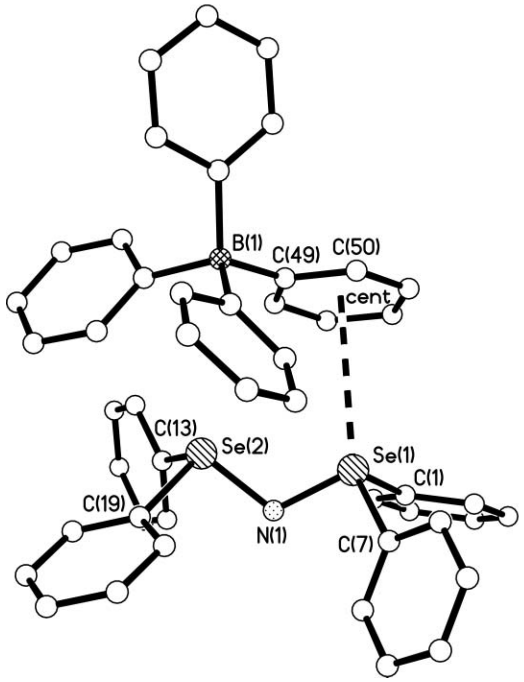

Fig. 1 The X-ray crystal structure of one of the two independent cation–anion pairs within the unit cell of **2**.

Although the isolation of **2** allows the first full characterisation of the cation by X-ray crystallography, this is not the key feature of the result; after all, as already noted, this cation has been previously generated by other means. The key point is that reaction must proceed *via* the free selenimide and bromoselenimide. This conclusion is further bolstered by observations made when Ph_2S (rather than Ph_2Se) is added to the reaction mixture at the bromo selenimide stage. Such a reaction might be hoped to generate the aforementioned mixed chalcogen cation $[Ph_2SeNSPh_2]^+$; in fact there is no reaction and work up simply results in the formation of the thermal decomposition products of $Ph_2Se{=}NBr$. ^{77}Se NMR spectroscopy reveals these to be a mixture of $Ph_2Se{=}O$ and Ph_2Se; importantly, no $[Ph_2SeNSePh_2]^+$ is observed. In other words the isolation of **2** is not simply the result of a decomposition–rearrangement which occurs upon deprotonation of $[Ph_2Se{=}NH_2]^+$. Had that been the case then **2** would form irrespective of whether Ph_2Se was added into the reaction mixture or not. These observations show that $Ph_2Se{=}NBr$ must be forming and then reacting with Ph_2Se. As an aside, the inertness of $Ph_2Se{=}NBr$ towards Ph_2S mirrors that of $Ph_2S{=}NBr$, which only reacts upon prolonged heating.

In conclusion, we have demonstrated that reaction of MSH with Ph_2Se allows easy access to a selenimidium salt which can be deprotonated to the free selenimide. Although undoubtedly very sensitive (thermally as well as aerobically—note that, as was the case with $Ph_2Se{=}NBr$, $Ph_2Se{=}O$ and Ph_2Se also appear to form upon thermal decomposition of the free selenimide) the latter can be used as a synthon *in situ*, in this case *via* the corresponding bromoselenimide. Given the wealth of chemistry associated with $Ph_2S{=}NH$, both in a classical "organic" sense[1] and in terms of coordination chemistry,[14] it follows that utilisation of the selenium analogue will allow access to a significant amount of new chemistry, even if this will have to be performed *in situ* due to the instability of the material. Indeed, given the fact that unstable (*i.e.* dialkyl) sulfimides have been used as nitrene (NH) sources before,[8] it may well be that the instability of $Ph_2Se{=}NH$ may actually make it a potent reagent in this sense as well. Such potential is magnified by the fact that the chemistry of the related selenium diimides, RN=Se=NR, has also proved to be a fruitful area of investigation, both from structural[15a] and synthetic[15b] standpoints. Thus work to fully assess the chemistry of this new species is under way.‡

Acknowledgements

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Notes and references

‡ All reactions were performed under an atmosphere of dry nitrogen using standard Schlenk techniques and appropriately dried solvents. MSH was prepared by the literature route[16] and Ph_2Se used as received (Aldrich). **Safety note!**: Solid MSH can spontaneously (and unpredictably) decompose, resulting in an explosive pressure change. Samples should be kept in small amounts in loosely sealed containers, thereby minimising the risks should decomposition occur.

$[Ph_2Se(NH_2)][mesSO_3]$. Ph_2Se (0.902 g, 3.87 mmol) was dissolved in Et_2O (50 cm^3), and MSH (1.04 g, 4.83 mmol) added as a solid in several portions. The mixture was stirred vigorously overnight, after which the precipitate formed was filtered under N_2 and dried under reduced pressure. Yield: 1.232 g (71%). Microanalysis: found C 55.5, H 5.5, N 3.1%; $C_{21}H_{23}NO_3SSe$ requires: C, 56.3; H, 5.2; N, 3.1%. ν_{max}(KBr)/cm^{-1}: 2970, 1476, 1448, 1226, 1171, 1085, 850, 754, 686, 584, 486; δ_{Se} (CD_3OD) = 934 ppm.

$[Ph_2SeNSePh_2][BPh_4]$. $[Ph_2Se(NH_2)][mesSO_3]$ (0.300 g, 0.67 mmol) was dissolved in THF–MeCN (9 : 1, 15 cm^3), and the solution temperature reduced to *ca.* −50 °C, resulting in some precipitation of material. LDA (0.33 cm^3 of a 2 M solution, 0.67 mmol) was added with stirring; within a minute all solid had dissolved leaving a clear, yellow solution, at which point NBS (0.119 g, 0.67 mmol) was added. The resulting mixture was stirred for *ca.* 2 min., after which Ph_2Se (0.156 g, 0.67 mmol) was added. After stirring for 1 h, the mixture was reduced to dryness, MeOH (2–3 cm^3) added, and an excess of $Na[BPh_4]$ (0.287 g, 0.84 mmol) added as a solid. The mixture was stirred for 1 h, and the resulting precipitate filtered and dried *in vacuo.* Yield 0.201 g (38%). Microanalysis: found C 72.6, H 5.4, N 2.2%; $C_{48}H_{40}Se_2BN$ requires C 72.1, H 5.0, N 1.8%; ν_{max}(KBr)/cm^{-1}: 3214, 3003, 1578, 1476, 1440, 1201, 1184, 1095, 1020, 844, 783, 730, 715, 683, 611, 600; δ_H (dmso) = 7.96 (d, 8H, 8 × PhSe Ar-H), 7.56 (br s, 12H, 12 × PhSe Ar-H), 7.23 (br s, 8H, 8 × BPh_4 Ar-H), 6.96 (t, 8H, 8 × BPh_4 Ar-H), 6.82 (t, 4H, 4 × BPh_4 Ar-H); δ_C (dmso) = 163.6 ppm (1 : 1 : 1 : 1 q, BPh_4 Ar-C), 139.8 (s, PhSe Ar-C), 135.5, 121.5 (s, BPh_4 Ar-CH), 129.8 (s, PhSe Ar-CH), 127.5 (s, PhSe Ar-CH) 125.3 (d, BPh_4 Ar-CH); δ_{Se} ($CDCl_3$) = 731 ppm. m/z (ES^+): 481 ($C_{24}H_{20}Se_2N$ requires 481).

Crystal data for **$[Ph_2SeNSePh_2][BPh_4]$**. $C_{48}H_{40}BNSe_2$, M 799.54; triclinic, $P\bar{1}$; $a = 10.9985(4)$, $b = 15.9145(6)$, $c = 24.0519(10)$ Å, $\alpha = 85.7218(6)$, $\beta = 76.9512(6)$, $\gamma = 71.9053(6)°$, $Z = 4$, $V = 3898.4(3)$ Å^3; $\rho_{cal} = 1.362$ g cm^{-3}; μ(Mo-Kα) = 1.931 mm^{-1}; $\lambda = 0.71073$ Å, $T = 150(2)$ K; 47137 reflections were collected on a Bruker APEX 2 CCD diffractometer using narrow ω-scans, 24038 of which were independent ($R_{int} = 0.0256$).[17,18] The structure was solved by direct methods and refined on F^2 values to give a final $R = 0.0365$ for 17868 data with $F^2 > 2\sigma(F^2)$; $wR_2 = 0.0918$ for all data.[19]

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