Caged Explosives: Metal-Stabilized Chalcogen Nitrides

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1 Introduction

The chemistry of chalcogen–nitrogen (*i.e.* S/Se/Te–N) systems spans more than 150 years. The most important single species in this class, S_4N_4 (Figure 1a), was first reported in 1835.[1a] However, it was not until 116 years after the synthesis of S_4N_4 that the related compound S_4N_2[1b] was fully characterized. Similarly, whilst Se_4N_4 has been known for many years,[2a] the preparation of Se_4N_2 has only been reported in the past few months.[2b] The combination of the historical and the contemporary is one of the reasons why this particular class of compounds continues to provoke keen interest. One aspect of their chemistry which has recently resulted in renewed interest is the conductivity and superconductivity of $(SN)_x$ polymer.

Metal sulfur–nitrogen complexes can now be prepared with a variety of S–N ligands, as well as for complexes containing the heavier chalcogens (Se or Te). However, little is understood about the mechanisms of many of these reactions since one can rarely, if ever, write balanced equations to describe them. As a result, even after almost a century of metal–sulfur–nitrogen chemistry it is often very difficult to predict the course of reactions, even in quite simple systems. This review will highlight recent developments in the chemistry of both sulfur–nitrogen and heavier chalcogen-containing ligands together with related advances in the chemistry of non-coordinated systems.

2 Metal–Sulfur–Nitrogen Compounds

The last two decades have witnessed rapid advances in the understanding of the chemistry of metalla-sulfur–nitrogen systems, prompted to a large extent by the application of modern X-ray crystallographic and spectroscopic techniques. Intriguingly, the knowledge accumulated during this time has not diminished the ability of these compounds, in particular S_4N_4, to reveal new aspects of their chemical behaviour. A number of reviews have covered the literature up to a few years ago[3] and so this work will concentrate upon very recent developments, in particular, reactions involving S_4N_4. The reactions in question belong to two basic categories: oxidative addition reactions, in which the S_4N_4 unit stays intact and is present in the product as the $S_4N_4{}^{2-}$ ligand, and those in which there is more extensive disruption of the structure resulting in smaller sulfur–nitrogen ligands.

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David Williams has interests in all aspects of structural chemistry especially the relationship between solid state structure and the properties of molecules. Although his first degree was in physics he regards himself as a chemical crystallographer. After studying for her BSc and PhD at Imperial College, Alexandra Slawin was appointed as the departmental Experimental Officer in this area. Paul Kelly entered university after a promising career with Bolton Wanderers was cut short through injury. He has worked on S–N and Se–N chemistry for the past eight years.
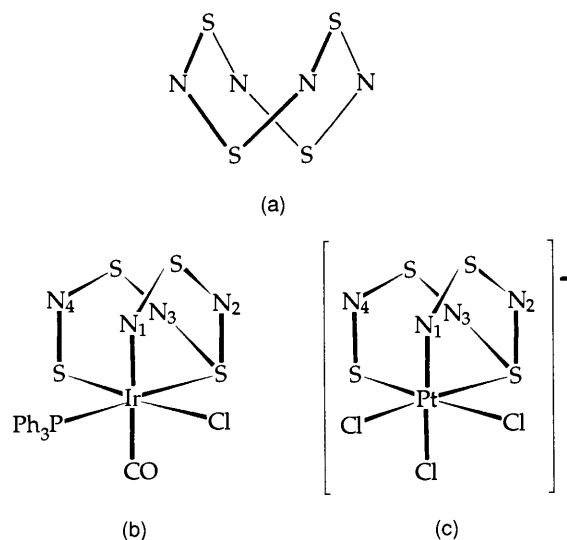
Figure 1 The structures of (a) S_4N_4, (b) $IrCl(CO)(PPh_3)(S_4N_4)$, and (c) $[PtCl_3(S_4N_4)]^-$.

In 1970 McCormick and Anderson reported the reaction of $IrCl(CO)(PPh_3)_2$ with S_4N_4 which yielded an intensely red coloured product formulated as $IrCl(CO)(PPh_3)(S_4N_4)$.[4] Until recently this was assumed to be a complex of neutral S_4N_4 bound to the metal by one nitrogen, in the manner of other complexes in which S_4N_4 acts as a Lewis base. However, work by Roesky *et al.*[5] revealed that the complex is actually an Ir^{III} species containing the previously unknown $S_4N_4{}^{2-}$ ligand. The ligand is bound to the iridium by two sulfurs and one nitrogen in a *facial* arrangement (Figure 1b); the fundamental geometry of the S_4N_4 moiety is, however, unchanged. The Ir–S bonds are unequal in length, an effect which has been correlated with the electron density, *i.e.* coordination number, at each sulfur. Thus the shorter of the two bonds is associated with the sulfur of coordination number 2, though it should be borne in mind that the authors add the *caveat* that the presence of different ligands *trans* to the two sulfurs should also be taken into consideration. We have measured the ^{31}P and ^{15}N NMR spectra of $IrCl(CO)PPh_3(S_4{}^{15}N_4)$ (*vide infra*); three of the four nitrogen atoms show significant coupling to the phosphorus atom while there are $^{15}N-^{15}N$ interactions within the pairs of nitrogen atoms on either side of the P–Ir–S axis. In addition to the chloro species, the bromo and iodo analogues can also be prepared from the appropriate starting materials.

The $S_4N_4{}^{2-}$ anion is also stabilized in $K[Pt^{IV}Cl_3(S_4N_4)]$, which we have prepared from the reaction (equation 1) of Zeises' salt, $K[PtCl_3(C_2H_4)]$, with S_4N_4 in thf.[6]

$$K[Pt^{II}Cl_3(C_2H_4)] + S_4N_4 \rightarrow K[Pt^{IV}Cl_3(S_4N_4)] + C_2H_4 \quad (1)$$
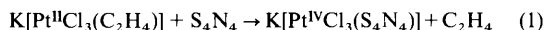
Metathesis yields the $[PPh_4]^+$ salt of the anion which can be crystallized but which unfortunately could not be characterized by X-ray crystallography because of disorder problems. However, we have assigned the structure shown in Figure 1c by the use of ^{14}N and ^{15}N spectroscopy. The ^{15}N spectrum of $[PPh_4][PtCl_3(S_4{}^{15}N_4)]$ is very similar to that of $IrCl(CO)(PPh_3)(S_4{}^{15}N_4)$ in terms of the chemical shifts of the four

Table 1 ^{15}N NMR data for IrCl(CO)(PPh$_3$)(S$_4$^{15}N$_4$) and [PPh$_4$][PtCl$_3$(S$_4$^{15}N$_4$)]

Nitrogen atom	δ/ppm	$J\{^{15}N-^{15}N\}/Hz$	$J\{^{31}P-^{15}N\}/Hz$
Ir N(1)	405	3	0
N(2)	270	3	3.4
N(3)	179	5.6	4.3
N(4)	355	5.6	1.7
Pt N(1)	435	3.2	—
N(2)	287	3.1	—
N(3)	170	5.8	—
N(4)	351	5.9	—

nitrogens (Table 1), which are inequivalent. The presence of a large ^{195}Pt$-^{15}$N coupling to the nitrogen at 435 ppm indicates that this is the metal-bound nitrogen and leads us to the somewhat unexpected conclusion that the one nitrogen in the iridium species which does not couple to the phosphorus is in fact the iridium-bound nitrogen. Again $^2J\{^{15}N-^{15}N\}$ N(1)–N(2) and N(3)–N(4) couplings are observed and are of comparable magnitude to those seen in the iridium compound. Figure 2 compares the ^{14}N and ^{15}N NMR spectra of [PtCl$_3$(S$_4$N$_4$)]$^-$ and reveals the different line widths obtained by the two techniques as well as the close correlation of chemical shifts. The analogous bromo and iodo complexes [PPh$_4$][PtX$_3$(S$_4$N$_4$)] have also been prepared by using [PPh$_4$]$_2$[Pt$_2$X$_6$] as the starting material.
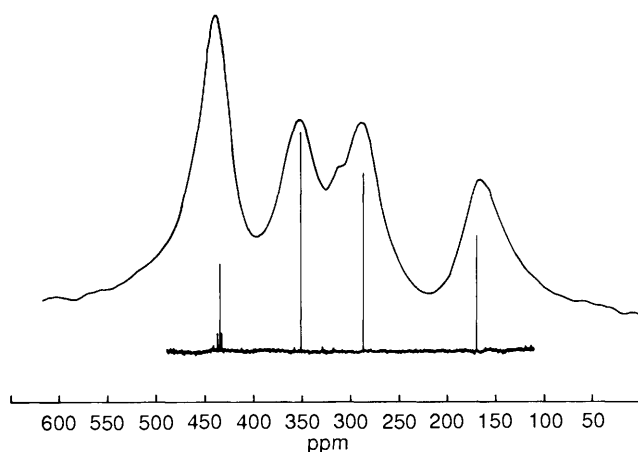
Figure 2 Comparison of ^{14}N and ^{15}N NMR spectra of [PtCl$_3$(S$_4$N$_4$)]$^-$ (upper) and [PtCl$_3$(S$_4$^{15}N$_4$)]$^-$.

x-axis: 600 550 500 450 400 350 300 250 200 150 100 50 ppm

Reaction of the dimeric Pt^{II} species [PtCl$_2$(PMe$_2$Ph)]$_2$ with S$_4$N$_4$ in CH$_2$Cl$_2$ at ambient temperature yields Pt^{IV}Cl$_2$(S$_4$N$_4$)(PMe$_2$Ph) in which the geometry of the S$_4$N$_4$$^{2-}$ ligand is radically different to that in the above cases (Figure 3).[7] The ligand is meridionally coordinated and is, with the exception of one sulfur and one nitrogen atom, planar. The Pt–S bond lengths are very similar to the Ir–S distances in IrCl(CO)(PPh$_3$)(S$_4$N$_4$) with the shorter of the two again being to the two-coordinate sulfur; the Pt–N distance is, however, significantly longer than the Ir–N distance. The ^{15}N NMR spectrum of the *mer* complex reveals a greater degree of ^{15}N–^{15}N interaction than is observed for the *facial* cases; five of the six possible $\{^{15}N-^{15}N\}$ couplings are observed and all of the nitrogens couple to the phosphorus.

Whereas *mer*-PtCl$_2$(S$_4$N$_4$)(PMe$_2$Ph) is very stable in the solid state, in CH$_2$Cl$_2$ solution it slowly isomerizes over a period of days at room temperature or in a few hours at 90 °C. The nature of this isomerization can be deduced by NMR studies on the ^{15}N labelled complex. The ^{31}P NMR spectrum reveals that in the
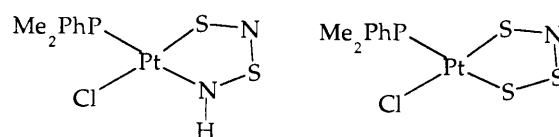
Figure 3 The structure of PtCl$_2$(S$_4$N$_4$)(PMe$_2$Ph) showing the meridionally bound S$_4$N$_4$$^{2-}$ ligand.
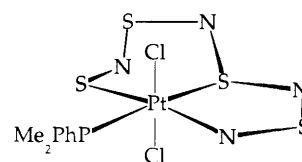
new species only two nitrogens couple to the phosphorus (*cf.* all four in the original species). This observation initially led us to the erroneous conclusion that the complex was simply a facially coordinated analogue of the starting material (Figure 4a).[8] However, ^{15}N and ^{195}Pt NMR studies suggest that the correct structure actually involves coordination by two nitrogens and one sulfur (Figure 4b),[9] although we cannot unequivocably assign a *mer* or *fac* geometry to the complex. This constitutes the first example of such a coordination mode and could be very significant in terms of the understanding of reaction mechanisms for S$_4$N$_4$ with a variety of metal species. The structure in Figure 4b has the potential to disproportionate to give either S$_2$N$_2$$^{2-}$ or S$_2$N$_3$$^{3-}$ complexes, depending upon the fragmentation path; both of these anions are known in coordination complexes. We believe that S$_4$N$_4$$^{2-}$ complexes may well be formed as short-lived intermediates in many reactions.

(a)   (b)

Figure 4 Comparison of the structure originally proposed for the isomer of PtCl$_2$(S$_4$N$_4$)(PMe$_2$Ph) (a) with that now known to be the true structure (b).

Finally, a recent report[10] suggests that reaction of the titanium species [Ti(Cp)$_2$(AsF$_6$)$_2$] with S$_4$N$_4$ in SO$_2$ results in the formation of [Ti(Cp)$_2$F(AsF$_6$)] and S$_4$N$_4$·AsF$_5$ which equilibrate with [Ti(Cp)$_2$(S$_4$N$_4$)][AsF$_6$]$_2$. The ^{14}N NMR spectrum of the latter species contains two peaks, indicating two different chemical environments for the nitrogens. This observation suggests that the (neutral) S$_4$N$_4$ is symmetrically coordinated to the titanium by two nitrogens although this has yet to be confirmed by X-ray crystallography.

Complexes of the type *cis*-PtCl$_2$(PR$_3$)$_2$ have proved to be amongst the most successful reagents for the preparation of metalla-sulfur–nitrogen species, *via* reaction with a variety of synthons. They are, however, inert to S$_4$N$_4$ unless the mixture is subjected to either high temperatures (> 140 °C) or UV photolysis.[11,12] When PR$_3$ = PMe$_2$Ph the main products are PtCl(S$_2$N$_2$H)(PMe$_2$Ph) and PtCl(S$_3$N)(PMe$_2$Ph) (Figure 5). The use of UV photolysis to activate S$_4$N$_4$ at below room temperature is obviously the safer of the two reactions and should be applicable to many other systems involving S$_4$N$_4$ which have so far been deemed inert. ^{15}N labelling studies

Figure 5 The structures of PtCl(S$_2$N$_2$H)(PMe$_2$Ph) and PtCl(S$_3$N)(PMe$_2$Ph), the main products of the photolysis of a mixture of PtCl$_2$(PMe$_2$Ph)$_2$ and S$_4$N$_4$.

indicate that the photolysis reaction proceeds *via* a short-lived intermediate S−N species which can rapidly exchange nitrogens before reacting; the nature of this intermediate has yet to be ascertained. A similar situation must also apply to the high-temperature reaction; we have shown that mixtures of $S_4{}^{15}N_4$ and S_4N_4 when heated intermix their nitrogens, possibly *via* short-lived chain species. If solutions of S_4N_4 are irradiated in the absence of metal species then a variety of products are obtained, depending upon concentration and solvent. For example, irradiation of a saturated cyclohexane solution yields S_4N_2, S_7NH, and sulfur whilst the same experiment performed in methanol results in only S_7NH.

We noted above that halogen-bridged complexes of the type $[PPh_4]_2[Pt_2X_6]$ (X = Br, I) react with S_4N_4 *via* oxidative addition to give $S_4N_4{}^{2-}$ complexes. If the analogous palladium complexes are used instead then the reactions proceed in a completely different manner and result in Pd^{II} complexes; indeed we have yet to prepare any Pd^{IV} complexes of $S_4N_4{}^{2-}$ since the other potential reagent for such a product, $[PdCl_2(PMe_2Ph)]_2$, is inert to S_4N_4 at room temperature.

The reaction of S_4N_4 with $[PPh_4]_2[Pd_2X_6]$ (X = Cl or Br) in CH_2Cl_2 proceeds readily at ambient temperatures and gives a variety of species; in particular we have characterized $[PPh_4]_2[Pd_2X_6(S_2N_2)]$, $[PPh_4]_2[Pd_2X_4(S_3N_2)]$, and $[PPh_4]_2$-$[PdX_2(S_2N_2H)]$.[13] These can be crystallized from the reaction mixture by slow diffusion of hexane into the CH_2Cl_2 solution and then readily separated from each other by hand. The predominant product is $[PPh_4]_2[Pd_2X_6(S_2N_2)]$ which crystal-lizes as brown plates and contains a neutral, bridging S_2N_2 ligand (Figure 6) coordinated *via* its two nitrogen atoms. A feature of the crystal structure of both the chloro[13a] and bromo[13b] species is a strong interaction between two of the halogens and the sulfur atoms of the S_2N_2 ring. In both cases the N−Pd−X' angle is substantially less than 90° (84.7° and 85.7° for Cl and Br respectively), an effect which has been noted in other S_2N_2 bridged systems.[14] Also significant is the fact that in both cases the anion is almost perfectly planar, which raises the possibility of utilizing them in stacking systems with appropriate cations.
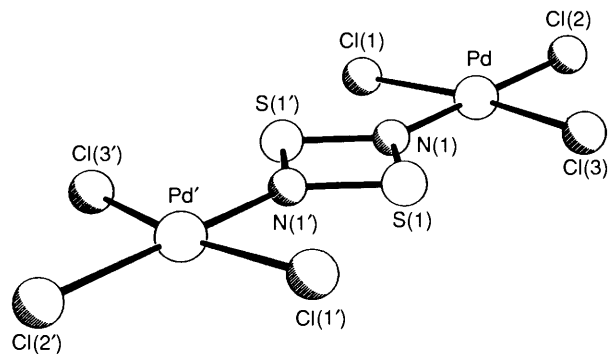

Figure 7 The structure of the $[Pd_2Cl_4(S_2N_2)]^{2-}$ anion.

Figure 8 The structure of the $[PdCl_2(S_2N_2H)]^-$ anion.

Figure 6 The structure of the $[Pd_2Cl_6(S_2N_2)]^{2-}$ anion.

Significant amounts (*ca.* 20% yield) of $[PPh_4]_2[Pd_2X_4(S_3N_2)]$ in the form of bright orange needles (X = Cl) or plates (X = Br) are also obtained. The crystal structure of the chloro species reveals the presence of two $PdCl_2$ units bridged by a planar $S_3N_2{}^{2-}$ ligand, which coordinates *via* two sulfurs (Figure 7). Within the S_3N_2 unit there are two short and two long S−N bonds whilst the plane of this unit is inclined at 119° from both coordination planes. This is only the second example of a complex of the $S_3N_2{}^{2-}$ ligand. A low-yield by-product of the reaction[15] of $PdCl_2$ with S_4N_4 in refluxing McOH is $Pd_2(S_3N)_2(S_3N_2)$, which contains two $Pd(S_3N)$ units bridged by S_3N_2.

The lowest-yield product is also potentially the most useful. In both the chloro and bromo cases red crystals of $[PPh_4][PdX_2(S_2N_2H)]$ can be isolated; the crystal structure of
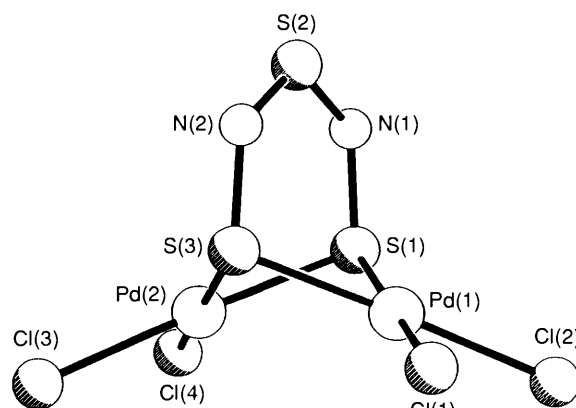
the chloro compound shows it (Figure 8) to be analogous to the many other $S_2N_2H^-$ complexes we have prepared, with the proton attached to the metal-bound nitrogen. In view of the ability of $S_2N_2H^-$ to promote stacking properties in its complexes[16] it seems likely that these complexes will find a use as synthons in the preparation of new 1-D materials.

Finally in this section we shall consider a reaction which, although it falls outside the precise brief defined earlier, has great potential for future development. If a thf solution of S_4N_4 is treated with the highly reducing 19-electron species cobaltocene, also in thf, one obtains an immediate precipitate of dark maroon coloured $[CoCp_2][S_3N_3]$.[17] This is not a particularly surprising result since it has long been established that reduction of S_4N_4 can readily generate salts of the cyclic $S_3N_3{}^-$ anion. However, the nearly black colour of the solid product suggests that its structure is unusual, especially since most salts of either $[CoCp_2]^+$ or $[S_3N_3]^-$ are yellow. The crystal structure reveals the reason for this anomalous colour (Figure 9). The cations and anions are arranged to form continuous stacks of alternating $[CoCp_2]^+$ cations and $[S_3N_3]^-$ anions with an array of hydrogen bonds between the C−H groups on the Cp rings and the nitrogens in the S_3N_3 rings. Clearly, there is potential for extending this chemistry to systems involving other metals, and we have already made some tentative progress in this field. For example, *bis*-benzene chromium, $Cr(C_6H_6)_2$, reacts with S_4N_4 to give $[Cr(C_6H_6)_2][S_3N_3]$ which is obtained as a dark green solid.[18] This is not a colour associated with either the cation or anion and so it is reasonable to conclude that this too contains strong cation–anion interactions in the solid state. Although this result is encouraging, it should be noted that it is not a foregone conclusion that such products will be stable. For example, we have found that while the reaction of $Na[S_3N_3]$ with $[FeCp_2]Cl$

does proceed *via* elimination of NaCl, the desired product, namely [FeCp$_2$][S$_3$N$_3$], is unstable and readily disproportionates to ferrocene and S$_4$N$_4$.

3 Chemistry of the Heavy Chalcogen Nitrides

In view of the wealth of chemistry of S$_4$N$_4$ and related sulfur–nitrogen systems it would, on the face of it, appear logical to
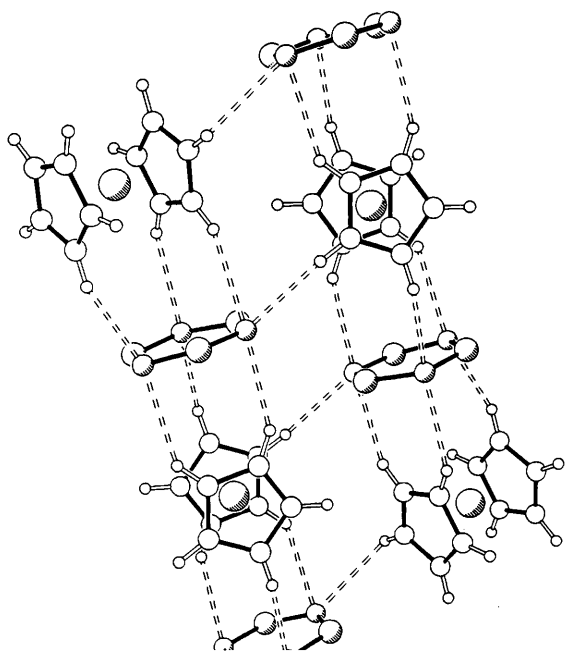

(a)

(b)   (c)

Figure 10 Mixed sulfur–selenium–nitrogen rings: the structures of (a) [SSe$_2$N$_2$]$_2^+$, (b) [SSe$_2$N$_2$]$^{+\cdot}$, and (c) [S$_2$SeN$_2$]$^{+\cdot}$.

Figure 11 The structure of complexes of the type Pt(SSeN$_2$)(PR$_3$)$_2$.

Figure 9 The stacking structure observed in [CoCp$_2$][S$_3$N$_3$]. Ball and stick representation (top) showing the C–H$\cdots$N contacts, and space filling representation (bottom).

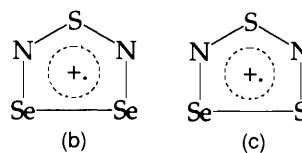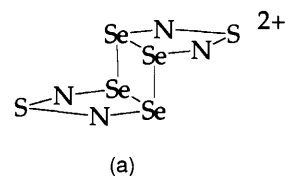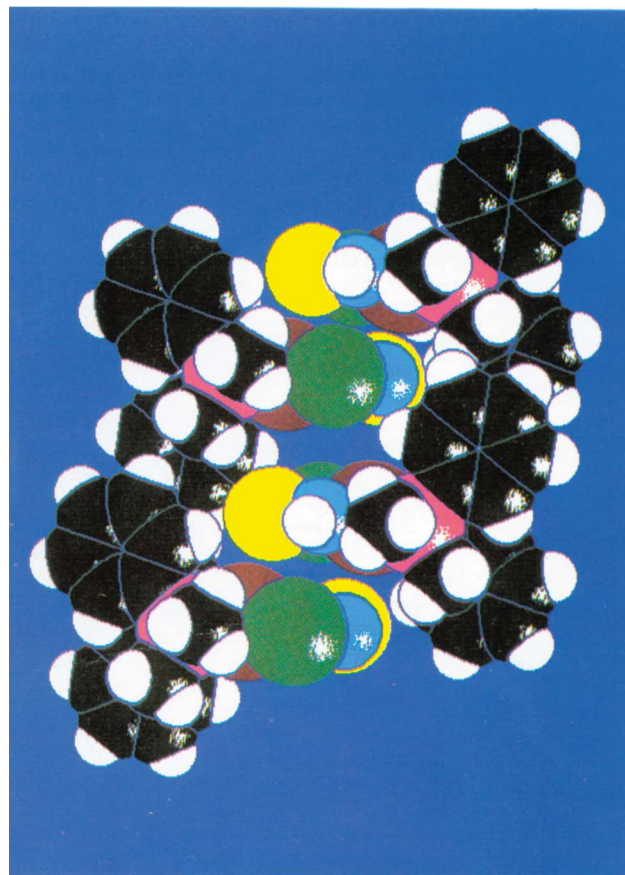**Figure 12** Space filling representation of the stacking array observed in the crystal structure of [Pt(SSeN$_2$H)(PMe$_2$Ph)$_2$]BF$_4$.

study heavier chalcogen systems. However, such a progression is fraught with difficulties, and has only recently yielded significant results. Tetraselenium-tetranitride, Se$_4$N$_4$, has been known for many years but for most of that time it has remained undeveloped as a synthetic reagent, due in part to a combination of its insolubility and instability. This latter property is expecially noteworthy since we have found that the destructive ability of amounts as small as 20 mg warrants extreme caution and compression of particles < 100 µg in weight produces an audible explosion. Recent work has, however, indicated that whilst it is

undoubtedly more chemically inert than S_4N_4, Se_4N_4 does have the potential for interesting chemistry in its own right. Furthermore, other binary selenium–nitrogen systems have come to light together with hetero-chalcogen–nitrogen systems which contain sulfur and selenium or tellurium, suggesting that there is great scope for development in this area.

3.1 Sulfur–Selenium–Nitrogen Systems

This class of compound has its origin in the late seventies when it was noted by Street et al,[19] that reaction of $[(Me_3Si)_2N]_2S$ with selenium halides results in insoluble salts of the type $[SSe_2N_2]_2X_2$ (X = Cl or Br). It was subsequently shown that similar salts can be generated by reaction of S_4N_4 with $Se_4(AsF_6)_2$, and contain a dimeric cation (Figure 10a);[20] in solution the $(SSe_2N_2)^{+\cdot}$ radical is generated (Figure 10b) and has been monitored by EPR.[21] The related mono-selenium radical cation $(S_2SeN_2)^{+\cdot}$ (Figure 10c) has also been observed by the latter technique – it results when the product of the reaction between $Se_8(AsF_6)_2$ and four equivalents of $(NS)AsF_6$ in SO_2 is dissolved in SO_2.

We have shown that the insoluble salt $[SSe_2N_2]_2Cl_2$ reacts with cis-$PtCl_2(PR_3)_2$ in liquid ammonia to generate complexes of the $SSeN_2^-$ ligand.[22] Figure 11 shows the structure of one of these complexes; note that the single selenium present is invariably bound to the metal. More conveniently, the same products result from the reaction of the platinum compounds with $SeCl_4/$ $[S_4N_3]Cl$ mixtures in ammonia. If this reaction is performed using $[S_4{}^{15}N_3]Cl$ then a product with ca. 33% ^{15}N enrichment can be obtained and values for $^{15}N-^{31}P$ couplings can be measured by ^{31}P NMR. In the case of $Pt(SSeN_2)(PMe_2Ph)_2$ the metal-bound nitrogen couples to both the cis and trans phosphorus atoms (with magnitudes 6 and 24 Hz respectively) whilst the other nitrogen couples solely to the latter phosphorus (12 Hz). Interestingly, these couplings are virtually identical to those seen in the analogous $S_2N_2{}^{2-}$ complexes, indicating that the substitution of one selenium for sulfur has little effect upon the electronic environment about the two nitrogens. This is further confirmed by the fact that the basicity of the metal-bound nitrogen is similar in both types of complex.

Reaction of the above species with acids such as HBF_4 yields complexes of $SSeN_2H^-$ in which the metal-bound nitrogen is protonated.[22] We have undertaken detailed studies of the solid-state properties of complexes of the type $[Pt(S_2N_2H)(PMe_2Ph)_2]X$ (where X = Cl$^-$, $BF_4{}^-$, etc.) which form infinite stacking arrays.[23] In the solid state $[Pt(SSeN_2H)(PMe_2Ph)_2]BF_4$ also stacks (Figure 12) with significant interactions between adjacent cations.

3.2 Selenium–Nitrogen Systems

Until quite recently the only binary selenium nitride known was Se_4N_4, a reddish orange insoluble solid with the same molecular structure as S_4N_4 but an order of magnitude more explosive. Traditionally it is prepared by the reaction of selenium halides with liquid ammonia at high pressure, though in our experience the 'wet' method[24] involving the passage of ammonia through a toluene solution of $[Et_2O]_2SeO$ is preferable. The first example of a reaction with a metal species was the preparation of $[WCl_4(NSeCl)]_2$[25] (Figure 13) from WCl_6 and Se_4N_4; the
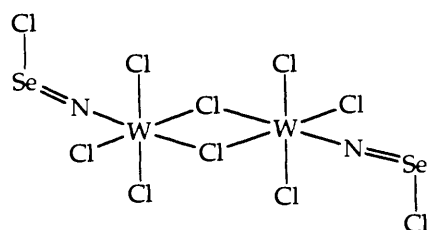

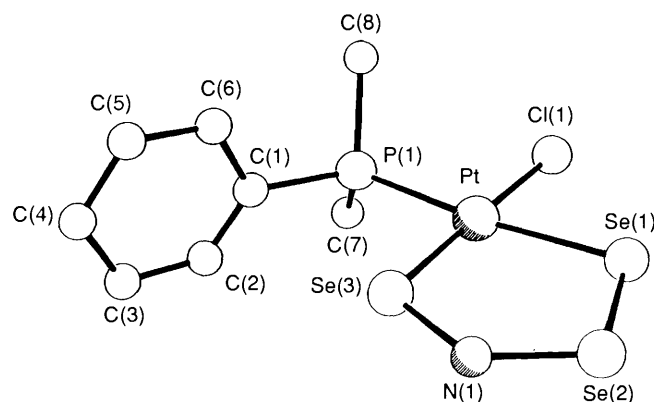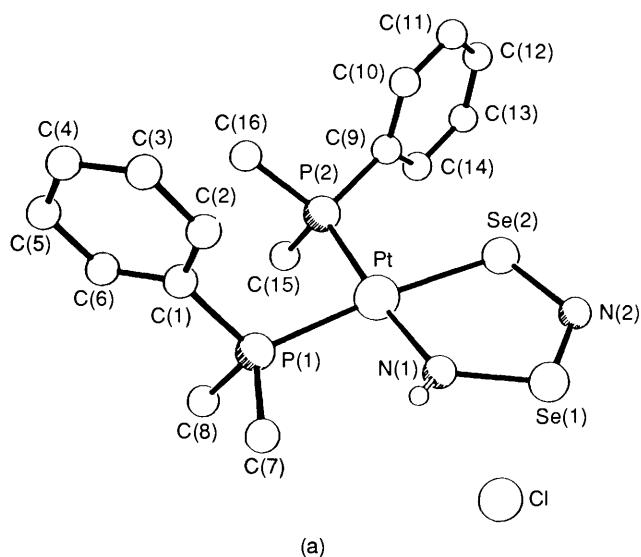
Figure 13 The structure of $[WCl_4(NSeCl)]_2$.

Figure 14 The structure of $Pt(Se_3N)Cl(PMe_2Ph)$, the first example of a metal–selenium–nitrogen metallocycle.

complex contains the NSeCl ligand which is analogous to NSCl which has been characterized as a ligand in numerous systems.[3] A similar reaction involving $MoCl_5$ in refluxing CH_2Cl_2 leads to the black complex $[MoCl_4(NSeCl)]_2$.[26]
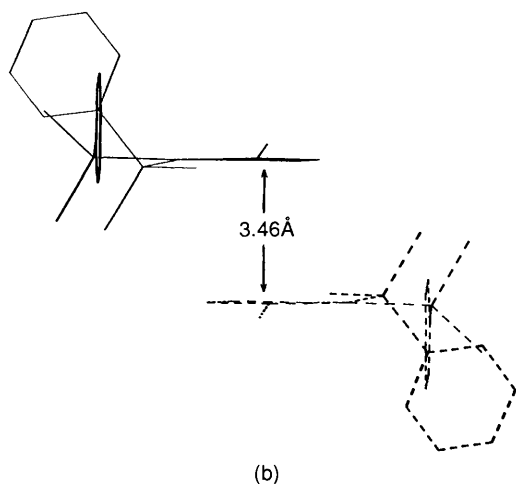
The reactive chloro-bridged platinum species $[PtCl_2(PMe_2Ph)]_2$ was referred to earlier in this review with regard to its ability to react with S_4N_4 to give complexes of $S_4N_4{}^{2-}$. The latter reaction is performed at room temperature; in contrast Se_4N_4 only reacts upon heating to ca. 90 °C in $CHCl_3$ and does not retain its structure in the form of an $Se_4N_4{}^{2-}$ ligand. Instead the molecule fragments to smaller anions which can be detected by TLC as intense purple (low R_f) and green (high R_f) bands. After purification by gel-permeation and preparative TLC, X-ray crystallography reveals the green complex to be $Pt(Se_3N)Cl(PMe_2Ph)$ (Figure 14)[27] and mass spectrometry indicates that the purple complex formed is $Pt(Se_2N_2H)Cl(PMe_2Ph)$,[28] though it is not stable long enough in solution to be crystallized. It may, however, be derivatized by addition of PMe_2Ph to give the readily crystallizable $Pt(Se_2N_2H)(PMe_2Ph)_2]Cl$ (Figure 15). The structure of this again shows the metal-bound nitrogen to be protonated, and as in analogous mono- and di-sulfur species there are significant interactions between cations. However, these interactions do not result in the formation of continuous stacks as is the case in the latter complexes; instead discrete pairs of cations pack with their $PtSe_2N_2$ rings parallel and overlapping (Figure 15).

A better, and safer, route to complexes of the $Se_2N_2{}^{2-}$ and $Se_2N_2H^-$ ligands comes with the use of $SeCl_4{}^{29a}$, or better still $SeOCl_2$,[29b]/liquid ammonia mixtures to generate the desired anions in situ. These anions may be trapped by the addition of the platinum complexes cis-$PtCl_2(PR_3)_2$ and the resulting species isolated in good yield. Thus addition of $PtCl_2(PMe_2Ph)$ to liquid ammonia at -78 °C followed by cooling with liquid nitrogen and addition of $SeOCl_2$ generates a mixture which, when allowed to heat to room temperature under pressure, produces $Pt(Se_2N_2)(PMe_2Ph)_2$ in quantitative yield. The reaction can be extended to form complexes of other phosphines in similar yield and has allowed the study of some of the fundamental chemistry associated with these systems. These studies show that there is often a marked contrast between the properties of the selenium-containing complexes and their $S_2N_2{}^{2-}$ analogues. For example, their reactivity towards halogens; whereas the $S_2N_2{}^{2-}$ complexes react via oxidative addition to give relatively stable Pt^{IV} species, their $Se_2N_2{}^{2-}$ counterparts lose the latter ligand in the form of Se_4N_4 and generate simple dihalogen Pt^{II} species.[30] Another difference is in the basicity of the metal-bound nitrogen, which is far greater in the selenium-containing ligand. Thus $Se_2N_2{}^{2-}$ complexes readily deprotonate their $S_2N_2H^-$ counterparts.

The reaction between S_4N_4 and $Pt(PPh_3)_3$ has been extensively studied. When it is performed in CH_2Cl_2 the initial products include $Pt(S_2N_2)(PPh_3)_2$ and an intermediate species which decomposes via loss of PPh_3 to give the dimeric complex

(a)

3.46Å

(b)

Figure 15 The *X*-ray crystal structure of [Pt(Se$_2$N$_2$H)(PMe$_2$Ph)$_2$]Cl together with the stacking array exhibited by the cations.

[Pt(S$_2$N$_2$)(PPh$_3$)]$_2$.[31] We have now found that the analogous reaction occurs if Se$_4$N$_4$ is used instead;[32] thus if solid Se$_4$N$_4$ is stirred with a solution of Pt(PPh$_3$)$_3$ in CH$_2$Cl$_2$ at room temperature the colour of the mixture rapidly darkens and ^{31}P NMR can be used to detect the presence of Pt(Se$_2$N$_2$)(PPh$_3$)$_2$ together with another species characterized by a singlet and doublet (with appropriate [195]Pt satellites). By analogy with conclusions drawn from work on the S$_4$N$_4$ reaction this latter species could well be Pt$_2$(Se$_2$N$_2$)$_2$(PPh$_3$)$_3$; it rapidly decomposes with loss of PPh$_3$ to give an insoluble green compound which we have shown by *X*-ray crystallography to be [Pt(Se$_2$N$_2$)(PPh$_3$)]$_2$ (Figure 16). The important feature of this reaction is that it involves Se$_4$N$_4$ reacting in *exactly* the same manner as S$_4$N$_4$. This is particularly striking when one notes that the reaction is actually performed under very mild conditions – indeed it is the only metal reaction involving Se$_4$N$_4$ so far discovered that does not require the use of refluxing solvent. We can conclude that many other systems in which S$_4$N$_4$ reacts may well be accessible to Se$_4$N$_4$ and clearly the chemistry of this molecule awaits development.

Apart from Se$_4$N$_4$ there are only two species which contain just selenium and nitrogen: Se$_4$N$_2$ and (Se$_3$N$_2$)$_n^+$ (*n* = 1 or 2). The former compound has been prepared by Dehnicke *et al.* (equation 2).[2b] It is obtained as a black micro-crystalline solid which has a stability similar to that of S$_4$N$_4$ and which is thought to have a structure analogous to that of S$_4$N$_2$ (Figure 17). No further chemistry has been reported to date but the compound clearly has great potential as a reagent, particularly as it is apparently substantially less explosive than Se$_4$N$_4$.
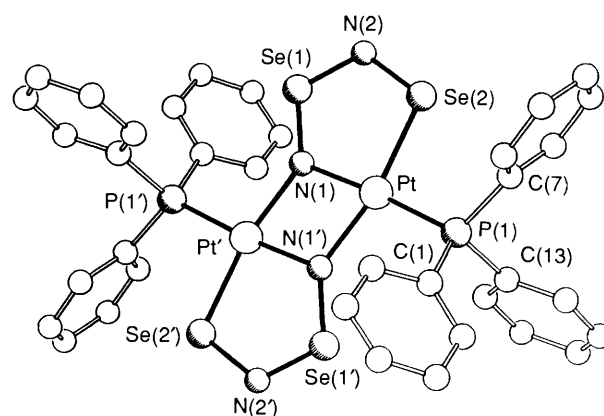

Figure 16 The structure of the dimeric Se$_2$N$_2{}^{2-}$ complex [Pt(Se$_2$N$_2$)(PPh$_3$)]$_2$.

Figure 17 The proposed structure of Se$_4$N$_2$.

$$2Se_2Cl_2 + 4Me_3SiN_3 \rightarrow Se_4N_2 + 5N_2 + 4Me_3SiCl \quad (2)$$

Finally, the species (Se$_3$N$_2$)$_n^+$ have been reported to form as shown in equation 3.[33] In solution the *n* = 1 species generates the 6π radical (Se$_3$N$_2$)$^{2+\cdot}$ whereas the *n* = 2 compound gives the 7π (Se$_3$N$_2$)$^{+\cdot}$. Both have the same basic structure (Figure 18).

$$Se_4N_4 + Se_4(AsF_6)_2 \rightarrow [Se_3N_2]_2[AsF_6]_2$$
$$[Se_3N_2]_2[AsF_6]_2 + 3AsF_5 \rightarrow [Se_3N_2][AsF_6]_2 + AsF_3 \quad (3)$$
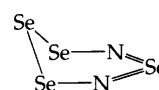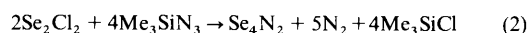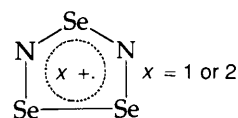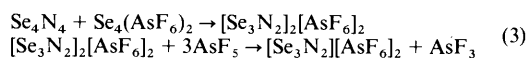

Figure 18 The structure of selenium–nitrogen rings of the type [Se$_3$N$_2$]$^{x+\cdot}$, where *x* = 1 or 2.

3.3 Tellurium–Sulfur–Nitrogen Compounds

Two Te–S–N species have been prepared by similar routes which involve reacting TeCl$_4$ with the sulfur(II) and sulfur(IV) compounds [(Me$_3$Si)$_2$N]$_2$S and (Me$_3$SiN)$_2$S. The first of these gives rise to a dark insoluble compound formulated as Te$_3$N$_2$SCl$_2$.[34] The proposed structure (Figure 19a) is somewhat tentative and awaits elucidation. However, we have used this compound to generate a complex of the novel anion TeSN$_2^{2-}$ *via* reaction with *cis*-PtCl$_2$(PMe$_2$Ph)$_2$ and the base DBU.[35] The resulting species, Pt(TeSN$_2$)(PMe$_2$Ph)$_2$, was characterized by micro-analysis and ^{31}P NMR, which reveals the first reported examples of [2]J[[125]Te–^{31}P] couplings.[36] As in the previous sulfur and selenium cases the metal-bound nitrogen may be protonated using HBF$_4$ to give [Pt(TeSN$_2$H)(PMe$_2$Ph)$_2$]BF$_4$, the structure of which has been determined (Figure 19b). The tellurium is metal-bound with a Pt–Te bond length of almost exactly 2 Å. Inclusion of one heavy chalcogen does not appear to affect the basicity of the metal-bound nitrogen. We have yet to find a route to complexes of the di-tellurium species (Te$_2$N$_2$)$^{2-}$

Finally, reaction of TeCl$_4$ with (Me$_3$SiN)$_2$S affords (TeN$_2$SCl)$_3$N[37] which differs from Te$_3$N$_2$SCl$_2$ in being somewhat soluble and bright yellow in colour. The intriguing stucture of this compound (Figure 20) has no parallel in sulfur–nitrogen chemistry, indicating that the inclusion of tellurium into these
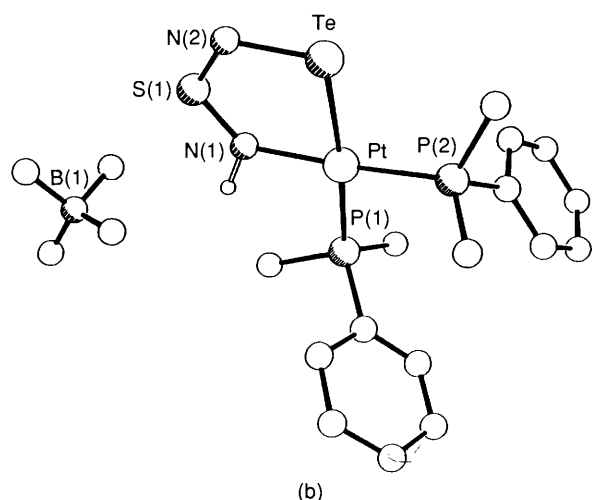
(a)

Figure 20 The structure of $(TeN_2SCl)_3N$.

(b)
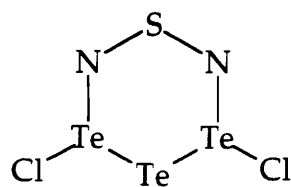
Figure 19 The proposed structure of $Te_3N_2SCl_2$ (a) together with the crystal structure of the cation in $[Pt(TeSN_2H)(PMe_2Ph)_2]BF_4$ (b).

systems generates the potential for the appearance of novel bonding arrangements.

4 Conclusion

There has been an explosion in activity in metal–chalcogen nitride chemistry in the past few years. This has been due, in part at least, to the increased interest in solid-state properties of inorganic heterocycles coupled with improved synthetic methods and the availability of rapid structural characterization. The combination of X-ray crystallography and multi-element NMR is extremely powerful and has enabled the correlation of spectra with structure to such an extent that the prospects for mechanistic and solution studies are now good. The ability of the metal centre to stabilize otherwise unknown chalcogen nitride anions places M–E–N chemistry at the forefront of chalcogen nitride chemistry, encouraging the synthesis of the free anions. The past few years have laid the foundations for the development of exciting new molecules and materials over the next decade.

5 Note Added in Proof

Recent months have seen a number of significant advances in this area, resulting in the preparation of potentially important new reagents. In particular, the work of Haas et al. has proved especially fruitful, resulting in a range of novel $Se-N$ and $Te-N$ systems. Thus Se_2Cl_2 reacts with Me_3SiNSO to generate $Se(NSO)_2$ and with $Li[N(SiMe_3)_2]$ to give $Se[N(SiMe_3)_2]_2$; both these species are potentially useful synthetic reagents in their own right. The former has already been the subject of intensive study:[38] it reacts with AsF_5 to generate a salt of dimeric $[(SSe_2N_2)_2]^{2+}$ cation which in turn reacts with halogens to give species of the type $[XSe_2N_2S]^+$ which contain exocyclic halogen atoms bound to the five-membered ring. The same product $(X = Cl)$ is also obtained directly by reaction of $Se(NSO)_2$ with $SbCl_5$ in CH_2Cl_2 whilst the dichloro compound $Cl_2Se_2N_2S$ results when $POCl_3$ is used instead. The facile loss of SO_2 from
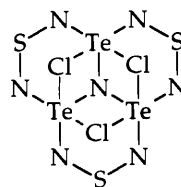
$Se(NSO)_2$ makes it a potent source of the $SSeN_2$ fragment, which can be stabilized as an adduct with $TiCl_4$; reaction of this species with AsF_5 results in the novel cation $[SeS_3N_5]^+$ which has a structure similar to that of $[S_4N_5]^+$ with one sulfur replaced by selenium. The $SeSN_2$ fragment can also be incorporated into tellurium-containing systems; thus reaction of $Se(NSO)_2$ with $TeCl_4$ results in $Cl_2TeSeSN_2$,[39] in which the two chlorines are covalently bound to the tellurium atom which is itself part of a five-membered ring. Also produced in this reaction is $Cl_6Te_2N_2S$,[40] which has an unusual structure based around a TeNSNTe unit with two bridging chlorine atoms. This species reacts with Ph_3Sb to generate $Cl_2Te_2N_2S$ which is a five-membered ring system with a $Te-Te$ bond and both chlorines attached to one of the tellurium atoms.[41] Interestingly, this same compound has been identified as the product of the reaction of $TeCl_4$ with $S[N(SiMe_3)_2]_2$ in CH_2Cl_2, implying that the original structure proposed by Zibarev et al. (Figure 19a)[34] is in error.

Roesky et al. have shown that the tellurium analogue of $Se[N(SiMe_3)_2]_2$ can be prepared by reaction of $TeCl_4$ with $Li[N(SiMe_3)_2]$;[42] the $Te[N(SiMe_3)_2]_2$ thus produced may be purified by sublimation and has clear potential as an important reagent. The same workers have also prepared $[FTeNSN]_3N$ by reaction of TeF_4 with $[Me_3SiN]_2S$ and have shown it to have a structure analogous to its chloro counterpart.[43] The first examples of reactions involving Se_4N_2 have been reported:[44] treatment with $SnCl_4$ or $TiCl_4$ leads to $SnCl_4(Se_4N_2)_2$ and $TiCl_4$ (Se_4N_2) respectively. We have shown that ^{15}N-labelled ammonia gas is an efficient source of the latter isotope for chalcogen–nitrogen systems.[45] Thus introduction of $^{15}NH_3$ into a solution of $(EtO)_2SeO$ in xylene, under reduced pressure, leads to $Se_4{}^{15}N_4$; if the reaction is performed in the presence of $PtCl_2(PMe_2Ph)_2$ then $Pt(Se_2{}^{15}N_2)(PMe_2Ph)_2$ is obtained. This technique does appear to be very versatile – for example if the latter reaction is repeated with $SOCl_2$ present rather than $(EtO)_2SeO$, the product is $Pt(^{15}NSO)_2(PMe_2Ph)_2$. Finally, we have found that ammonia at high pressure acts as an efficient solvent for Se_4N_4.[46] A mixture of the latter with $PtCl_2(PMe_2Ph_2)_2$ in ammonia at 50 Atm pressure results in the efficient preparation of $Pt(Se_2N_2)(PMe_2Ph)_2$. Interestingly, if $Se_4{}^{15}N_4$ is dissolved in ammonia at this pressure and then recrystallized by cooling the resulting product is still fully labelled indicating that, unlike S_4N_4, Se_4N_4 does not react with ammonia as it dissolves.

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