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Use of Se_4N_4 and $Se(NSO)_2$ in the preparation of palladium adducts of diselenium dinitride, Se_2N_2; crystal structure of $[PPh_4]_2[Pd_2Br_6(Se_2N_2)]$ †

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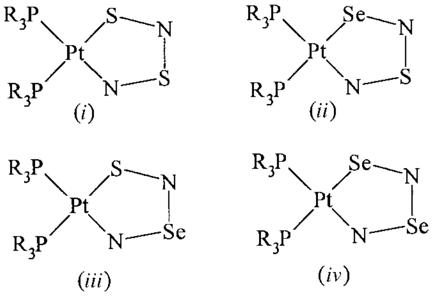
Reaction of Se_4N_4 with $[NBu^n_4]_2[Pd_2Br_6]$ at 100 °C in CH_2Cl_2 resulted in $[NBu^n_4]_2[Pd_2Br_6(Se_2N_2)]$ **1a** in high yield (67%). In contrast to the reaction of $[PPh_4]_2[Pd_2Br_6]$ with S_4N_4, which generates a number of products, the tetrabutylammonium salt generated only $[NBu^n_4]_2[Pd_2Br_6(S_2N_2)]$ **1b**; comparison of the IR spectra of **1a** and **1b** allows unambiguous identification of the two bands due to E_2N_2 vibrations. While reaction of $S(NSO)_2$ with $[Pt(PPh_3)_3]$ leads to a mixture of $[Pt(S_2N_2)(PPh_3)_2]$ and $[Pt(NSO)_2(PPh_3)_2]$, only the latter species forms in the analogous reaction of $Se(NSO)_2$. Two different results were also found in reactions with $[PPh_4]_2[Pd_2Br_6]$; while $S(NSO)_2$ appears surprisingly inert to this reagent, $Se(NSO)_2$ reacts, when present in excess, to give the unexpected product $[PPh_4]_2[Pd_2Br_6(Se_2N_2)]$ **1c**. The crystal structure of the latter confirms the presence of the adducted diselenium dinitride unit.

A number of significant inroads into the co-ordination chemistry of selenium–nitrogen and mixed selenium–sulfur–nitrogen ligands have been reported in recent years.[1] The nature of these advances suggests that, ultimately, the range and structural diversity of such complexes will rival that of their sulfur–nitrogen congeners. By way of example, one of the best known and most studied S–N ligands is $[S_2N_2]^{2-}$, which occurs in complexes such as $[Pt(S_2N_2)(PR_3)_2]$ [Scheme 1(*i*)]. Recent work has demonstrated the stability of complexes of the selenium analogue, $[Se_2N_2]^{2-}$ [as in Scheme 1(*iv*)], and of the mixed ligand $[SeSN_2]^{2-}$ (ref. 2) [it is noteworthy that in the latter case only the isomer illustrated in Scheme 1(*ii*) has been observed]. The recent report of the preparation of the first examples of adducts of neutral diselenium dinitride, Se_2N_2, added weight to this conclusion.[3] The adducts in question, salts of $[Pd_2Cl_6(Se_2N_2)]^{2-}$, form in the high-temperature reaction of Se_4N_4 with simple halide-bridged palladium salts, and appear to be stable both to air and friction (in marked contrast to Se_4N_4 which is a particularly pernicious explosive).

Here we report on the preparation of the bromide analogues of these adducts, *i.e.* salts of $[Pd_2Br_6(Se_2N_2)]^{2-}$ with either $[PPh_4]^+$ or $[NBu^n_4]^+$ as cations. The advantage of the latter cation is its markedly less complicated IR spectrum and this, in conjuction with the presence of bromine in the system, allows a more complete analysis of the spectrum than was previously possible. In addition, we present the results of investigations into the chemistry of a potentially important synthon: $Se(NSO)_2$. First prepared by Haas *et al.*[4] in 1991, this air-sensitive material has been shown to react with $TiCl_4$ to generate an adduct of $(SSeN_2)$. Here we report on investigations into its reactivity towards simple platinum and palladium complexes and contrast the results with those obtained for the sulfur analogue, $S(NSO)_2$.

Experimental

Unless otherwise stated all reactions were performed under an inert atmosphere. The ^{31}P NMR measurements were performed on a JEOL FX90Q spectrometer operating at 36.21 MHz and run in $CDCl_3$. The tetrabutylammonium and tetraphenylphosphonium salts of $[Pd_2Br_6]^{2-}$ were prepared from $PdBr_2$ by the action of KBr in water followed by addition of either $[PPh_4]Br$ or $[NBu^n_4]Br$. Tetraselenium tetranitride was prepared from the action of ammonia upon diethyl selenite,[5] compounds $S(NSO)_2$[6] and $Se(NSO)_2$[4] by the literature routes. Infrared spectra were recorded using a PE 2000 FT spectrometer.



Scheme 1 Metallocycles containing the $[S_2N_2]^{2-}$, $[Se_2N_2]^{2-}$ and $[SSeN_2]^{2-}$ ligands; note that isomer (*iii*) is as yet unknown

CAUTION: Se_4N_4 is a severely explosive material; the risk of detonation is exacerbated during reaction at high temperatures.

Preparation

$[NBu^n_4]_2[Pd_2Br_6(Se_2N_2)]$ 1a. A mixture of Se_4N_4 (61 mg, 0.16 mmol) and $[NBu^n_4]_2[Pd_2Br_6]$ (193 mg, 0.16 mmol) in CH_2Cl_2 (50 cm^3) was sealed in a thick-walled tube fitted with a Young's joint and heated to 100 °C using an oil-bath. After thorough stirring at this temperature for 1.5 h the resulting dark mixture was cooled, filtered through Celite (in air) and the volume of the solvent reduced to *ca.* 5–10 cm^3 *in vacuo*. At this point the mixture was briefly heated to redissolve any solid and then cooled overnight in a freezer. This resulted in a crop of well formed claret coloured crystals which were isolated by decanting the mother-liquor. The latter was allowed to evaporate slowly in air, yielding a mixture of crystalline material and an oily residue. Washing this mixture with cold CH_2Cl_2 (3 × 5 cm^3) yielded the pure crystals which were combined with the original crop. Total yield 150 mg (67% based on palladium) {Found: C, 28.1; H, 5.1; N, 4.3. Calc. for $[NBu^n_4]_2[Pd_2Br_6(Se_2N_2)]$: C, 28.2; H, 5.3; N, 4.1%}. IR: 2964s, 2929s, 2873s, 1471s, 1382m, 1182mw, 1168m, 1110mw, 1065mw, 1032mw, 895m, 882m, 753ms, 740ms and 323m cm^{-1}.

$[NBu^n_4]_2[Pd_2Br_6(S_2N_2)]$ 1b. A mixture of $[NBu^n_4]_2[Pd_2Br_6]$ (160 mg, 0.14 mmol) and S_4N_4 (50 mg, 0.27 mmol) in CH_2Cl_2 (50 cm^3) was stirred overnight and the resulting dark red solution reduced in volume to 5 cm^3. Slow diffusion of diethyl ether

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into this solution resulted in the formation of dark red crystals of $[NBu^n{}_4]_2[Pd_2Br_6(S_2N_2)]$ (115 mg, 66% based on palladium) (Found: C, 30.1; H, 5.5; N, 4.7. Calc.: C, 30.3; H, 5.7; N, 4.4%). IR: 2961s, 2931ms, 2873ms, 1470s, 1381m, 1169m, 1109mw, 1064mw, 1033mw, 895m (sh), 882m, 855ms, 739m and 441mw cm^{-1}.

The mother-liquor from this crystallisation was reduced to dryness and infrared spectroscopy used to compare this crude material with the crystalline compound (see text).

$[PPh_4]_2[Pd_2Br_6(Se_2N_2)]$ 1c. Solid Se_4N_4 (150 mg, 0.4 mmol) was added to a solution of $[PPh_4]_2[Pd_2Br_6]$ (272 mg, 0.2 mmol) in CH_2Cl_2 (50 cm^3) in a thick-walled reaction tube fitted with a Young's greaseless joint. The mixture was stirred at room temperature under a nitrogen atmosphere; more CH_2Cl_2 was added to just below the seal of the joint which was then closed and the tube immersed in a pre-heated oil-bath at 100 °C. After *ca.* 1 h with continuous stirring the mixture consisted of a dark solution with dark coloured suspension. After cooling the solution was filtered through Celite in air and reduced in volume to 2 cm^3; layering with ether followed by slow diffusion yielded a crop of well formed dark red-orange crystals of compound **1c**. Yield 65 mg (21% based upon Pd) {Found: C, 37.2; H, 2.3; N, 1.8. Calc. for $[PPh_4]_2[Pd_2Br_6(Se_2N_2)]$: C, 37.0; H, 2.6; N, 1.8%}.

Reaction of $[Pt(PPh_3)_3]$ with $S(NSO)_2$. Solid $S(NSO)_2$ (14 mg, 0.09 mmol) was added, with stirring, to a solution of $[Pt(PPh_3)_3]$ (90 mg, 0.09 mmol) in toluene (60 cm^3) and the mixture stirred overnight. The solvent was removed *in vacuo* to give a yellow solid. Phosphorus-31 NMR measurements revealed the presence of *cis*-$[Pt(NSO)_2(PPh_3)_2]$[7] [δ 8.8, $^1J(^{195}Pt-^{31}P)$ 3190], $[Pt(S_2N_2)(PPh_3)_2]$[8] [δ_A 11.5, δ_x 24.1; $^1J_A(^{195}Pt-^{31}P_A)$ 2995, $^1J_x(^{195}Pt-^{31}P_x)$ 2825 Hz] together with $P(S)Ph_3$ and PPh_3.

Reaction of $[Pt(PPh_3)_3]$ with $Se(NSO)_2$. Solid $Se(NSO)_2$ (15 mg, 0.07 mmol) was added, with stirring, to a solution of $[Pt(PPh_3)_3]$ (72 mg, 0.07 mmol) in toluene (60 cm^3) to give a suspension which was stirred overnight. The solvent was removed from the reaction mixture *in vacuo* to give a yellow solid. Phosphorus-31 NMR spectroscopy revealed the presence of *cis*-$[Pt(NSO)_2(PPh_3)_2]$ [δ 8.8, $^1J(^{195}Pt-^{31}P)$ 3190], and $P(Se)Ph_3$ [δ 35.38, $^1J(^{77}Se-^{31}P)$ 730 Hz].

Reaction of $Se(NSO)_2$ with $[PPh_4]_2[Pd_2Br_6]$. Solid $Se(NSO)_2$ (35 mg, 0.17 mmol) was added to a solution of $[PPh_4]_2[Pd_2Br_6]$ (36 mg, 0.02 mmol) in CH_2Cl_2 (50 cm^3) and the mixture stirred overnight. At this point the solution was reduced in volume to 2 cm^3 and layered with Et_2O. After 48 h of slow diffusion a mixture of red crystals and a non-crystalline solid (15 mg) was generated. X-Ray crystallography and microanalysis revealed the red crystals to be $[PPh_4]_2[Pd_2Br_6(Se_2N_2)]$ **1c** (Found: C, 36.6; H, 2.2; N, 1.75; S, 0.0%). The non-crystalline solid was also shown to be predominantly $[PPh_4]_2[Pd_2Br_6(Se_2N_2)]$ by microanalysis and IR spectroscopy (the latter identical to those for samples prepared from Se_4N_4 as above). Total yield 15 mg, 37% based upon Pd.

When the reaction was performed in a 1:1 or 2:1 ratio of $Se(NSO)_2:[PPh_4]_2[Pd_2Br_6]$ most of the $[PPh_4]_2[Pd_2Br_6]$ remained unchanged (as shown by microanalysis and IR spectroscopy).

X-Ray crystallography

Crystal data for compound 1c. $C_{48}H_{40}Br_6N_2P_2Pd_2Se_2$, $M = 1556.95$; orthorhombic, space group *Pbca* (no. 61), $a = 18.200(7)$, $b = 20.653(8)$, $c = 13.496(10)$ Å, $U = 5072(3)$ Å^3, $Z = 4$, $D_c = 2.04$ g cm^{-3}. Red block of dimensions 0.10 × 0.10 × 0.10 mm, μ(Cu-Kα) = 137.7 cm^{-1}, $\lambda = 1.541\ 78$ Å, $F(000) = 2968$.

Data collection and processing. All measurements were made on a Rigaku AFC7S diffractometer with graphite-monochromated Cu-Kα radiation using the ω–2θ scan technique to a maximum 2θ value of 120.1°. Of 4231 measured reflections 1456 were unique [$I > 3\sigma(I)$]. Data were corrected for Lorentz-polarisation effects and an empirical absorption correction was applied resulting in transmission factors ranging from 0.62 to 1.00.

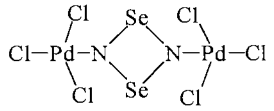
Structure analysis and refinement. The structure was solved by, and expanded, using Fourier techniques. Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically; hydrogen atoms were included but not refined. Refinement was by full-matrix least squares to $R = 0.046$ [$\Sigma(|F_o| - |F_c|)/\Sigma|F_o|$], $R' = 0.039$. The maximum and minimum residual electron densities in the final ΔF map were 0.86 and -0.78 e Å^{-3} while the largest parameter shift in the final refinement cycle was 0.05 times its e.s.d. All calculations were performed using the TEXSAN crystallographic package.[9]

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/355.

Results and Discussion

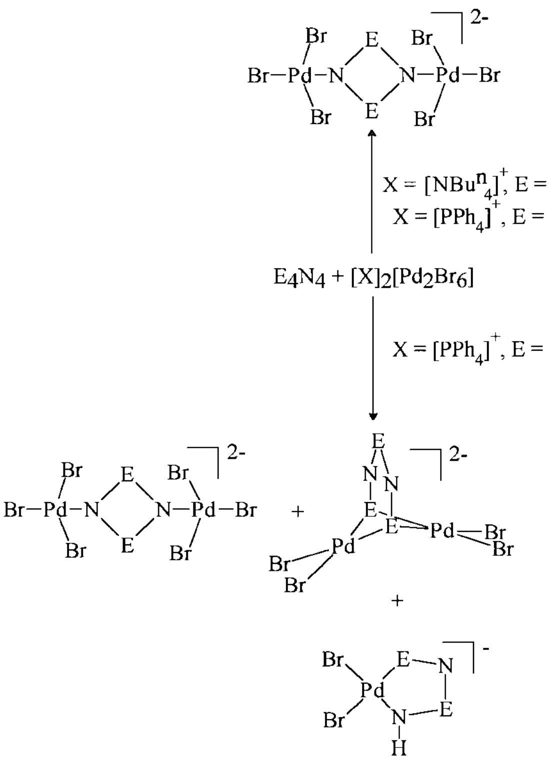
Reactions of Se_4N_4

The last few years have seen an increase in interest in the chemistry of selenium–nitrogen systems,[1] fuelled, in part, by the realisation that the chemistry of the main parent compound, Se_4N_4, is far more diverse that had been previously thought. A good example of the increased range of chemistry associated with this material came with the isolation of the first adducts of diselenium dinitride, a compound which, unlike its sulfur analogue, has yet to be prepared in the free state.[3] Thus, the high-temperature reaction of Se_4N_4 with salts of $[Pd_2Cl_6]^{2-}$ results in adducts of the type $[Pd_2Cl_6(Se_2N_2)]^{2-}$, with the $[PPh_4]^+$ salt of the latter characterised by X-ray crystallography.



We have now extended this reaction to salts of the bromo species $[Pd_2Br_6]^{2-}$. The tetraphenylphosphonium salt of the latter reacts to give $[PPh_4]_2[Pd_2Br_6(Se_2N_2)]$ in much the same yield as the chloro analogue; we have also characterised this species by X-ray techniques after its unexpected formation from reactions involving $Se(NSO)_2$ (see below). The corresponding tetrabutylammonium salt, $[NBu^n{}_4]_2[Pd_2Br_6(Se_2N_2)]$ **1a**, may also be prepared by the reaction of $[NBu^n{}_4]_2[Pd_2Br_6]$ with Se_4N_4 (Scheme 2). Two features make this the most interesting of the palladium species so far isolated. First, the yield is high; a typical reaction generates the high-purity crystalline material in some 67% yield (based on palladium), around three times that of its $[PPh_4]^+$ analogue. This is an important consideration, bearing in mind that the safety aspects of the use of Se_4N_4 (especially at such elevated temperatures) dictate that quantities of <150 mg should be used. With this kind of yield, however, such amounts of Se_4N_4 still allow the ready isolation of >100 mg of product, thus facilitating the investigation of its chemical properties.

The other key feature of compound **1a** is its infrared spectrum. By analogy with the spectra of salts of $[Pd_2X_6(S_2N_2)]^{2-}$ we should expect to see two vibrational peaks associated with the Se_2N_2 moiety.[10] These are not apparent with, for example, $[PPh_4]_2[Pd_2Cl_6(Se_2N_2)]$ due to the presence of the strong cation bands. We have previously shown that one of the desired bands



Scheme 2 The reactivity of salts of $[Pd_2Br_6]^{2-}$ towards S_4N_4 and Se_4N_4

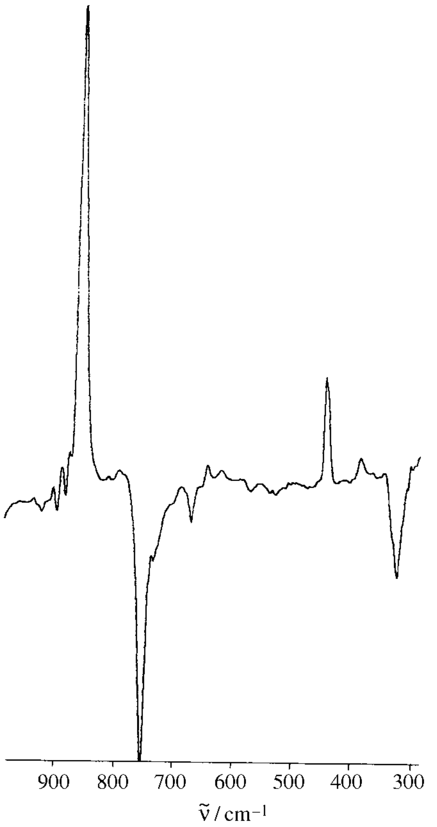
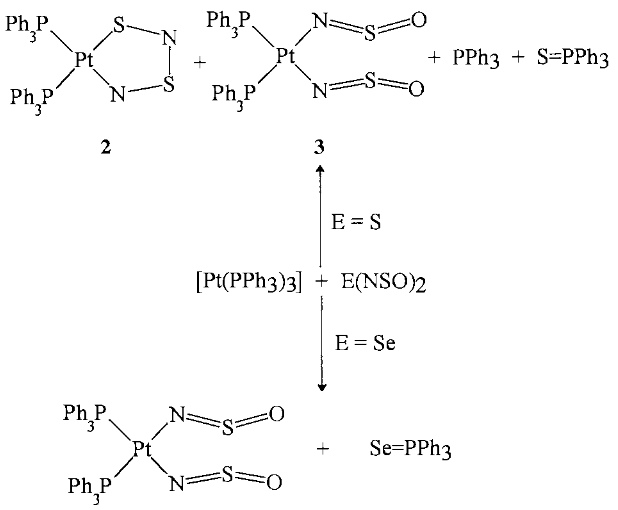


Fig. 1 Difference IR spectrum in which the spectrum of compound **1a** has been substracted from that of **1b**, revealing the two bands due to the (E_2N_2) vibrations



Scheme 3 The reactivity of $[Pt(PPh_3)_3]$ towards $S(NSO)_2$ and $Se(NSO)_2$

may be revealed by substituting $[NBu^n_4]^+$ for $[PPh_4]^+$ but postulated that the other was obscured by the Pd–Cl vibration. This is confirmed by the spectrum of **1a**; now the lack of intrusive cation vibrations *and* the shift of the metal–halogen stretch to lower frequency allow both bands to be resolved. As Fig. 1 shows, they are conveniently displayed by means of a difference spectrum wherein the spectrum of **1a** is subtracted from that of its sulfur analogue, $[NBu^n_4]_2[Pd_2Br_6(S_2N_2)]$ **1b** (prepared by the reaction of S_4N_4 with $[NBu^n_4]_2[Pd_2Br_6]$, see below). Owing to excellent correlation of the cation bands in each, only the two chalcogen–nitrogen bands are left. As expected there is a shift to low frequency on introducing the heavier chalcogen; thus the bands at 855 and 441 cm^{-1} of **1b** shift to 753 and 323 cm^{-1} for **1a**.

The formation of compound **1b** in the reaction of $[NBu^n_4]_2[Pd_2Br_6]$ with S_4N_4 is not a surprising result *per se*; what is unexpected, however, is the fact that this appears to be the *only* isolable product. By analogy with the reaction of $[PPh_4]_2[Pd_2Br_6]$ with S_4N_4, the generation of salts of $[Pd_2Br_4(S_3N_2)]^{2-}$ and $[PdBr_2(S_2N_2H)]^-$ would also be expected to occur.[10] Neither of these species crystallises from the crude product nor are any of the characteristic IR bands associated with them present for this material {for example, the medium-strength band at 642 cm^{-1} indicative of $[Pd_2Br_4(S_3N_2)]^{2-}$}. Quite why the change in cation should have such a drastic effect upon reaction products is not obvious. It is unlikely that either cation can affect the course of reaction by direct chemical means, indeed when the reaction of $[PPh_4]_2[Pd_2Br_6]$ with S_4N_4 is monitored by ^{31}P NMR spectroscopy then only the signal due to unchanged $[PPh_4]^+$ is observed in the reaction mixture. It is possible that small amounts of monomeric $[PdBr_4]^{2-}$ are present in either case and that this can influence the course of the reactions, though we have yet to prove this.

Reactions of $Se(NSO)_2$

Both $S(NSO)_2$ and $Se(NSO)_2$ are very reactive towards the platinum(0) species $[Pt(PPh_3)_3]$. The course of such reactions may be conveniently monitored by ^{31}P NMR spectroscopy which reveals a clear difference in the complexity of the two spectra, with more signals being present in the reaction involving $S(NSO)_2$. In the latter case the products appear to mirror those reported by Chivers *et al.*[11] for the reaction with $[Pt(PPh_3)_2(C_2H_4)]$, *i.e.* the most abundant species present is the metallocyclic $[Pt(S_2N_2)(PPh_3)_2]$ **2** (Scheme 3).[11] The only other identifiable metal species present in any significant amount is the $[NSO]^-$ complex $[Pt(NSO)_2(PPh_3)_2]$ **3**, which is seen as a singlet (with appropriate ^{195}Pt satellites) at δ 8.8 and is about half as abundant as **2**. The other main components of the spectrum are PPh_3 and $P(S)Ph_3$ which are present in the approximate ratio 2:3.

In the light of the above observations it was hoped that reaction of $Se(NSO)_2$ with $[Pt(PPh_3)_3]$ would proceed in a similar manner and generate a metallocycle. In view of the likelihood (albeit difficult to prove absolutely) that the order of S and N

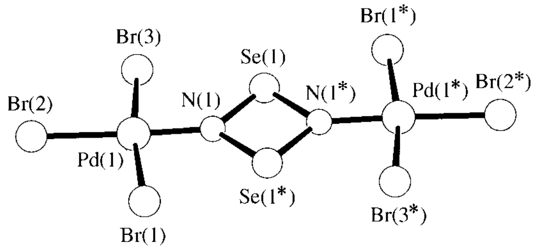


Fig. 2 Crystal structure of compound **1c**

atoms in **3** mirrors that in the starting material it might be hoped that the hitherto unseen isomer shown in Scheme 1(*iii*) would result. In fact, this is not the case. The reaction is far simpler than that involving $S(NSO)_2$; complex **3** results in very high yield alongside triphenylphosphine selenide (Scheme 3). No free PPh_3 is left; neither is there any evidence for the production of *any* metallocycle of the type shown in Scheme 1.

It is possible to speculate that the difference in the two reactions outlined above hinges on the relative strengths of the chalcogen–nitrogen bonds in the starting materials. If we assume that the reaction progresses *via* co-ordination/reduction of the $E(NSO)_2$ then a transitory complex of the type $[Pt\{E(NSO)_2\}(PPh_3)_2]$, containing the $[E(NSO)_2]^{2-}$ ligand, might be envisaged. If the latter were bidentate through the two nitrogens then the final rearrangement could proceed either through loss of ‘E’ to give **3** and $P(E)Ph_3$ (by reaction with free PPh_3) or through loss of sulfur and oxygen (presumably as SO_2) and formation of the metallocycle. The strength of the E–N bond would, of course, be a key factor in determining which of these two courses occurs; presumably in the case of $Se(NSO)_2$ the weakness of the Se–N bond, and the inherent stability of the NSO unit, conspire to generate the observed products. This casts some doubt on the efficacy of $Se(NSO)_2$ as a reagent for the preparation of new species under conditions involving oxidative addition.

Given that, as we have already seen, S_2N_2 and Se_2N_2 adducts readily form from $[Pd_6Br_6]^{2-}$, and given that both $S(NSO)_2$ and $Se(NSO)_2$ have been shown to react with $TiCl_4$ to generate adducts of S_2N_2[12] and $SSeN_2$[4] respectively, it would seem reasonable to expect similar products to predominate when $[PPh_4]_2[Pd_2Br_6]$ is treated with $E(NSO)_2$ (E = S or Se). In fact, in both cases unexpected results are observed. In the case of E = S there appears to be no reaction with $[PPh_4]_2[Pd_2Br_6]$, even when the former is present in excess and the reagents are allowed to stir in solution overnight. In contrast, $Se(NSO)_2$ reacts in an equimolar ratio to give a crude mixture from which two species may be crystallised by slow diffusion of ether into the dichloromethane solutions. One of these is simply the starting material, $[PPh_4]_2[Pd_2Br_6]$. Rather than the $SeSN_2$ adduct one might expect (*cf.* the $TiCl_4$ products, see above), the other compound actually proves to be $[PPh_4]_2[Pd_2Br_6(Se_2N_2)]$ **1c** *i.e.* the diselenium dinitride adduct.

The identity of compound **1c** has been confirmed by a number of techniques. X-Ray crystallography reveals the structure shown in Fig. 2, consistent with the presence of two selenium atoms in the central ring. In addition, microanalysis results in a zero sulfur content, while infrared spectroscopy reveals a spectrum identical to that of a sample of $[PPh_4]_2[Pd_2Br_6(Se_2N_2)]$ prepared by the reaction of Se_4N_4 with $[PPh_4]_2[Pd_2Br_6]$. When an eight-fold excess of $Se(NSO)_2$ is used then **1c** is the only isolable palladium species. From a mechanistic point of view it is very difficult to suggest how such a reaction is proceeding; suffice it to say that the palladium species must catalyse substantial decomposition (and subsequent rearrangement) of $Se(NSO)_2$. The ultimate fate of the sulfur atoms in the reaction is unknown.

Table 1 Selected bond distances (Å) and angles (°) in complex **1c**

Pd(1)–Br(1)	2.424(2)	Pd(1)–N(1)	1.875(9)
Pd(1)–Br(2)	2.294(2)	N(1)–Se(1)	1.809(10)
Pd(1)–Br(3)	2.428(2)	N(1)–Se(1*)	1.920(9)
N(1)–Pd(1)–Br(1)	88.0(1)	Pd(1)–N(1)–Se(1*)	136.9(5)
N(1)–Pd(1)–Br(3)	84.0(3)	Se(1*)–N(1)–Se(1)	94.2(4)
Pd(1)–N(1)–Se(1)	128.5(5)	N(1)–Se(1)–N(1*)	85.8(4)

The structure of compound **1c** is very much analogous to that of $[PPh_4]_2[Pd_2Cl_6(Se_2N_2)]$, with one intriguing difference. In the latter case an asymmetry within the anions was noted and ascribed to the presence of long-range intermolecular interactions. Though an even more pronounced asymmetry appears in **1c** (witness the two Se–N bond lengths of 1.81 and 1.92 Å, Table 1) there is no concomitant intermolecular interaction. It appears that in this case the asymmetry is inherent to the anions and is not the result of the crystal packing. Both these bond lengths are significantly larger than those in the chloro analogue (average length 1.79 Å) and in Se_4N_4. It is not clear why the asymmetry exists, though it is perhaps noteworthy that in $[(AlBr_3)_2(Se_2N_2)]$, the only other adduct of Se_2N_2 so far characterised by X-ray techniques, there is substantially less asymmetry in the bond lengths.[13]

The main conclusion to be drawn from this work is that the efficiency of formation of Se_2N_2 adducts by reaction of Se_4N_4 with palladium complexes is dependent upon both the cations and the halide ligands present in the starting material. The Se_4N_4–$[NBu^n_4]_2[Pd_2Br_6]$ system appears to be the most efficient; this is also the most useful in assigning the IR stretches of the product. In addition, while it is clear that $Se(NSO)_2$ has great promise as a new synthon, its chemistry does not mirror that of its sulfur analogue and the isolation of the Se_2N_2 adduct **1c** highlights its ability to exhibit unexpected reaction pathways.

Acknowledgements

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References

1 T. M. Klapötke, in *The Chemistry of Inorganic Ring Systems; Studies in Inorganic Chemistry*, ed. R. Steudel, Elsevier, Amsterdam, 1992, vol. 14, p. 409; T. Chivers, *Main Group Chem. News*, 1993, **1**, 6.

2 P. K. Kelly, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *Chem. Soc. Rev.*, 1992, 245.

3 P. F. Kelly and A. M. Z. Slawin, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1758.

4 A. Haas, J. Kasprowski, K. Angermund, P. Betz, C. Kruger, Y. Tsay and S. Werner, *Chem. Ber.*, 1991, **124**, 1895.

5 J. Adel, C. Ergezinger, R. Figge and K. Dehnicke, *Z. Naturforsch., Teil B*, 1988, **43**, 639.

6 D. A. Armitage and A. W. Sinden, *Inorg. Chem.*, 1972, **11**, 1151.

7 I. P. Parkin, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *Polyhedron*, 1989, **8**, 835.

8 R. Jones, P. F. Kelly, D. J. Williams and J. D. Woollins, *Polyhedron*, 1985, **4**, 1947.

9 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1985 and 1992.

10 V. C. Ginn, P. F. Kelly, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1992, 963.

11 T. Chivers, F. Edelmann, U. Behrens and R. Drews, *Inorg. Chim. Acta*, 1986, **116**, 145.

12 H. W. Roesky, J. Anhaus and W. S. Sheldrick, *Inorg. Chem.*, 1984, **23**, 75.

13 P. F. Kelly and A. M. Z. Slawin, *J. Chem. Soc., Dalton Trans.*, 1996, 4029.

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