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## Metal complexes of chalcogen-nitrogen ligands

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# **METAL COMPLEXES OF CHALCOGEN-NITROGEN LIGANDS**

**by**

**Antonio Soriano Rama**

**A Master's Thesis**

**Submitted in partial fulfilment of the requirements  
for the award of**

**Master of Philosophy of the Loughborough University of Technology**

**Department of Chemistry**

**February, 1996**

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**Dedicado con cariño a mis padres, Toni y Joaquina,  
y hermanas Silvia y Bea**

**"Mientras la ciencia a descubrir no alcance  
las fuentes de la vida,  
y en el mar o en el cielo haya un abismo  
que al cálculo resista;**

**mientras la humanidad, siempre avanzando,  
no sepa a dó camina;  
mientras haya un misterio para el hombre  
¡habrá poesía!"**

**G. A. Bécquer**

## **ACKNOWLEDGEMENTS**

Above all, I would like to give thanks to Dr. Paul Kelly, excellent supervisor and even better human being. I could have never completed this work without his advice and guidance.

Many thanks to Professor Derek Woollins for giving me the chance to be a member of his research group. I am also grateful to Alex Slawin for X-ray Crystal Structures.

Dr. Martin Smith deserves special mention for his patience. I am in your debt. Thanks very much to Andy Ross and Tuan Ly for being as they are and to the rest of the inhabitants of the inorganic lab: Robin, Mark, Alex, Dr. Jon Parr and Dr. Maria Loza.

I could not finish without naming three wonderful friends I had the luck to live with: Carsten, Dinos and K. L. There will be always a place in my heart for you.

## ABSTRACT

Reaction of  $\text{Me}_3\text{SiNSNSNSNSiMe}_3$  with  $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_6]$  results in a mixture of  $[\text{PPh}_4][\text{PdCl}_2(\text{S}_2\text{N}_3)]$  and  $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_4(\text{S}_3\text{N}_2)]$ ; in addition to the analogous bromo species, reaction with  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6]$  also generates  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6(\text{S}_2\text{N}_2)]$ . The crystal structure of  $[\text{PPh}_4][\text{PdBr}_2(\text{S}_2\text{N}_3)]$ , only the second full characterisation of a complex of  $[\text{S}_2\text{N}_3]^-$ , confirms the presence of two distinct S-N bond lengths (1.49 and 1.60 Å). The crystal structure of  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_4(\text{S}_3\text{N}_2)]$  is also described. Potential mechanisms for these reactions are discussed. The chemistry of the novel complex  $[\text{PPh}_4][\text{PdBr}_2(\text{S}_2\text{N}_3)]$  is briefly studied. The reactivity of  $\text{Me}_3\text{SiNSNSNSNSiMe}_3$  versus *cis*- $[\text{PtCl}_2(\text{PMe}_2\text{Ph})_2]$ ,  $[\text{PtCl}_2(\text{PMe}_2\text{Ph})]_2$  and  $[\text{Pt}(\text{PPh}_3)_3]$  is also reported.

The chemistry of 'BuNSNSNSN'Bu is studied in comparison to that of  $\text{Me}_3\text{SiNSNSNSNSiMe}_3$ .

Reaction of  $\text{Se}(\text{NSO})_2$  with  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6]$  gives  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6(\text{Se}_2\text{N}_2)]$ . This compound is the second example of a  $\text{Se}_2\text{N}_2$  adduct. Its crystal structure reveals that the bond lengths within the  $\text{Se}_2\text{N}_2$  moiety are not equivalent. Reaction of  $\text{Se}(\text{NSO})_2$  with  $[\text{Pt}(\text{PPh}_3)_3]$  affords  $\text{P}(\text{Se})\text{Ph}_3$  and  $[\text{Pt}(\text{NSO})_2(\text{PPh}_3)_2]$ .



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## ABBREVIATIONS

Å	Angstrom unit, $10^{-10}$ m
Bu	Butyl
$\text{cm}^{-1}$	wave number
dppe	1, 2-bis(diphenylphosphino) ethane
Et	Ethyl
FAB	fast atomic bombardment
Hz	Hertz, $\text{sec}^{-1}$
IR	Infrared
Me	Methyl
MO	molecular orbital
NMR	Nuclear Magnetic Resonance
Ph	Phenyl
ppm	parts per million
S-N	sulphur-nitrogen
X	halogen
$\delta$	NMR chemical shift

## GENERAL EXPERIMENTAL CONDITIONS

Unless stated otherwise all reactions were performed under an inert atmosphere ( $\text{N}_2$ ) using standard Schlenk techniques. Solvents were dried and distilled before use: toluene from Na,  $\text{Et}_2\text{O}$  from Na/benzophenone and  $\text{CH}_2\text{Cl}_2$  from calcium hydride. IR spectra were recorded as KBr discs using a PE 2000 FT IR spectrometer.  $^{31}\text{P}\{^1\text{H}\}$  and  $^1\text{H}$  NMR spectra were recorded on a Jeol FX90Q machine operating at 36.21 and 89.55 MHz respectively. Microanalysis was performed by the LUT chemistry departmental service. X-ray crystallography was performed by A. M. Z. Slawin at LUT.

The complexes  $[\text{Pt}(\text{PPh}_3)_3]$ ,  $[\text{PtCl}_2(\text{PMe}_2\text{Ph})]_2$  and *cis*- $[\text{PtCl}_2(\text{PMe}_2\text{Ph})_2]$  were prepared by the literature methods.<sup>1,2,3</sup>

## CHAPTER 1. INTRODUCTION

### 1.1 Unsaturated Sulphur-Nitrides

Unsaturated sulphur-nitrides<sup>4</sup> fall into two groups: cages and planar rings. They are classified as unsaturated because they cannot be described making use of single bonds only. The S-N bond orders in these compounds are usually non-integral and it is not unusual to find different bond multiplicities along different bonds in the same molecule or ion. Therefore attempts to represent them by canonical formulas are usually misleading.

By far the most important sulphur-nitride is  $S_4N_4$  which is usually described as a cage where the nitrogen atoms are lying in a square-plane arrangement within a tetrahedron of sulphur atoms (Fig. 1.1).

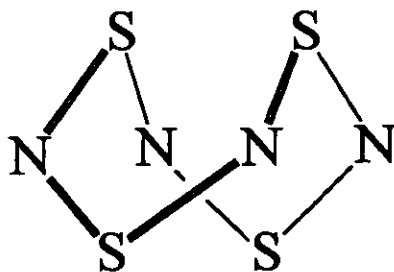


Figure 1.1 *The structure of  $S_4N_4$*

The most convenient laboratory synthesis is direct reaction of ammonia gas with sulphur dichloride in  $CCl_4$ .<sup>5</sup> This is a multi-stage process where several planar S-N heterocycles are probably involved (  $[S_3N_2Cl]Cl$  and  $[S_4N_3]Cl$  ).

The unusual geometrical and electronic structures of  $S_4N_4$  have been the object of study by theoretical chemists. In particular, there are two approaches that are attractive and which, in simple terms, account for the observations that: i) all the N-S bonds are

equivalent (*ca.* 1.62 Å), ii) there is no N-N bonding, iii) there is a substantial bonding interaction between the transannular sulphurs.

a) Banister's treatment.<sup>4</sup> The structure is treated with emphasis on the number of delocalised electrons. Each atom is assigned a lone pair and each S-N connection uses one pair of electrons, leaving six pairs which are then delocalised along the edges of the S<sub>4</sub> tetrahedron (Fig. 1.2). Unfortunately, this electron count fails to provide eight electrons to each nitrogen to complete an octet.

b) Mingos<sup>4</sup> has proposed a different scheme. Mingos regards the S<sub>4</sub>N<sub>4</sub> structure as a unit. Tetrasulphur-tetranitride has 44 valence electrons, *i.e.* four more than required for the electron-precise twelve edge structure of cuneane, C<sub>8</sub>H<sub>8</sub>. The extra two pairs of electrons go into antibonding orbitals to break two bonds in the cuneane structure resulting in two fewer bonds (Fig. 1.2).

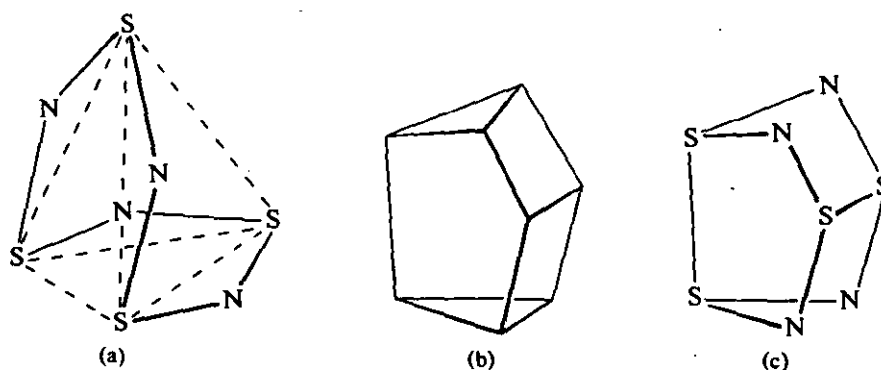


Figure 1.2 "Cage" or "cluster" viewpoints on the bonding of S<sub>4</sub>N<sub>4</sub>.<sup>4</sup> a) based on a tetrahedron of sulphur atoms; b) the skeleton of cuneane, C<sub>8</sub>H<sub>8</sub>; c) S<sub>4</sub>N<sub>4</sub> depicted as a cuneane-like skeleton with two edge bonds missing

The importance of S<sub>4</sub>N<sub>4</sub> arises from its ability to act as a precursor to many other sulphur-nitrides. However, it must be handled with care as it is prone to explode when ground, struck or suddenly heated. According to MO studies the S-N bonds in S<sub>4</sub>N<sub>4</sub> are polar with a charge transfer from sulphur to nitrogen, yielding S<sup>+</sup>-N<sup>-</sup> bonds. Therefore, it is

to be expected that electrophilic reagents should attack the nitrogen atom whereas nucleophilic reactions should proceed at the sulphur. Tetrasulphur-tetranitride undergoes three basic types of reactions:<sup>6,7</sup>

1) Addition reactions. Reactions in which the original eight-atom structure is conserved either with ring retention or ring expansion (eg. the ions  $S_5N_5^+$  and  $S_4N_5^-$ ), (Fig. 1.3).

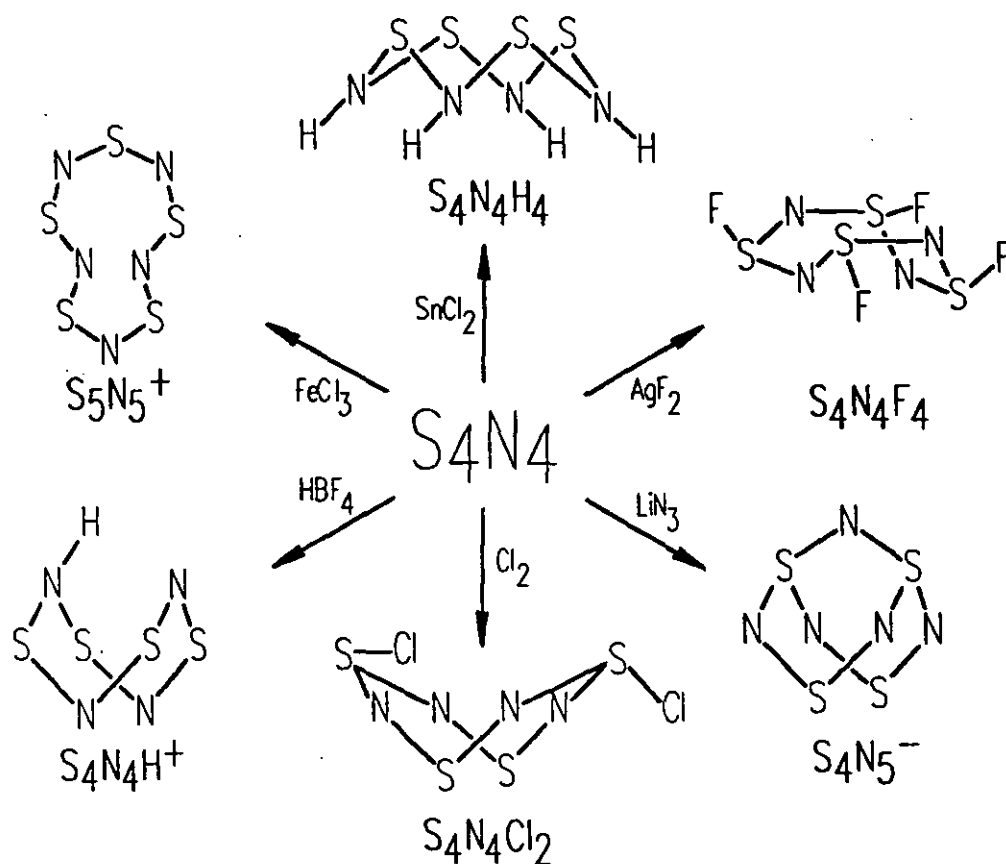


Figure 1.3 Addition reactions of  $S_4N_4$

2) Reactions with ring contraction. Some examples of this type of reaction are shown in Figure 1.4.

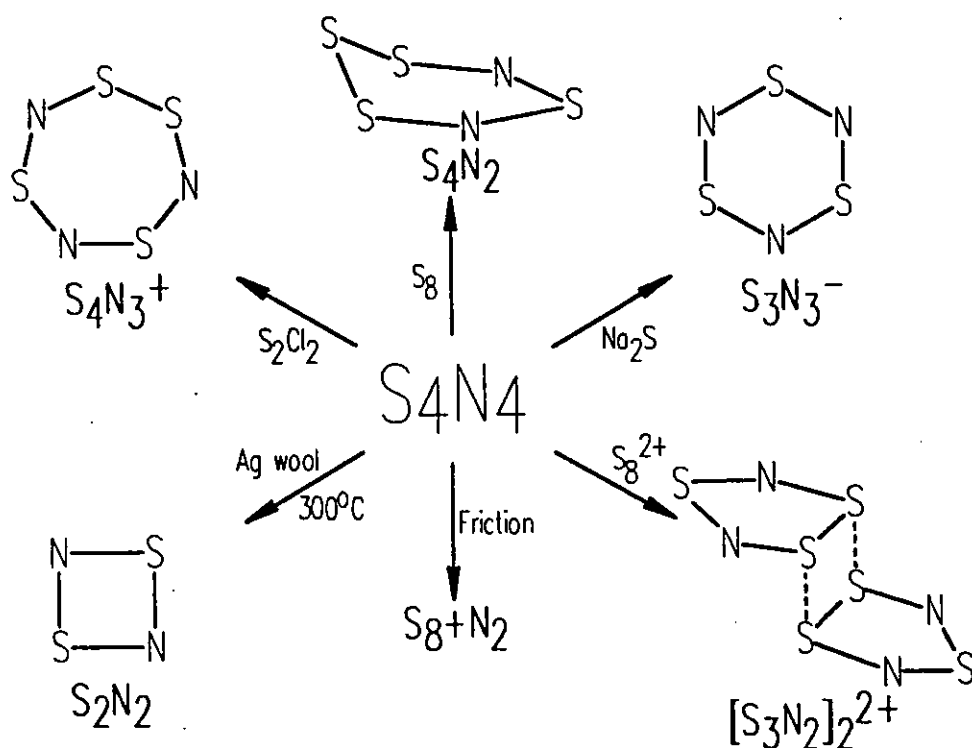


Figure 1.4 Reactions with ring contraction of  $S_4N_4$

3) Reactions with ring cleavage. Organic nucleophiles react with  $S_4N_4$  to afford compounds containing unsaturated chains of alternating sulphur and nitrogen atoms. The reaction of  $S_4N_4$  with  $(CH_3)_3SiNR_2$  (with  $R=CH_3, C_2H_5$ ) yields  $(CH_3)_3Si-N=S=N-SNR_2$ . Nucleophilic attack on  $S_4N_4$  by Grignard reagents leads to  $R-S-N=S=N-S-R$ . Reaction of diaryldiazomethanes with  $S_4N_4$  produces compounds having the formula  $R=N-S-N=S=N-S-N=R$ .

Planar-ring sulphur-nitrogen species are of interest to theoreticians because of their pseudo-aromaticity. The Huckel theory of aromaticity can be applied to such species by considering each nitrogen and each 2 co-ordinate sulphur to contribute one and two electrons respectively to the  $\pi$  system. For instance  $S_2N_2$  is, on this basis, a  $6\pi$  aromatic system. This compound is the most convenient precursor to  $(SN)_x$ <sup>8</sup> which is an anisotropic conductor and superconductor at low temperatures.

## 1.2 Metal Sulphur-Nitrogen Complexes

The continued interest in the co-ordination chemistry of sulphur-nitrogen ligands is testimony to the ability of the resulting complexes to exhibit a range of bonding modes and structural properties.<sup>7,9</sup> Tetrasulphur tetranitride is again, the main precursor to metal sulphur-nitrogen complexes and these may be categorised into two main structural types: Lewis acid-Lewis base adducts and cyclometallathiazenes. In the former category the ligand is bonded to the metal via a nitrogen atom. This group includes adducts of heterocycles, such as  $S_4N_4$  and  $S_2N_2$ , and monodentate ligands such as the thionitrosyls (Fig. 1.5).

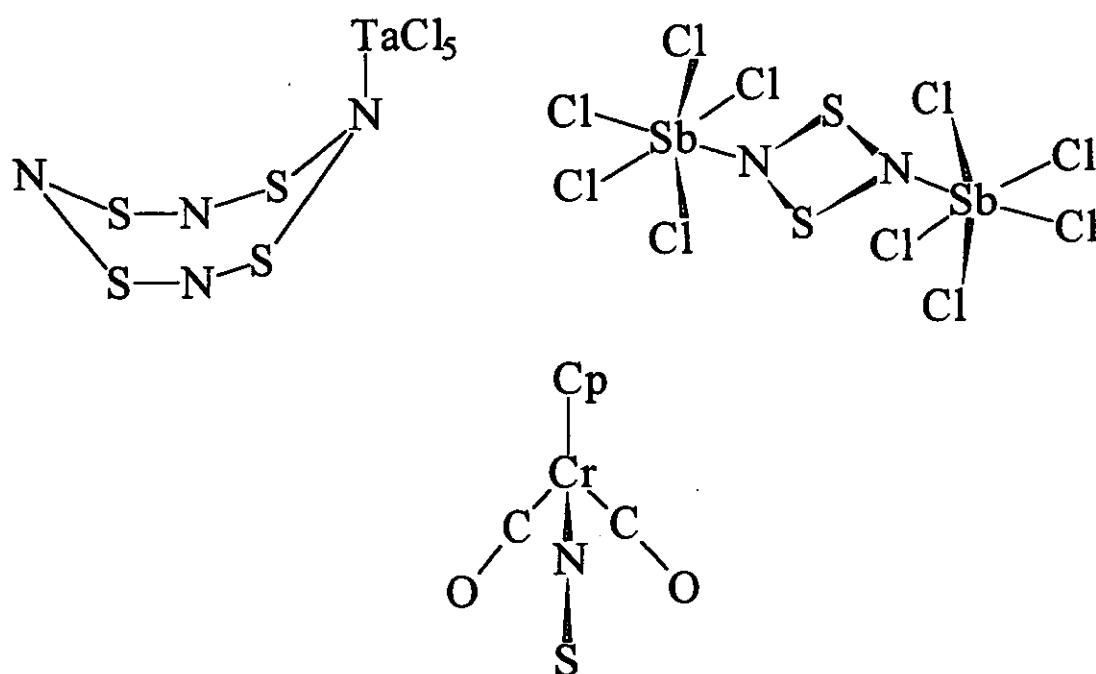


Figure 1.5 Some examples of non-metallacyclic S-N complexes; a)  $TaCl_5 \cdot S_4N_4$ , b)  $S_2N_2 \cdot 2SbCl_3$  and c)  $Cr(CO)_2Cp \cdot NS$

In the case of the cyclometallathiazenes the S-N ligand forms part of a metallacycle. In these complexes the metal ion is a constituent of a S-N ring and the ligand can be considered as a binary S-N anion (Fig. 1.6).

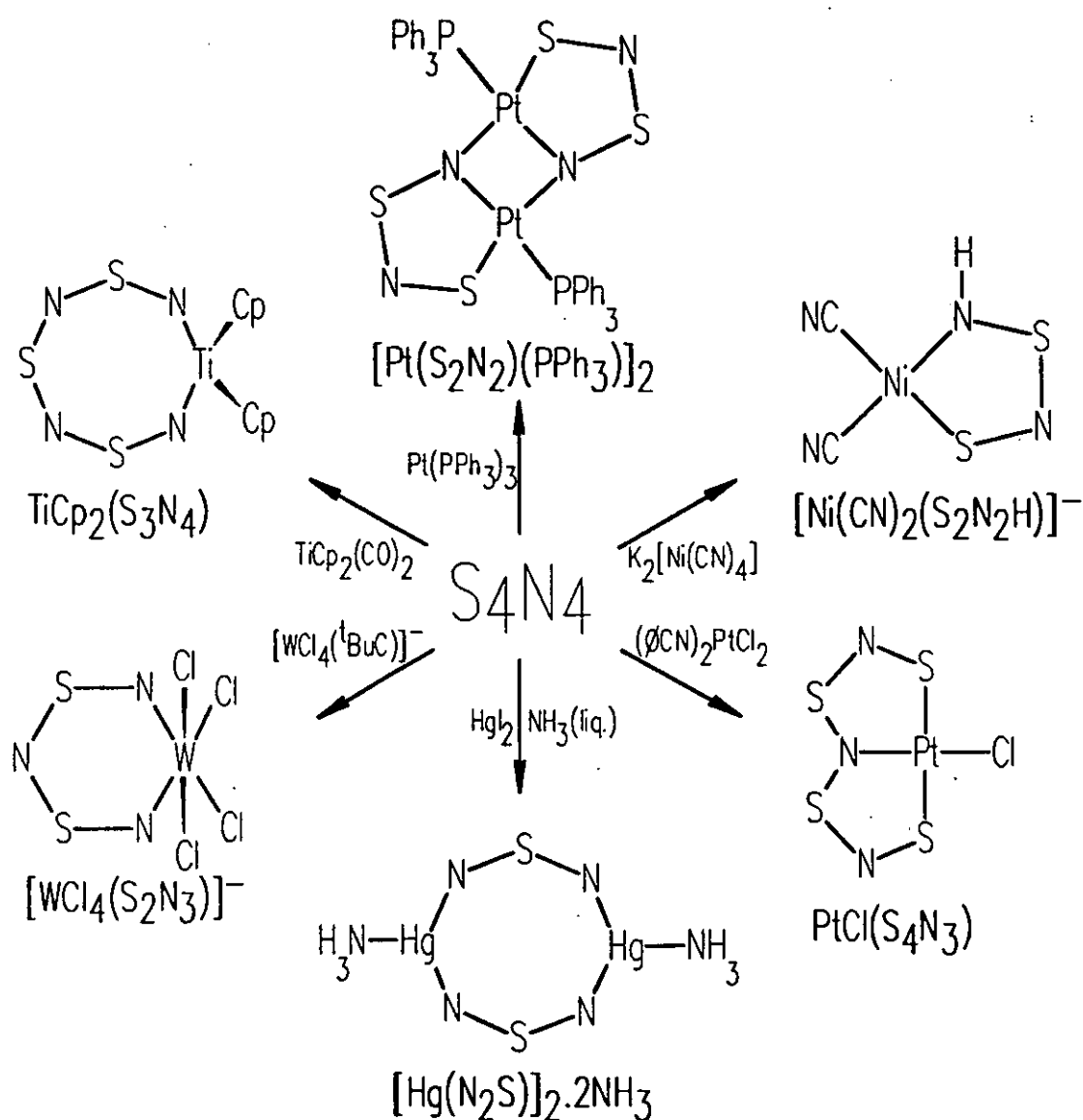


Figure 1.6 Some examples of cyclometallathiazenes prepared by reaction of  $\text{S}_4\text{N}_4$  with metal complexes

These complexes are important because they often enable us to study otherwise unstable S-N anions which cannot be obtained as a single salt. In addition, these complexes may act as a source of the novel fragments in further reactions.



Reactions involving the synthesis of metal sulphur-nitrogen complexes very often proceed through obscure routes. Consequently, this has challenged the imagination of chemists to propose mechanisms that account for the nature of the products obtained. The reaction of  $S_4N_4$  with  $MCl_2$  ( $M=Pt$ ,  $Pd$ ,  $Ni$  and  $Co$ ) in methanol is a good example to illustrate the complexity of this area of co-ordination chemistry. Three different compounds are formed:  $M(S_2N_2H)_2$ ,  $M(S_2N_2H)(S_3N)$  and  $M(S_3N)_2$  (Fig. 1.7) which can be separated from each other by preparative thin-layer chromatography.<sup>10</sup>

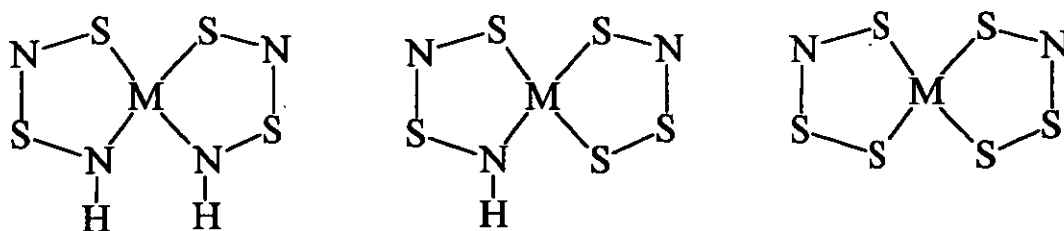


Figure 1.7 The structures of  $M(S_2N_2H)_2$ ,  $M(S_2N_2H)(S_3N)$  and  $M(S_3N)_2$

Halogen-bridged dimeric  $Pt(II)$ <sup>11</sup> and  $Pd(II)$ <sup>12</sup> complexes are an important class of reagents for reactions with S-N species as they effectively act as a source of the coordinatively unsaturated metal centre. In this study the dimers  $[PPh_4]_2[Pd_2X_6]$ , where  $X=Cl$ ,  $Br$  or  $I$ , have been prepared from  $PdCl_2$  in a two step process (see Chapter 2) avoiding the use of  $M_2[PdX_4]$ . This reduces costs and introduces a new approach to their synthesis. Simple halide species such as compounds of the general class  $[MCl_2(PR_3)_2]$ <sup>13</sup> ( $M=Pt$  or  $Pd$ ) and low valent metal species such as  $Pt(0)$ <sup>14</sup> have proved to be useful too.

### 1.3 Selenium-Nitride compounds

The development of selenium-nitrogen chemistry has been slow compared to the substantial advances that have been made in the area of sulphur-nitrogen chemistry in the last twenty years. The number of species containing just Se and N is limited to  $\text{Se}_4\text{N}_4$ ,  $\text{Se}_4\text{N}_2$  and the cations present in the salts  $(\text{Se}_3\text{N}_2)(\text{AsF}_6)_2$  and  $(\text{S}_3\text{N}_2)_2(\text{AsF}_6)_2$  (Fig. 1.8). This is in contrast to the numerous sulphur-nitrides which have been prepared and structurally characterised.

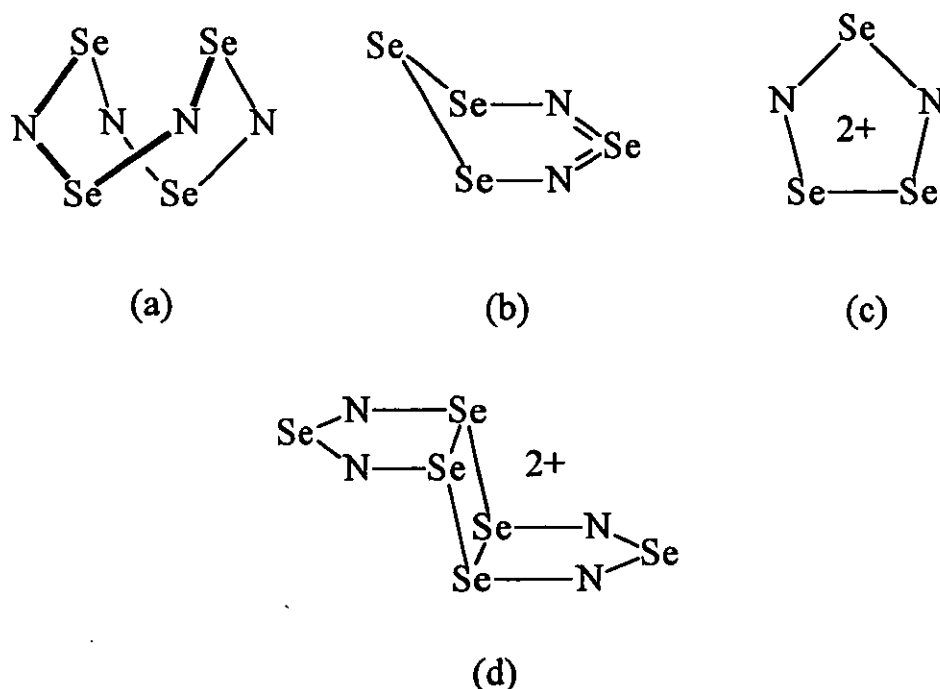


Figure 1.8 Structures of (a)  $\text{Se}_4\text{N}_4$ , (b)  $\text{Se}_4\text{N}_2$ , (c)  $(\text{Se}_3\text{N}_2)^{2+}$  and (d)  $(\text{Se}_3\text{N}_2)_2^{2+}$

The compound  $\text{Se}_4\text{N}_4$  adopts the same cage structure described for  $\text{S}_4\text{N}_4$  by replacement of the S atoms for Se. However, their crystal structures belong to different space groups, reflecting the differences in molecular packing.<sup>15</sup> The crystal structure of  $\text{Se}_4\text{N}_4$  reveals strong intermolecular  $\text{Se}\cdots\text{N}$  contacts between the cage molecules which seem to be essential to explain the low solubility of  $\text{Se}_4\text{N}_4$  in many solvents. The insolubility of  $\text{Se}_4\text{N}_4$  and its extreme instability, an order of magnitude more explosive than

$S_4N_4$ , have restricted the use of  $Se_4N_4$  as a reagent. In fact, only a few reactions involving  $Se_4N_4$  have been reported.<sup>16</sup>

The compound  $Se_4N_4$  would perhaps be expected to react with a given metal species in the same manner as  $S_4N_4$ , but this is not always observed. An example of  $Se_4N_4$  mimicking  $S_4N_4$  is found in its reaction with  $[Pt(PPh_3)_3]$  in which  $[Pt(Se_2N_2)(PPh_3)_2]$  and  $[Pt(Se_2N_2)(PPh_3)]_2$  are formed (Fig. 1.9).

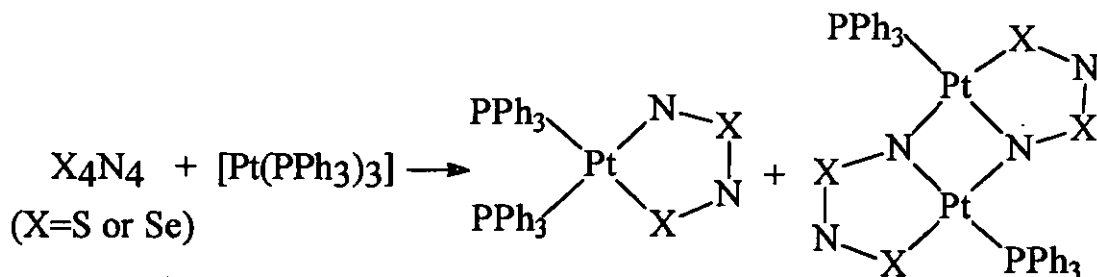


Figure 1.9 Products of the reaction of  $S_4N_4$  and  $Se_4N_4$  with  $[Pt(PPh_3)_3]$

However, the selenium analogue to the Pt(IV) complex *mer*- $[PtCl_2(S_4N_4)(PPhMe_2)]$ , obtained by reacting  $S_4N_4$  with  $[PtCl_2(PPhMe_2)]_2$ , is not formed when  $Se_4N_4$  is used instead. In this case  $[Pt(Se_3N)Cl(PPhMe_2)]$  and  $[Pt(Se_2N_2H)Cl(PPhMe_2)]$  are the species generated (Fig. 1.10).

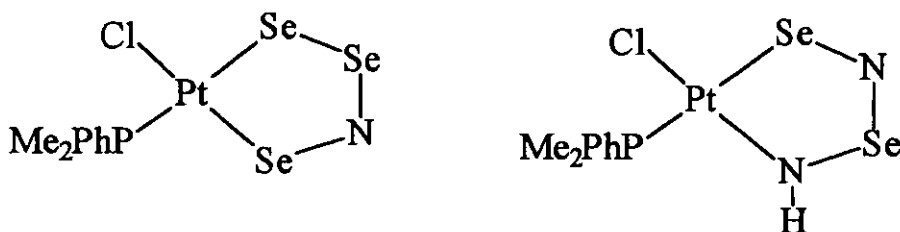


Figure 1.10 The structures of  $[Pt(Se_3N)Cl(PPhMe_2)]$  and  $[Pt(Se_2N_2H)Cl(PPhMe_2)]$

Due to the pernicious properties of  $\text{Se}_4\text{N}_4$ , research was undertaken to prepare less harmful selenium-nitride reagents. This research led to the synthesis of  $\text{Se}_4\text{N}_2$ <sup>17</sup> and  $[\text{Se}_3\text{N}_2]_n[\text{AsF}_6]_2$  ( $n=1$  or  $2$ ).<sup>18</sup> The former is generated by reaction of  $\text{Se}_2\text{Cl}_2$  with  $\text{Me}_3\text{SiN}_3$  in  $\text{CH}_2\text{Cl}_2$  and the latter by making use of  $\text{Se}_4\text{N}_4$ , which is likely to be a drawback in the development of its chemistry. The compound  $\text{Se}_4\text{N}_2$  reacts with  $\text{SnCl}_4$  or  $\text{TiCl}_4$  to form  $[\text{SnCl}_4(\text{Se}_4\text{N}_2)_2]$  and  $[\text{TiCl}_4(\text{Se}_4\text{N}_2)]$  respectively.<sup>19</sup> In both complexes, the  $\text{Se}_4\text{N}_2$  unit is preserved (Fig. 1.11).

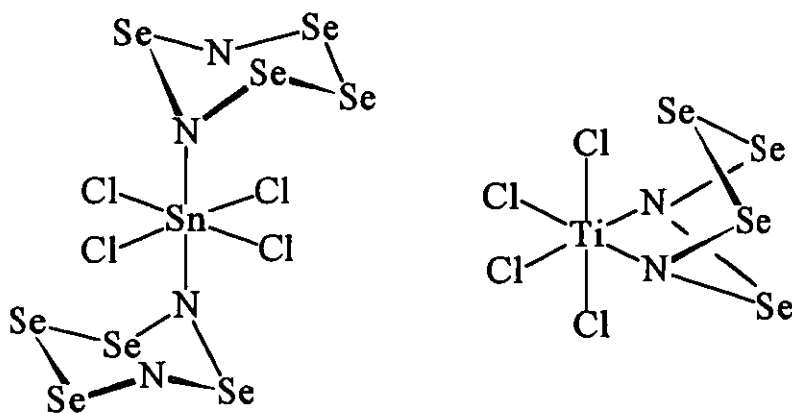


Figure 1.11 The donor-acceptor complexes  $[\text{SnCl}_4(\text{Se}_4\text{N}_2)_2]$  and  $[\text{TiCl}_4(\text{Se}_4\text{N}_2)]$

#### 1.4 Aims

A wide variety of complexes of transition metals with chalcogen-nitrogen (*i.e.* S/Se-N) ligands have been described. In general, they have been prepared using a handful of reagents such as  $\text{S}_4\text{N}_4$ ,  $(\text{NSCl})_3$  or  $\text{Se}_4\text{N}_4$  and not much attention has been devoted to the study of new precursors.

The aim of this work was to gain an insight into the chemistry of three of these new species such as  $(\text{Me}_3\text{SiNSN})_2\text{S}$ ,  $(^t\text{BuNSN})_2$  and  $\text{Se}(\text{NSO})_2$ . In view of the results obtained, we can anticipate that the above compounds have an encouraging future as a source of novel chalcogen-nitrogen complexes.

## CHAPTER 2. CHEMISTRY OF $(\text{Me}_3\text{SiNSN})_2\text{S}$

### 2.1 Introduction

Reactions involving S-N species have been known for many years. Most of these can be described as "non-rational" because no balanced equations can be proposed to give an explanation of the products obtained. One of the few S-N reagents which reacts following a logical pattern is bis(trimethylsilyl) sulphur diimide,  $\text{Me}_3\text{Si-N}=\text{S}=\text{N-SiMe}_3$ , which is a yellow-green liquid prepared by the reaction:<sup>20</sup>



Bis(trimethylsilyl) sulphur diimide acts as a source of  $-\text{N}=\text{S}=\text{N}-$  groups. Its reactivity hinges around the potential loss of  $\text{Me}_3\text{SiX}$  where  $\text{X}=\text{Cl}$ ,  $\text{Br}$  or  $\text{I}$ . The driving force seems to be the weakness of the Si-N bond relative to the Si-X formed.<sup>4</sup> Some examples of its utility are shown in Figure 2.1.

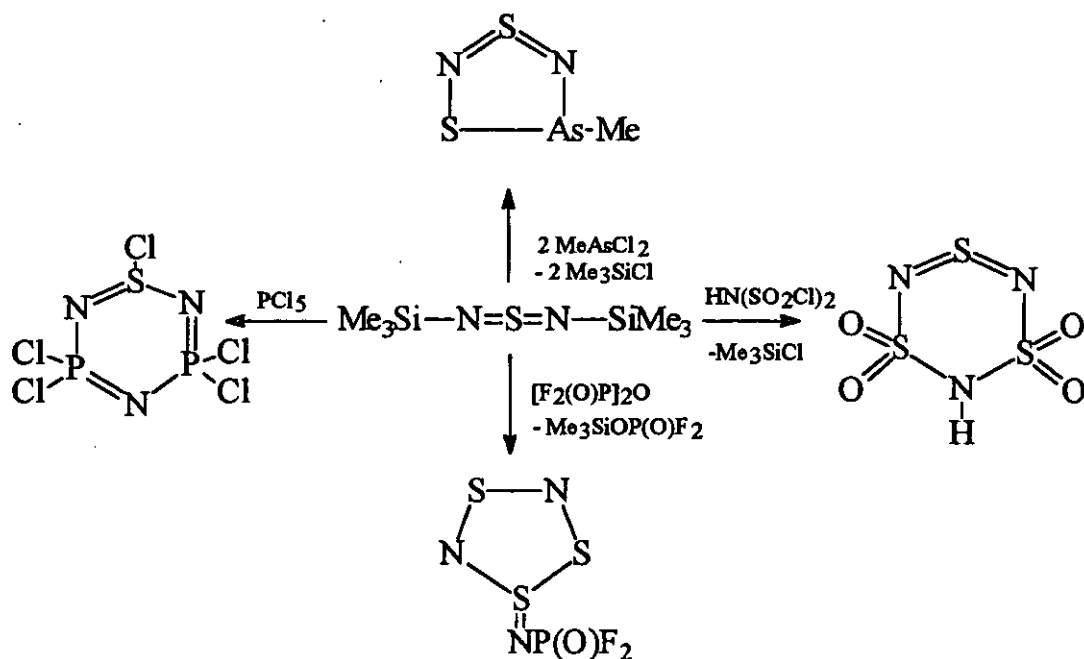


Figure 2.1 *Synthesis of inorganic heterocycles using bis(trimethylsilyl) sulphur diimide*

An interesting reaction of  $(\text{Me}_3\text{SiN})_2\text{S}$  is the preparation of bis(trimethylsilyl) trisulphur tetraimide<sup>21</sup> **1**,  $\text{Me}_3\text{Si-N}=\text{S}=\text{N-S-N}=\text{S}=\text{N-SiMe}_3$ , by reaction of two equivalents of  $(\text{Me}_3\text{SiN})_2\text{S}$  with one of sulphur dichloride. Bis(trimethylsilyl) trisulphur tetraimide is as an orange solid which crystallises readily when pure, with a melting point of 69°C. To date, all attempts to resolve its crystal structure have failed, probably because of the multiple conformations that the chain may adopt within the unit cell. However, the structure of the <sup>t</sup>Bu derivative is known.<sup>22</sup> Assuming the same conformation then, **1** should be as shown in Figure 2.2. The bond lengths reported for  $(^t\text{BuNSN})_2\text{S}$  can be used to draw single and double bonds in the N-S chain.

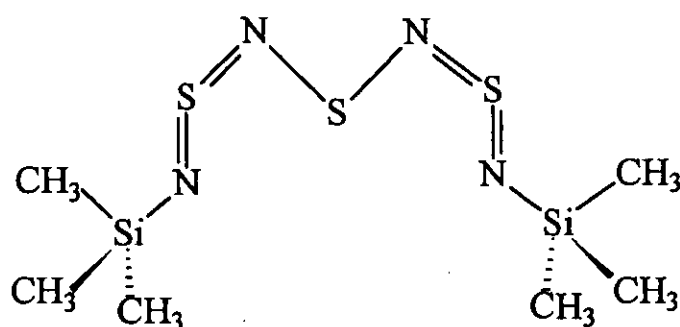


Figure 2.2 Possible structure of  $(\text{Me}_3\text{SiNSN})_2\text{S}$

The superconductive behaviour of  $(\text{SN})_x$  has caused great interest with the physical and structural properties of this polymer recently reviewed.<sup>8</sup> Polymeric sulphur-nitride consists of chains of unknown length of alternating sulphur and nitrogen atoms. More recently, the preparation of oligomeric analogues of  $(\text{SN})_x$  with known chain length,  $\text{Ar-S}_k(-\text{N}=\text{S}=\text{N-S-})_l-\text{N}=\text{S}=\text{N-S}_m-\text{Ar}$ , have been studied in depth since the formation of chains of the desired length could be applied in what has been called “molecular electronic devices”. The work of A.V.Zibarev *et al.* has proved that **1** is a useful starting material for the synthesis of oligomeric S-N chains.<sup>23</sup> Thus **1** reacts with two equivalents of  $\text{ArSCl}$ , where  $\text{Ar}$ =nitrophenyl, to generate  $(\text{ArSN}=\text{S}=\text{N})_2\text{S}$ . The crystal structure of

$(\text{ArSN}=\text{S}=\text{N})_2\text{S}$  shows common features with  $(\text{SN})_x$ , having both compounds an alternating configuration *i.e.* Z, E, Z, E, ... and similar bond lengths along the chain.

It is surprising that the co-ordination chemistry of **1** has been hardly developed, especially considering that the facile displacement of the silyl groups in **1** makes this compound a potential precursor to metal sulphur-nitrogen complexes. Only very few reactions have been described in the literature. Amongst others, **1** reacts with  $\text{SnCl}_4$  to initially form  $\text{SnCl}_4 \cdot \text{SN}_2(\text{SiMe}_3)_2$ ; upon longer reaction times,  $\text{SnCl}_4 \cdot 2\text{S}_4\text{N}_4$  appears.<sup>24</sup> Clearly the presence of the NSNSNSN unit in **1** provides some similarity to  $\text{S}_4\text{N}_4$  but there is potential for **1** to react in a subtly different way. In this chapter we report on reactions of **1** with a range of metal species and we propose a mechanism for the reaction of **1** with  $[\text{PPh}_4]_2[\text{Pd}_2\text{X}_6]$  where  $\text{X}=\text{Cl}$  and  $\text{Br}$ .

## 2.2 Results and Discussion

### 2.2.1 Preparation of Starting Materials

Although all starting materials are known, we have investigated a number of ways of preparing compound **1** in higher yields. The standard preparation of the Pd dimers have been modified too.

#### 2.2.1.1 Preparation of $(\text{MeSiNSN})_2\text{S}$

Bis(trimethylsilyl) trisulphur tetraimide **1** is an orange solid prepared by the reaction of  $(\text{Me}_3\text{SiN})_2\text{S}$  **2** with sulphur dichloride, in  $\text{CH}_2\text{Cl}_2$ , in a 2:1 ratio.<sup>21</sup> The yield of **1** is low due to the preferential formation of  $(\text{SN})_x$  as a by-product. This difficulty arises as both **1** and **2** have very similar reactivity towards  $\text{SCl}_2$ , which is to be expected. Hence, once **1** is formed a fraction of it reacts further with  $\text{SCl}_2$  to afford  $(\text{SN})_x$  leaving some unreacted **2**. The deep blue polymer is easily removed by filtration through Celite. Then, it appears that **1** is soluble in the unreacted **2** giving a red oil. In this work, we found that the

best means to obtain pure 1 is to expose the red oil mixture to air on a watch-glass overnight. As 2 evaporates off well formed orange needles of 1 appear.

All attempts to separate out compound 1 from 2 by passing the red oil through a Bio-Beads gel-permeation column (this chromatography method works on the size of the molecules) fail. This result may be understood if we take into consideration that the globular size of compounds 1 and 2 is mainly determined by the Me<sub>3</sub>Si groups. Thus, the penetration ratio of both chains in the gel is very similar, leading to the poor separation observed.

We have found that the more concentrated the solutions of starting materials the higher the yield of 1 (Table 2.1).

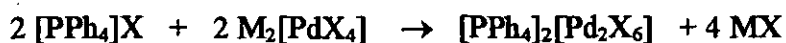
Moles SCl <sub>2</sub> .(1x10 <sup>3</sup> )	M SCl <sub>2</sub>	Moles 2.(1x10 <sup>3</sup> )	M 2	Yield 1. (%)
11.96	0.48	2x11.96	0.79	13
8.03	1.61	2x8.03	1.61	16
23.03	4.60	2x23.03	2.30	34

Table 2.1 Yields of 1 varying the concentration of the solutions of starting materials.

*Concentration expressed in Molarity (M)*

#### 2.2.1.2 Preparation of [PPh<sub>4</sub>]<sub>2</sub>[Pd<sub>2</sub>X<sub>6</sub>] (X=Cl, Br and I)

Palladium species of the type [PPh<sub>4</sub>]<sub>2</sub>[Pd<sub>2</sub>X<sub>6</sub>] (X=Cl and Br) are usually prepared by addition of an aqueous solution of [PPh<sub>4</sub>]X to a solution of [PdX<sub>4</sub>]<sup>2-</sup> in the same solvent:



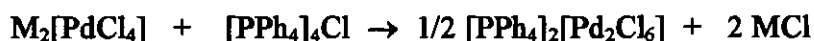
Due to the instability of M<sub>2</sub>[PdI<sub>4</sub>], [PPh<sub>4</sub>]<sub>2</sub>[Pd<sub>2</sub>I<sub>6</sub>] is prepared in a different fashion:



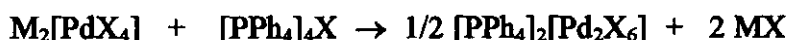
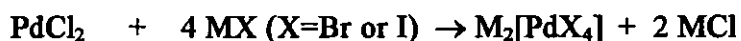


In this work we developed a different route which makes use of  $\text{PdCl}_2$  as the only precursor to all three palladium dimers. This preparation avoids the use of both  $\text{M}_2[\text{PdX}_4]$  ( $\text{X}=\text{Cl}$  and  $\text{Br}$ ) and  $\text{PdI}_2$  which reduces costs and introduces a new approach to the synthesis of  $[\text{PPh}_4]_2[\text{Pd}_2\text{X}_6]$  (Scheme 2.1 and 2.2).

#### Scheme 2.1



#### Scheme 2.2



### 2.2.2 Reaction of $[\text{PPh}_4]_2[\text{Pd}_2\text{X}_6]$ ( $\text{X}=\text{Cl}$ , $\text{Br}$ or $\text{I}$ ) with two equivalents of $(\text{MeSiNSN})_2\text{S}$

#### 2.2.2.1 Reaction of $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_6]$ with two equivalents of $(\text{MeSiNSN})_2\text{S}$

Work in our group has demonstrated the versatility of  $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_6]$  in the preparation of sulphur-nitrogen complexes. Thus reaction of  $\text{S}_4\text{N}_4$  with  $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_6]$  results in the isolation of  $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_6(\text{S}_2\text{N}_2)]$ ,  $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_4(\text{S}_3\text{N}_2)]$  and  $[\text{PPh}_4][\text{PdCl}_2(\text{S}_2\text{N}_2\text{H})]$  (Fig. 2.3).<sup>12</sup>

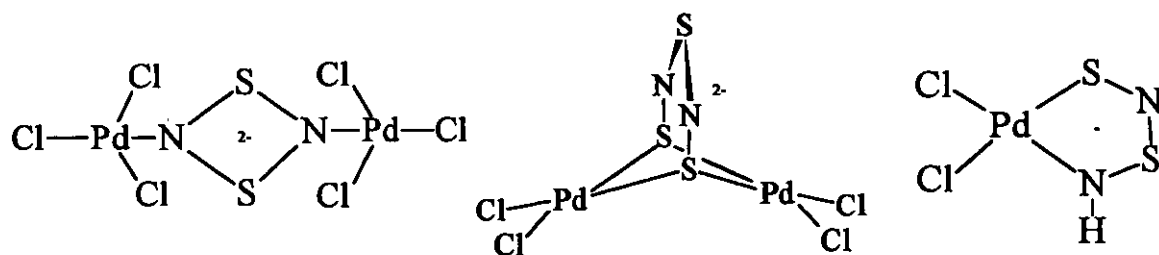


Figure 2.3 The structures of the anions in  $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_6(\text{S}_2\text{N}_2)]$ ,  $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_4(\text{S}_3\text{N}_2)]$  and  $[\text{PPh}_4][\text{PdCl}_2(\text{S}_2\text{N}_2\text{H})]$

We have found that  $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_6]$  readily reacts with **1** to give a variety of species. Thus when the starting materials are mixed in  $\text{CH}_2\text{Cl}_2$  and stirred for a few hours a brown coloured solution is obtained from which black crystals form by slow diffusion of diethyl ether into the concentrated solution. Microanalysis and IR spectroscopy reveal this product to be  $[\text{PPh}_4][\text{PdCl}_2(\text{S}_2\text{N}_3)]$  (Fig. 2.4; Table 2.2). In addition, a low yield of orange crystals is also obtained; these are formed in somewhat larger yield if either a) the above crude product mixture (including material which does not form well defined crystals) is recrystallised or b) the initial reaction is left to stir for a few days before crystallisation. IR spectroscopy reveals this compound to be  $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_4(\text{S}_3\text{N}_2)]$ . As Figure 2.4 also shows, if the reaction is performed in  $\text{CD}_2\text{Cl}_2$  then *in situ*  $^1\text{H}$  NMR spectroscopy reveals the presence of  $\text{SiMe}_3\text{Cl}$  and  $\text{Me}_3\text{SiSiMe}_3$  in the reaction mixture.

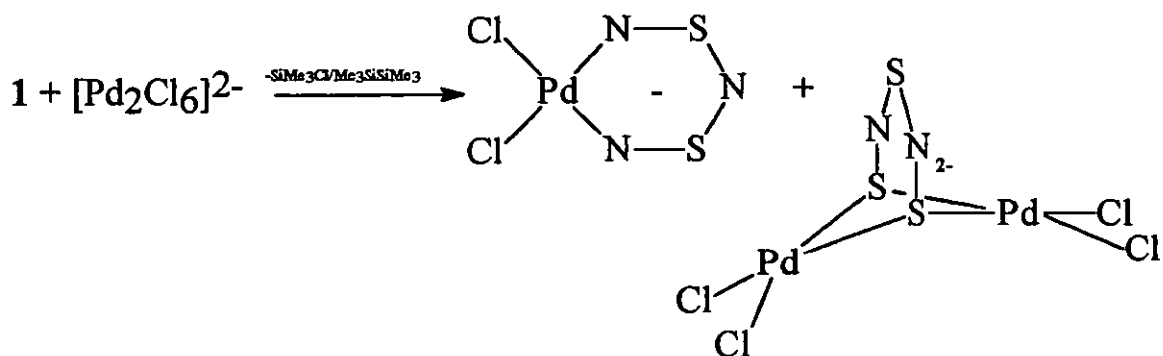


Figure 2.4 Products of the reaction of compound **1** with  $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_6]$

The complex  $[\text{PPh}_4][\text{PdCl}_2(\text{S}_2\text{N}_3)]$  was first prepared, in low yield, by reaction of  $\text{S}_5\text{N}_6$  with  $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_6]$ , being the first example of a compound containing the bidentate  $[\text{S}_2\text{N}_3]^-$  unit.<sup>25</sup> The new preparative route to  $[\text{PPh}_4][\text{PdCl}_2(\text{S}_2\text{N}_3)]$  has a number of distinct advantages over the only previously reported route. The primary advantage comes in the form of the S-N starting material which in this case is neither particularly air-sensitive nor explosive (in contrast to  $\text{S}_5\text{N}_6$  which is difficult to handle on both these fronts). In addition, the yield is higher and significantly more reproducible using **1**.

### 2.2.2.2 Reaction of $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6]$ with two equivalents of $(\text{MeSiNSN})_2\text{S}$

In the case of the reaction of  $\text{S}_4\text{N}_4$  with  $[\text{PPh}_4]_2[\text{Pd}_2\text{X}_6]$ , where  $\text{X}=\text{Cl}$  or  $\text{Br}$ , changing from the chloro species to bromo does not appear to make any significant difference to the progress of the reaction. Thus the bromine containing analogues of  $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_6(\text{S}_2\text{N}_2)]$ ,  $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_4(\text{S}_3\text{N}_2)]$  and  $[\text{PPh}_4][\text{PdCl}_2(\text{S}_2\text{N}_2\text{H})]$  are obtained.<sup>12</sup>

However, this is not the case with reactions of **1**. Here we find that reaction of **1** with  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6]$  in  $\text{CH}_2\text{Cl}_2$ , as above, followed by slow diffusion of diethyl ether, leads to a high yield of a mixture of  $[\text{PPh}_4][\text{PdBr}_2(\text{S}_2\text{N}_3)]$  and the  $\text{S}_2\text{N}_2$  adduct  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6(\text{S}_2\text{N}_2)]$ . Again, if the mixture is left longer before crystallisation then significant amounts of  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_4(\text{S}_3\text{N}_2)]$  form. Another contrast to the chloro reaction comes with the ultimate fate of  $\text{Me}_3\text{Si}$  groups; in this case only  $\text{Me}_3\text{SiSiMe}_3$  is formed (*i.e.* no  $\text{SiMe}_3\text{Br}$ ) (Fig. 2.5; Table 2.2).

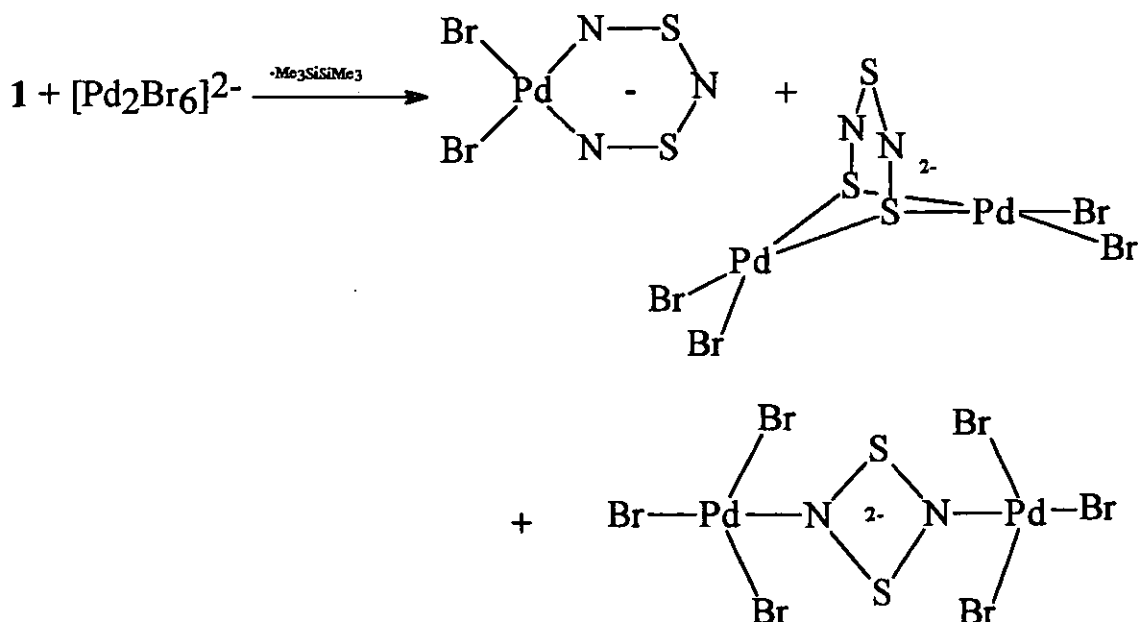


Figure 2.5 Products of the reaction of compound **1** with  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6]$

COMPOUND	PHYSICAL APPEARANCE	
	X=Cl	X=Br
$[\text{PPh}_4][\text{PdX}_2(\text{S}_2\text{N}_3)]$	Black plates	Black prisms
$[\text{PPh}_4]_2[\text{Pd}_2\text{X}_4(\text{S}_3\text{N}_2)]$	Orange needles	Orange flakes and needles
$[\text{PPh}_4]_2[\text{Pd}_2\text{X}_6(\text{S}_2\text{N}_2)]$	—	Brown plates

Table 2.2 *Physical appearance of the crystalline samples of the chloro and bromo species prepared by reaction of  $[\text{PPh}_4]_2[\text{Pd}_2\text{X}_6]$ , where  $X=\text{Cl}$  or  $\text{Br}$ , with 1*

The novel complex  $[\text{PPh}_4][\text{PdBr}_2(\text{S}_2\text{N}_3)]$  is the second example of a compound containing the  $[\text{S}_2\text{N}_3]^-$  ligand (Fig. 2.6, Table 2.3).

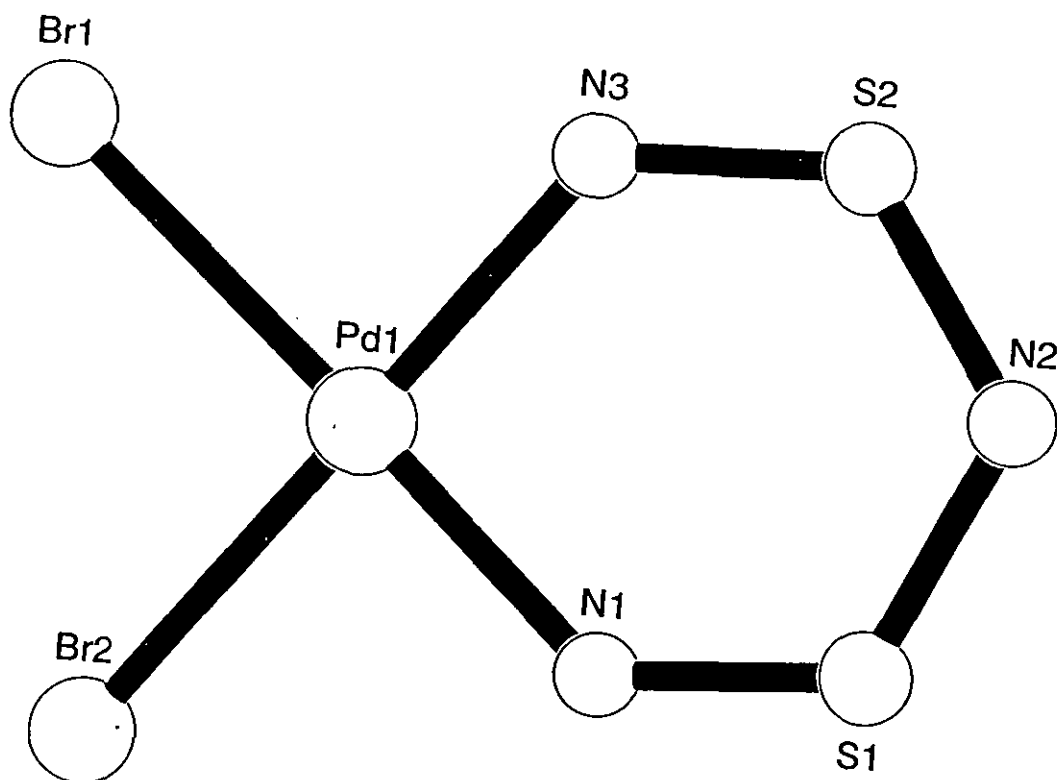


Figure 2.6 *The X-ray structure of the anion in  $[\text{PPh}_4][\text{PdBr}_2(\text{S}_2\text{N}_3)]$*

Pd-Br(1)	2.438(2)	Pd-Br(2)	2.461(2)
Pd-N(1)	1.921(12)	N(1)-S(1)	1.504(11)
S(1)-N(2)	1.607(13)	N(2)-S(2)	1.598(12)
S(2)-N(3)	1.489(11)	N(3)-Pd	1.979(12)
Br(1)-Pd-Br(2)	91.87(8)	Br(1)-Pd-N(3)	86.6(3)
N(3)-Pd-N(1)	94.51(46)	N(1)-Pd-Br(2)	87.08(35)
Pd-N(1)-S(1)	132.67(78)	N(1)-S(1)-N(2)	119.79(70)
S(1)-N(2)-S(2)	120.79(78)	N(2)-S(2)-N(3)	122.06(72)
S(2)-N(3)-Pd	129.10(69)		

Table 2.3 Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for  $[\text{PPh}_4][\text{PdBr}_2(\text{S}_2\text{N}_3)]$

The X-ray crystal structure of  $[\text{PPh}_4][\text{PdBr}_2(\text{S}_2\text{N}_3)]$  reveals bond distances and angles similar to those reported for  $[\text{PPh}_4][\text{PdCl}_2(\text{S}_2\text{N}_3)]$ , with the anion essentially planar (maximum deviation from the mean plane coming at S(1),  $-0.13 \text{ \AA}$ ). Comparison of these two sets of values with those for early transition metal complexes of the  $[\text{S}_2\text{N}_3]^{3-}$  ligand reveals an interesting contrast. In the latter the average S-N (metal-bound) and the S-N (bridgehead) lengths are fairly similar. Thus for the complexes  $[\text{WCl}_4(\text{S}_2\text{N}_3)]^-$  and  $[\text{WCl}_3(\text{S}_2\text{N}_3)(\text{THF})]$  these average out as 1.57 and 1.59  $\text{\AA}$  respectively.<sup>26,27</sup> In complexes  $[\text{PPh}_4][\text{PdBr}_2(\text{S}_2\text{N}_3)]$  and  $[\text{PPh}_4][\text{PdCl}_2(\text{S}_2\text{N}_3)]$ , however, these values average out as 1.49 and 1.60  $\text{\AA}$ , indicating a significant difference in the bonding arrangement.

Parallel work in our group has ruled out the possibility that the ligand in  $[\text{PPh}_4][\text{PdCl}_2(\text{S}_2\text{N}_3)]$  was actually a protonated version of  $[\text{S}_2\text{N}_3]^{3-}$  (a possibility not unambiguously dealt with by X-ray crystallography). The absence of NH groups was confirmed by recording the  $^{15}\text{N}$  NMR spectrum of partially  $^{15}\text{N}$  labelled  $[\text{PPh}_4][\text{PdCl}_2(\text{S}_2\text{N}_3)]$ .<sup>28</sup> As Figure 2.7 shows, this spectrum consists of the expected two singlets, present in the ratio 2:1, at  $\delta$  460 (metal-bound) and  $\delta$  355 (bridgehead nitrogen).

The key feature is that the spectrum is unchanged when run with or without proton decoupling. The presence of any protons on the nitrogens would invariably result in a substantial  $^1J(^1\text{H}-^{15}\text{N})$  coupling in the latter case.

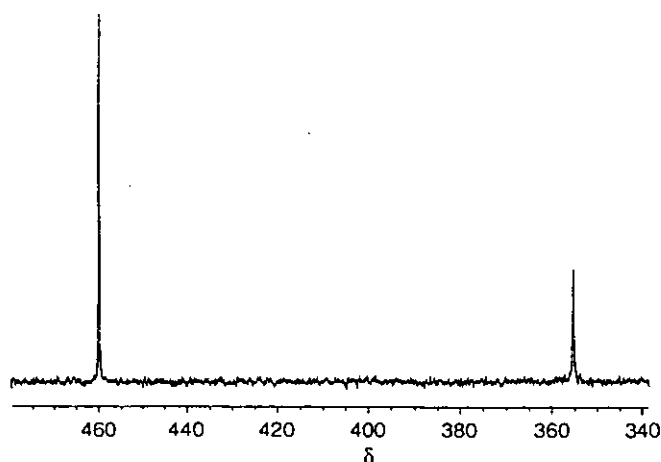


Figure 2.7 The  $^{15}\text{N}$  NMR spectrum of 66%  $^{15}\text{N}$  labelled  $[\text{PPh}_4][\text{PdCl}_2(\text{S}_2\text{N}_3)]$

When  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_4(\text{S}_3\text{N}_2)]$  was prepared for the first time, by making use of  $\text{S}_4\text{N}_4$  and  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6]$ , its crystal structure could not be elucidated.<sup>12</sup> In this work  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_4(\text{S}_3\text{N}_2)]$  forms as either orange flakes or orange needles. The latter are amenable to X-ray analysis and are obtained when the reaction mixture is left stirring several days before crystallisation (Fig. 2.8 ; Tables 2.4a and 2.4b). The X-ray structure of  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_4(\text{S}_3\text{N}_2)]$  shows a  $\text{S}_3\text{N}_2^{2-}$  ligand bridging two  $\text{PdBr}_2$  units with co-ordination through sulphur. The  $\text{Pd}_2\text{S}_3\text{N}_2$  fragment has two short ,N(1)-S(2) and N(2)-S(2), and two long ,S(1)-N(1) and N(2)-S(3), S-N bonds. Viewed from the S(1)....S(3) axis the co-ordination planes are inclined. On a whole,  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_4(\text{S}_3\text{N}_2)]$  has a very similar geometry to that of  $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_4(\text{S}_3\text{N}_2)]$ .<sup>29</sup>

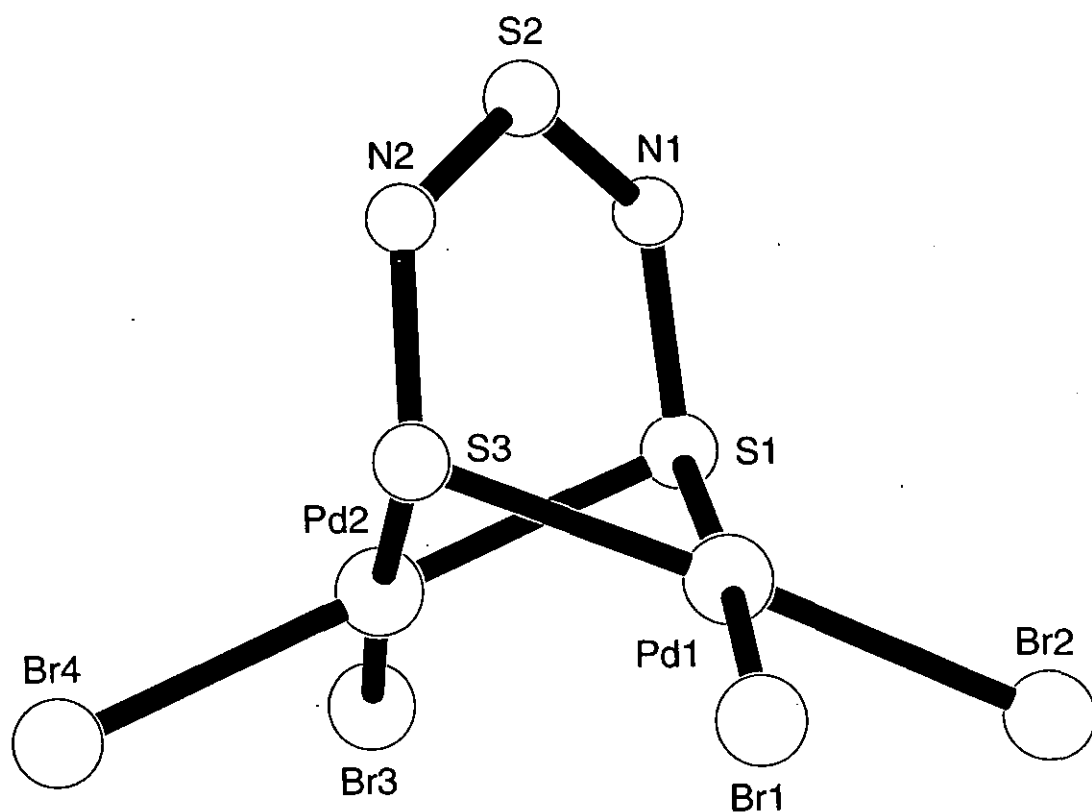


Figure 2.8 The X-ray structure of the anion in  $[PPh_4]_2[Pd_2Br_4(S_3N_2)]$

Pd(1)-Br(1)	2.473(5)	Pd(1)-Br(2)	2.457(5)
Pd(1)-S(1)	2.279(12)	Pd(1)-S(3)	2.279(11)
S(1)-N(1)	1.652(34)	N(1)-S(2)	1.563(37)
S(2)-N(2)	1.605(51)	N(2)-S(3)	1.638(48)
Pd(2)-S(1)	2.280(12)	Pd(2)-S(3)	2.270(12)
Pd(2)-Br(3)	2.473(6)	Pd(2)-Br(4)	2.475(6)

Table 2.4a Selected bond lengths (Å) for  $[PPh_4]_2[Pd_2Br_4(S_3N_2)]$

Br(1)-Pd(1)-Br(2)	94.88(17)	Br(1)-Pd(1)-S(3)	91.27(32)
S(3)-Pd(1)-S(1)	85.37(41)	S(1)-Pd(1)-Br(2)	88.42(30)
Pd(1)-S(3)-Pd(2)	77.83(36)	Pd(1)-S(1)-Pd(2)	77.62(39)
Pd(1)-S(3)-N(2)	111.27(158)	Pd(1)-S(1)-N(1)	107.35(130)
S(3)-N(2)-S(2)	123.64(236)	N(2)-S(2)-N(1)	120.77(207)
S(2)-N(1)-S(1)	127.23(225)		
Br(4)-Pd(2)-Br(3)	96.56(21)	Br(4)-Pd(2)-S(3)	89.04(35)
S(3)-Pd(2)-S(1)	85.55(44)	S(1)-Pd(2)-Br(3)	88.90(34)
Pd(2)-S(3)-N(2)	107.11(141)	Pd(2)-S(1)-N(1)	106.54(126)

Table 2.4b *Selected angles (°) for [PPh<sub>4</sub>]<sub>2</sub>[Pd<sub>2</sub>Br<sub>4</sub>(S<sub>3</sub>N<sub>2</sub>)]*

#### 2.2.2.3 Reaction of [PPh<sub>4</sub>]<sub>2</sub>[Pd<sub>2</sub>I<sub>6</sub>] with two equivalents of (MeSiNSN)<sub>2</sub>S

Stirring a mixture of [PPh<sub>4</sub>]<sub>2</sub>[Pd<sub>2</sub>I<sub>6</sub>] and 1 for a few hours, as above, followed by slow diffusion of diethyl ether into the concentrated solution, results in the precipitation of a black solid. This solid does not appear to be crystalline, preventing study by single crystal X-ray diffraction. <sup>1</sup>H NMR studies of the reaction mixture reveal that 1 does not degradate. This observation together with the negligible nitrogen content in the black solid, shown by microanalysis measurements, seem to indicate that 1 does not react with [PPh<sub>4</sub>]<sub>2</sub>[Pd<sub>2</sub>I<sub>6</sub>].

#### 2.2.2.4 Infrared Spectra

The IR spectra of all complexes obtained by reaction of [PPh<sub>4</sub>]<sub>2</sub>[Pd<sub>2</sub>X<sub>6</sub>], where X=Cl or Br, with 1 are dominated by strong absorptions due to the [PPh<sub>4</sub>]<sup>+</sup> counterion. However, it is possible to identify bands due to S-N and M-X vibrations.

Simple theory indicates that the positions of the bands due to Pd-X vibrations are expected to shift significantly to lower frequency when passing from Cl to Br. Thus any non-[PPh<sub>4</sub>]<sup>+</sup> band that remains unaffected by a change of halogen can be assume to be associated with the S-N fragment.



$[\text{PPh}_4][\text{PdCl}_2(\text{S}_2\text{N}_3)]$	$[\text{PPh}_4][\text{PdBr}_2(\text{S}_2\text{N}_3)]$	Assignment
858(vs){858} <sup>25</sup>	857(s)	N-S
675(sh)	671(sh)	N-S
	510(sh)	unknown
408(m){409}	401(w)	unknown
309(m){308}	317(w)	unknown

$[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_4(\text{S}_3\text{N}_2)]$	$[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_4(\text{S}_3\text{N}_2)]$	$[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6(\text{S}_2\text{N}_2)]$	Assignment
643(m){643} <sup>12</sup>	641(m){642} <sup>12</sup>	867(m){868} <sup>12</sup>	N-S
386(w){387}	381(m){383}	432(m){434}	N-S
309(w){309}		257(m){265}	Pd-X
290(w){291}	251(w){251}	249(m){251}	Pd-X

Table 2.5 *Vibrational frequencies ( $\text{cm}^{-1}$ ) for  $[\text{PPh}_4][\text{PdCl}_2(\text{S}_2\text{N}_3)]$ ,  $[\text{PPh}_4][\text{PdBr}_2(\text{S}_2\text{N}_3)]$ ,  $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_4(\text{S}_3\text{N}_2)]$ ,  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_4(\text{S}_3\text{N}_2)]$  and  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6(\text{S}_2\text{N}_2)]$ . Non  $[\text{PPh}_4]^+$  bands only, values reported in literature are given in {} brackets*

The synthesis of  $[\text{PdBr}_2(\text{S}_2\text{N}_3)]^-$  allows to compare its IR spectrum with that of  $[\text{PdCl}_2(\text{S}_2\text{N}_3)]^-$  and make an attempt to establish the identity of the bands observed (Table 2.5). The bands at  $858/857 \text{ cm}^{-1}$  and  $675/671 \text{ cm}^{-1}$  are common to both complexes and must be associated with the  $(\text{S}_2\text{N}_3)^-$  ligand. Both sets of bands are in ranges noted previously for S-N ligand vibrations, although it is difficult to ascertain precisely the modes responsible for each. The remaining two low frequency bands at  $408/401 \text{ cm}^{-1}$  and  $309/317 \text{ cm}^{-1}$  are more difficult to assign. They both fall in the area which one would expect to contain Pd-X stretches, however, the change from Cl to Br does not appear to affect the energy of these bands. We cannot, therefore, assign these bands unequivocally. It is possible, for example, that the  $408/401 \text{ cm}^{-1}$  band is actually due to a Pd-N

vibration.<sup>30</sup> One method of confirmation we could use is  $^{15}\text{N}$  labelling. Regrettably, there is not a feasible preparation of  $^{15}\text{N}$  labelled  $[\text{PdBr}_2(\text{S}_2\text{N}_3)]^-$  from compound 1.

It would have been interesting to compare the values of the bands due to  $(\text{S}_2\text{N}_3)^-$  with those of  $(\text{S}_2\text{N}_3)^{3-}$  in complexes in which they act as bidentate ligands. Such a comparison would throw some light on the bonding differences between the two. Differences which, as we have already noted, result in contrasting S-N bond lengths. Unfortunately, papers reporting the IR spectra of complexes containing the  $(\text{S}_2\text{N}_3)^{3-}$  unit do not make any reference to S-N vibrations. The lack of S-N values may be due to the particular symmetry of the complexes or to the presence of other bands that mask the S-N ones.

#### 2.2.2.5 $^1\text{H}$ NMR monitoring experiments of the reactions of $[\text{PPh}_4]_2[\text{Pd}_2\text{X}_6]$ $\text{X}=\text{Cl}, \text{Br}$ and 1 with two equivalents of $(\text{MeSiNSN})_2\text{S}$

The different range of products obtained when comparing  $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_6]$  to  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6]$  in their respective reactions with 1 indicates that the reaction pathway depends on the nature of the halogen. Monitoring the reactions to try to account for the products obtained or, in other words, to determine the mechanisms followed in both cases is hindered by the lack of NMR-active nuclei in the ultimate products; specifically it is difficult to envisage a realistic preparative route to  $^{15}\text{N}$  labelled 1, and hence we cannot use  $^{15}\text{N}$  NMR to probe intermediates (as was the case in the reactions of  $\text{S}_4\text{N}_4$ <sup>12</sup>, which is amenable to  $^{15}\text{N}$  enrichment, with  $[\text{PPh}_4]_2[\text{Pd}_2\text{X}_6]$ ). We can, of course, monitor the progress of the degradation of 1 by  $^1\text{H}$  NMR; Figure 2.9 contrasts the two reactions.

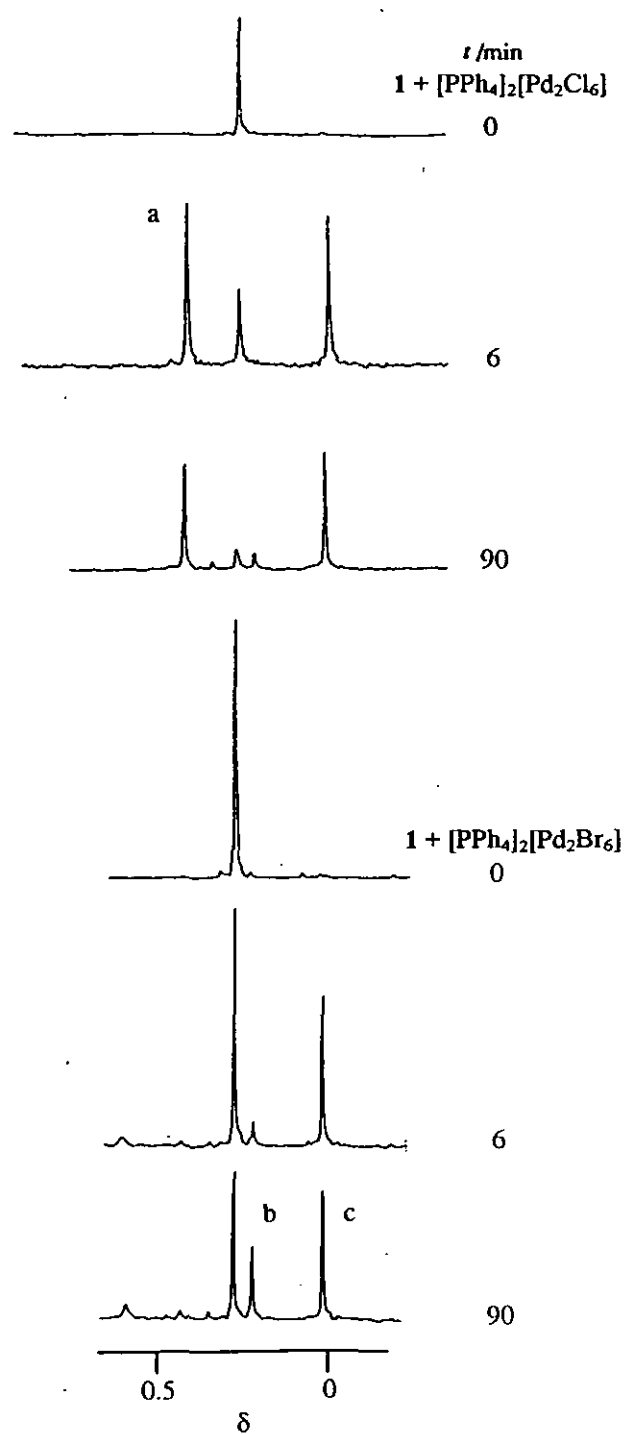


Figure 2.9 Comparison of the change with time of the  $^1\text{H}$  NMR spectra of solutions of 1 with  $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_6]$  and  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6]$  in  $\text{CD}_2\text{Cl}_2$  (peaks due to  $\alpha\text{-Me}_3\text{SiCl}$ ,  $b\text{-Me}_3\text{SiNSiMe}_3$ ,  $c\text{-Me}_3\text{SiSiMe}_3$ )

In the case of  $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_6]$  it can be seen that 6 minutes after mixing some 80% or so of **1** ( $\delta$  0.29 ppm) has reacted; by 90 minutes only a trace remains, together with a trace of  $(\text{Me}_3\text{SiN})_2\text{S}$  **b** ( $\delta$  0.24 ppm). By this stage the  $\text{Me}_3\text{Si}$  groups in **1** have effectively been converted to  $\text{Me}_3\text{SiCl}$  **a** ( $\delta$  0.42 ppm) and  $\text{Me}_3\text{SiSiMe}_3$  **c** ( $\delta$  0.06 ppm) (molar ratio 2:1). Degradation of **1** in the reaction with  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6]$  is clearly slower. After 6 minutes just over half of the ligand is still intact; appreciable amounts of  $\text{Me}_3\text{SiSiMe}_3$  are present together with a small amount of  $(\text{Me}_3\text{SiN})_2\text{S}$ . After 90 minutes **1** is still the predominant species, with  $(\text{Me}_3\text{SiN})_2\text{S}$  now present in significant amounts. Overnight reaction sees only  $\text{Me}_3\text{SiSiMe}_3$  remain. So whereas  $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_6]$  reacts with both equivalents of **1** in a matter of minutes,  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6]$  appears to use up only one equivalent on that time scale, with the final equivalent taking many hours to react.

It is worthwhile noting that **1** does not degrade when it is mixed with  $[\text{PPh}_4]_2[\text{Pd}_2\text{I}_6]$  in  $\text{CD}_2\text{Cl}_2$ ; this is consistent with the lack of reaction already noted.

#### 2.2.2.6 Reaction Mechanism

The following experimental observations must be accounted for in any proposed mechanism for the reaction between  $[\text{PPh}_4]_2[\text{Pd}_2\text{X}_6]$  ( $\text{X}=\text{Cl}$  and  $\text{Br}$ ) and **1**:

- a) the disparate nature of the resulting S-N ligands, and
- b) the observations recorded in the  $^1\text{H}$  NMR monitoring experiments.

In the case of the reaction of  $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_6]$  with **1** the above observations suggest that two equivalents of **1** react with a dimer to generate two mol of an adduct of the type  $[\text{PdCl}_3, \text{1}]$ . Clearly, this adduct is short lived (as no  $\text{Me}_3\text{Si}$  peaks associated with it are seen) and, given the preponderance of nitrogen-bound products eventually formed in these reaction, could well involve co-ordination of **1** *via* nitrogen (Fig. 2.10).

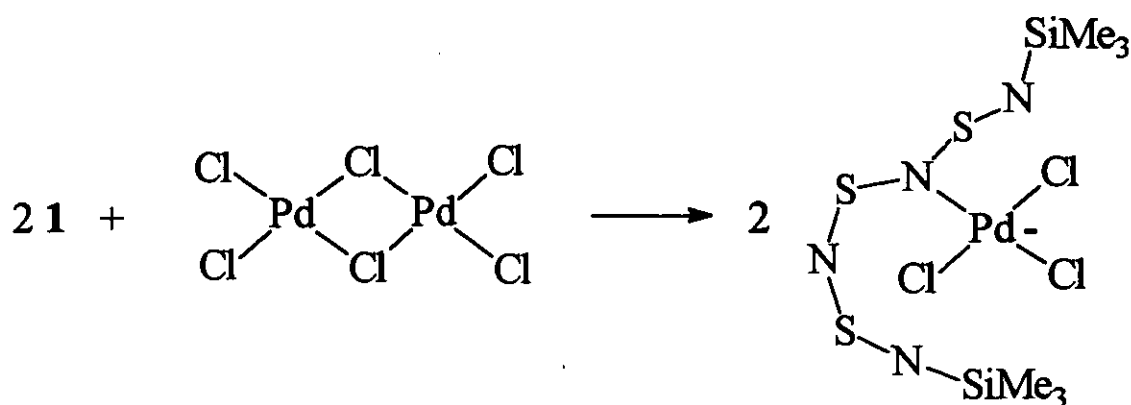


Figure 2.10 Proposed intermediate in the reaction of 1 with  $[PPh_4]_2[Pd_2Cl_6]$

Examples involving co-ordination of sulphur diimides *via* nitrogen with retention of the  $-N=S=N-$  group have been reported. Thus reaction of bis(benzonitrile)dichloropalladium (II) with  $(tBuN)_2S$  in  $CH_2Cl_2$  affords the complex  $[{(tBuN)_2S}_2PdCl_2]$  (Fig. 2.11).<sup>31</sup>

Reaction of one of the  $Me_3Si$  groups with a metal-halide bond would release the observed  $Me_3SiCl$ ; subsequent degradation of the resulting species to  $[PPh_4][PdCl_2(S_2N_3)]$  could then be achieved by loss of a  $Me_3Si$  unit (as half a mol of  $Me_3SiSiMe_3$ ) and a residual S-N fragment (presumably, ultimately, as  $S_4N_4$ ; the latter is indeed observed in the crude reaction mixture by IR spectroscopy).

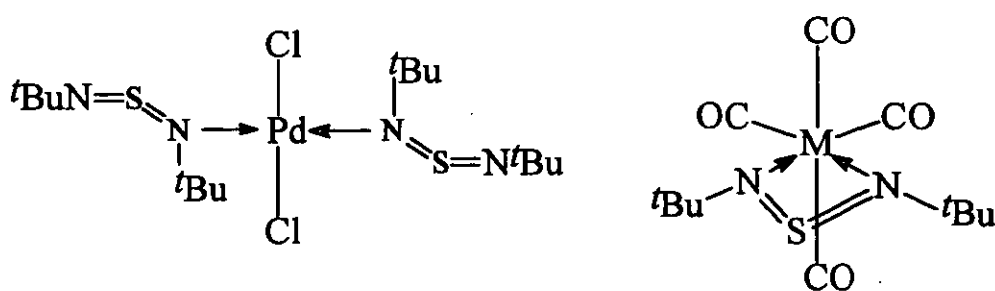


Figure 2.11 Co-ordination modes for  $[{(tBuN)_2S}_2PdCl_2]$  and  $[M(CO)_4{(tBuN)_2S}]$  where  $M=Cr, Mo$  and  $W$

In contrast, reaction of **1** with  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6]$  gives a subtly different cleavage of the original dimer, in this case we believe the initial products are a bidentate adduct of the type  $[\text{PdBr}_2.1]$ , which could clearly act as a source of  $[\text{PPh}_4][\text{PdBr}_2(\text{S}_2\text{N}_3)]$ , and the tetrabromo dianion  $[\text{PdBr}_4]^{2-}$  (Fig. 2.12).

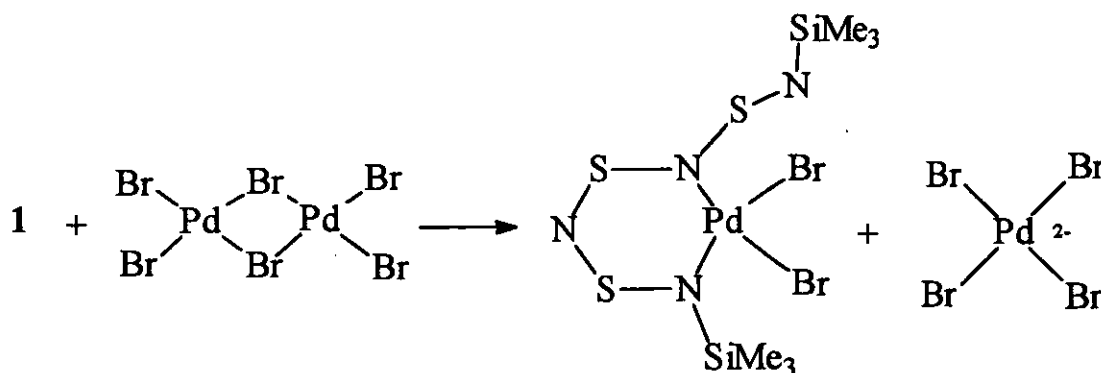


Figure 2.12 Proposed intermediate in the reaction of **1** with  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6]$

Sulphur diimide complexes have been reported to exhibit the same type of co-ordination, with the  $-\text{N}=\text{S}=\text{N}-$  moiety linked to a metal *via* two nitrogen atoms, that we suggest in the adduct  $[\text{PdBr}_2.1]$ . For instance, this fashion of co-ordination has been identified in  $[\text{M}(\text{CO})_4\{(\text{Bu}^t\text{N})_2\text{S}\}]$  where  $\text{M}=\text{Cr}$ ,  $\text{Mo}$  and  $\text{W}$  (Fig. 2.11).<sup>31</sup>

Comparison of the IR spectrum of the solid obtained by evaporation of the reaction mixture after one hour with that of  $[\text{PPh}_4]_2[\text{PdBr}_4]$  reveals a clear correlation of the Pd-Br stretch at  $247\text{cm}^{-1}$ , (the IR of  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6]$  shows two bands in this area, at  $239\text{cm}^{-1}$  and  $256\text{cm}^{-1}$ ). This explains why the  $^1\text{H}$  NMR results are as seen; one equivalent of **1** will be used up very quickly by reaction with the dimer, but the second will only be used up in the reaction with  $[\text{PdBr}_4]^{2-}$ , which would be expected to be markedly slower. If a sample of pure  $[\text{PPh}_4]_2[\text{PdBr}_4]$  is reacted with **1** a mixture of  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6(\text{S}_2\text{N}_2)]$  and some  $[\text{PPh}_4][\text{PdBr}_2(\text{S}_2\text{N}_3)]$  is obtained, indicating that the presence of  $[\text{PdBr}_4]^{2-}$  is indeed crucial to the formation of  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6(\text{S}_2\text{N}_2)]$ . It is noteworthy that in the reaction of **1** with  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6]$ , where large amounts of the  $\text{S}_2\text{N}_2$  adduct result,  $\text{Me}_3\text{SiNSNSiMe}_3$

is also formed as the reaction proceeds. Given that removal of a neutral  $S_2N_2$  unit from 1 would leave  $Me_3SiNSNSiMe_3$ , we can conclude that at some point an adducted molecule of 1 undergoes cleavage to these two products.

The presence of compounds  $[PPh_4]_2[Pd_2X_4(S_3N_2)]$  ( $X=Cl$  and  $Br$ ) clearly indicates that the above mechanistic arguments do not tell the whole story. In previous work<sup>12</sup> the appearance of  $[PPh_4]_2[Pd_2X_4(S_3N_2)]$  in the reaction of  $[PPh_4]_2[Pd_2X_6]$  with  $S_4N_4$  was explained by proposing a Pd(IV) intermediate containing the  $[S_4N_4]^{2-}$  ligand. It may be that adducts initially formed as in Figures 2.10 and 2.12 can undergo redox reactions to give unstable Pd(IV) species which then decompose back to Pd(II) with disruption of the ligand. It is also possible that some amounts of sulphur-bound adducts form in the initial reaction and then react further to give  $[PPh_4]_2[Pd_2X_4(S_3N_2)]$ ; or that the sulphur-nitrogen fragments lost as  $S_4N_4$  in the final degradation of the species in Figures 2.10 and 2.12 react to give  $[PPh_4]_2[Pd_2X_4(S_3N_2)]$  (although this is less likely, as one would expect to see  $[PPh_4]_2[Pd_2Cl_6(S_2N_2)]$  forming from  $[PPh_4]_2[Pd_2Cl_6]$ ). The fact that more  $[PPh_4]_2[Pd_2X_4(S_3N_2)]$  appears to form with time suggests that it results from degradation of an as yet unidentified intermediate. The latter must not contain  $Me_3Si$  groups (as these would be observed by NMR) and does not readily crystallise; this observation might suggest that it is neutral *i.e.* does not have the  $[PPh_4]^+$ , which tends to impart a greater ease of crystallisation, present. One result of this mode of formation of  $[PPh_4]_2[Pd_2Br_4(S_3N_2)]$  is that the crystalline samples are formed as needles rather than the flakes observed previously (or obtained upon recrystallisation of these samples). Clearly, the decomposition of the intermediate plays an important role during crystallisation and imparts this different crystal form; the crystals formed in this way are amenable to X-ray crystallography (Fig. 2.8).

#### 2.2.2.7 $^{31}P$ NMR study of the reaction of $[PPh_4][PdBr_2(S_2N_3)]$ with dppe [(dppe=1, 2 bis(diphenylphosphino) ethane)]

The above reactions give us access to significant amounts of complexes of  $[S_2N_3]^-$ , giving the opportunity to carry out a study of the chemistry of this ligand. The presence of

two reactive halogen atoms in  $[\text{PPh}_4][\text{PdX}_2(\text{S}_2\text{N}_3)]$  make these compounds potentially useful reagents in the preparation of new species *via* substitution with groups such as phosphines,  $(\text{S}_2\text{N}_2)^{2-}$  etc.

We have performed a preliminary investigation into this possibility by reacting  $[\text{PPh}_4][\text{PdBr}_2(\text{S}_2\text{N}_3)]$  with dppe in  $\text{CDCl}_3$ . The resulting product mixture contains, as shown by  $^{31}\text{P}$  NMR,  $[\text{Pd}(\text{dppe})(\text{S}_2\text{N}_2)]^{32}$ , a known complex of  $(\text{S}_2\text{N}_2)^{2-}$ ,  $[\text{Pd}(\text{dppe})\text{Br}_2]$  and of course  $[\text{PPh}_4]^+$  (Fig. 2.13).

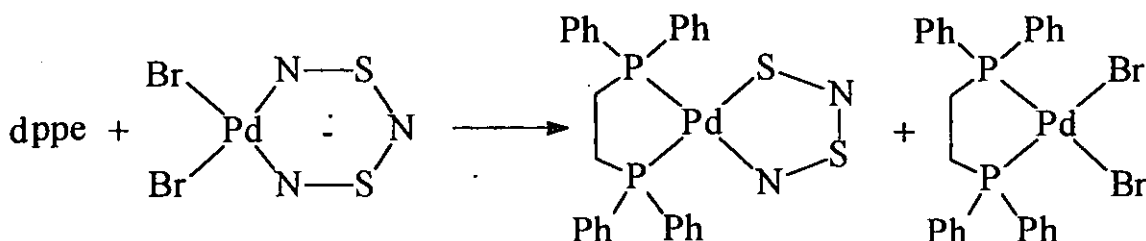


Figure 2.13 Products of the reaction of  $[\text{PPh}_4][\text{PdBr}_2(\text{S}_2\text{N}_3)]$  with dppe

This result suggests that the ligand is unstable both with respect to a ring contraction to the  $(\text{S}_2\text{N}_2)^{2-}$  ligand, and with respect to substitution for the dppe. The latter point emphasises the poor stability of this ligand. A conclusion backed up by the observation that, unlike the majority of palladium sulphur-nitrogen complexes, both species containing  $(\text{S}_2\text{N}_3)^-$  are actually air-sensitive. It is not easy to account for the fate of the third nitrogen atom in  $[\text{PPh}_4][\text{PdBr}_2(\text{S}_2\text{N}_3)]$ . This remaining nitrogen could have ended up linked to phosphorus or as  $1/4\text{S}_4\text{N}_4$ . The former possibility may be ruled out since there is not any signal in the  $^{31}\text{P}$  NMR spectrum of the crude mixture attributable to a compound such it. The formation of traces of  $\text{S}_4\text{N}_4$  is more likely, although no evidence of its presence was found.



### 2.2.3 Attempted photolytic activation of the reaction of *cis*-[PtCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] with (Me<sub>3</sub>SiNSN)<sub>2</sub>S

Photolytic activation of S<sub>4</sub>N<sub>4</sub> has been used in our group to prepare metal-sulphur-nitrogen complexes in reactions which otherwise require extreme conditions. Thus reaction of S<sub>4</sub>N<sub>4</sub> with *cis*-[PtCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>], which only occurs at temperatures over 100°C, can be achieved at 0°C by the use of UV photolysis. The reaction performed in this way leads to [Pt(S<sub>2</sub>N<sub>2</sub>H)Cl(PMe<sub>2</sub>Ph)] and [Pt(S<sub>3</sub>N)Cl(PMe<sub>2</sub>Ph)].<sup>13</sup>

In this work, irradiation with UV light of a mixture of *cis*-[PtCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] and **1**, in CH<sub>2</sub>Cl<sub>2</sub>, results in a colour change of the reaction mixture from orange to dark brown. After photolysis, the solution progressively returns to the original orange colour. <sup>31</sup>P NMR of the solid collected after concentration of the solution *in vacuo* only shows the presence of unreacted *cis*-[PtCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>]. Therefore, exposure to UV light does not promote reaction between both reagents, despite the distinct colour change observed. This observation implies that **1** does not undergo cleavage when photolysed because, if any intermediates had been formed by disruption of **1** they would have, almost certainly, reacted with *cis*-[PtCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>]. In fact, when **1** is irradiated with UV light in absence of *cis*-[PtCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] the same colour pattern described above is observed. The <sup>1</sup>H NMR spectrum of a sample of the dark brown solution and of the same solution once it has recovered the initial orange aspect are identical to that of compound **1**. Therefore, one possible explanation for these observations is that the colour change is caused by the electronic interaction of the UV light with the π-system in the chain rather than degradation of **1** to reactive intermediates; if such intermediates did form, they would be unlikely to rearrange back to **1**. Nevertheless, the formation of a small amount of a highly coloured unstable species cannot be completely ruled out, although such a compound is not detected by either <sup>1</sup>H or <sup>31</sup>P NMR spectroscopy. In conclusion, compound **1** survives when exposed to UV light which is a surprising result in itself. Undoubtedly, this reaction deserves further attention.

#### 2.2.4 Reaction of $[\text{PtCl}_2(\text{PMe}_2\text{Ph})]_2$ with two equivalents of $(\text{Me}_3\text{SiNSN})_2\text{S}$

The platinum bridged species  $[\text{PtCl}_2(\text{PMe}_2\text{Ph})]_2$  reacts with  $\text{S}_4\text{N}_4$  via oxidative cleavage of the bridging halide bonds to afford the Pt(IV) complex *mer*- $[\text{PtCl}_2(\text{S}_4\text{N}_4)(\text{PMe}_2\text{Ph})]$ , which contains the  $\text{S}_4\text{N}_4$  unit as a tridentate  $\text{S}_4\text{N}_4^{2-}$  bound to the metal via one nitrogen and two sulphur atoms.<sup>33</sup> In this complex the  $\text{S}_4\text{N}_4^{2-}$  ligand adopts a meridional geometry and it is almost planar, with the exception of one sulphur and one nitrogen atom (Fig. 2.14).

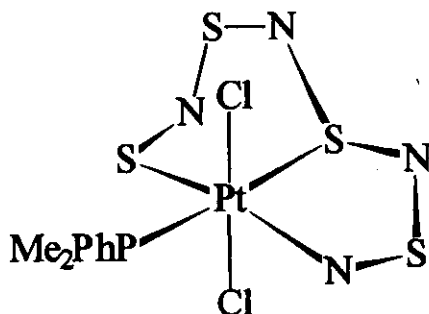


Figure 2.14 The structure of *mer*- $[\text{PtCl}_2(\text{S}_4\text{N}_4)(\text{PMe}_2\text{Ph})]$

If a mixture of  $[\text{PtCl}_2(\text{PMe}_2\text{Ph})]_2$  and 1 is dissolved in  $\text{CH}_2\text{Cl}_2$  the resulting solution immediately darkens from red to black. After stirring for a number of days, to assure complete reaction, a range of products are formed.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ) of the solid obtained after concentration *in vacuo* of the black solution reveals the presence of  $[\text{Pt}(\text{S}_2\text{N}_2\text{H})\text{Cl}(\text{PMe}_2\text{Ph})]$  ( $\delta$  -21.1 ppm,  $^1J(^{195}\text{Pt}-^{31}\text{P})$  3412 Hz), a known complex of  $[\text{S}_2\text{N}_2\text{H}]^-$ ,<sup>11</sup> and also an unknown complex ( $\delta$  -22.1 ppm,  $^1J(^{195}\text{Pt}-^{31}\text{P})$  3448 Hz) together with other species such as  $\text{P}(\text{S})\text{Me}_2\text{Ph}$ .

All attempts to isolate this new platinum complex failed. Thus elution of the crude reaction products through a Bio-Beads column with  $\text{CH}_2\text{Cl}_2$  leads to decomposition. Slow diffusion of hexane into a concentrated solution of the crude reaction mixture does not promote the growth of any crystals. Therefore, it is difficult to characterise the new complex by means of the information available; only the  $^{31}\text{P}$  NMR spectrum of the crude mixture may give a few clues to its nature. The size of the  $^1J(^{195}\text{Pt}-^{31}\text{P})$  coupling constant

in platinum-phosphine complexes is directly related to the oxidation state of the platinum. Typical values are in the region 4000, 3000 and 2000 Hz for Pt(0), Pt(II) and Pt(IV) respectively. For our complex the  $^1J(^{195}\text{Pt}-^{31}\text{P})$  is 3448 Hz so we may affirm that it contains Pt(II). In addition, the presence of only one peak (with  $^{195}\text{Pt}$  satellites) shows that it must be either a symmetrical *bis*-phosphine complex or a complex containing only one phosphine group bound to platinum. The chemical shift and  $^1J(^{195}\text{Pt}-^{31}\text{P})$  coupling constant of the new complex are comparable to that of  $[\text{Pt}(\text{S}_2\text{N}_2\text{H})\text{Cl}(\text{PMe}_2\text{Ph})]$ , so the former cannot differ much from the latter.

To sum up, in contrast to  $\text{S}_4\text{N}_4$  compound **1** does not react with  $[\text{PtCl}_2(\text{PMe}_2\text{Ph})]_2$  to give Pt(IV) complexes.

#### 2.2.5 Reaction of $[\text{Pt}(\text{PPh}_3)_3]$ with one equivalent of $(\text{Me}_3\text{SiNSN})_2\text{S}$

The reaction between  $\text{S}_4\text{N}_4$  and  $[\text{Pt}(\text{PPh}_3)_3]$  has been studied in depth.<sup>14</sup> When the reaction is performed in  $\text{CH}_2\text{Cl}_2$  the initial products include  $[\text{Pt}(\text{S}_2\text{N}_2)(\text{PPh}_3)_2]$  and an intermediate species which decomposes, *via* loss of  $\text{PPh}_3$ , affording the dimeric complex  $[\text{Pt}(\text{S}_2\text{N}_2)(\text{PPh}_3)]_2$  (Fig. 2.15).

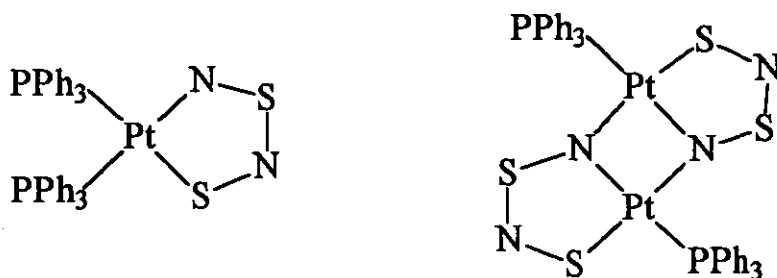


Figure 2.15 The structures of  $[\text{Pt}(\text{S}_2\text{N}_2)(\text{PPh}_3)_2]$  and  $[\text{Pt}(\text{S}_2\text{N}_2)(\text{PPh}_3)]_2$

In contrast to the reactions previously reported in this chapter, **1** appears to mimic  $\text{S}_4\text{N}_4$  in its reaction with the Pt(0) species  $[\text{Pt}(\text{PPh}_3)_3]$ . Thus, on mixing  $[\text{Pt}(\text{PPh}_3)_3]$  and **1**, in toluene, a green solution results which slowly changes colour to pale brown. Removal

of the toluene *in vacuo* and addition of  $\text{CH}_2\text{Cl}_2$  results in a yellow solution together with a red precipitate. IR analysis of the red precipitate reveals it to be  $[\text{Pt}(\text{S}_2\text{N}_2)(\text{PPh}_3)]_2$ .  $^{31}\text{P}$  NMR of the yellow solid collected after concentration *in vacuo* of the yellow solution and addition of hexane, shows the presence of the asymmetrical *cis-bis*-phosphine complex  $[\text{Pt}(\text{S}_2\text{N}_2)(\text{PPh}_3)_2]$  ( $\delta_{\text{A}}$  11.5 ppm,  $\delta_{\text{B}}$  24.1 ppm;  $^1J_{\text{A}}(^{195}\text{Pt}-^{31}\text{P}_{\text{A}})$  2995 Hz,  $^1J_{\text{B}}(^{195}\text{Pt}-^{31}\text{P}_{\text{B}})$  2825 Hz).

It is noteworthy that if the reaction is performed with two equivalents of **1** it seems to proceed through a more complicated route, since  $^{31}\text{P}$  NMR of the solution obtained after isolation of the insoluble  $[\text{Pt}(\text{S}_2\text{N}_2)(\text{PPh}_3)]_2$  reveals the presence of  $[\text{Pt}(\text{S}_2\text{N}_2)(\text{PPh}_3)_2]$  together with large amounts of  $\text{P}(\text{S})\text{Ph}_3$  and singlets at  $\delta$  24.9, 16.3 and 0.81 ppm which do not have  $^{195}\text{Pt}$  satellites. We have yet to ascertain whether these peaks are due to a phosphine-containing impurity or to the presence of a  $\text{PPh}_3$  on part of metallocycle, too far from the Pt to be coupled to the  $^{195}\text{Pt}$ . To date, we have been unable to either crystallise or isolate (using Bio-Beads) these products and so we have no real idea of its nature.

### 2.3 Conclusions

Although we can hope that compound **1** will act as a potent source of novel S-N fragments in a variety of reactions, there is always the chance that it will react in an identical manner to  $\text{S}_4\text{N}_4$ . Even in such situations, however, it could be argued that **1** is a more desirable reagent than  $\text{S}_4\text{N}_4$  due to the latter explosive nature.

## 2.4 Experimental

### 2.4.1 Preparation of Starting Materials

*(Me<sub>3</sub>SiNSN)<sub>2</sub>S* 1- A solution of freshly distilled SCl<sub>2</sub> (2.35 g, 23.03 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 ml) was added dropwise to a stirred solution of Me<sub>3</sub>SiNSNSiMe<sub>3</sub><sup>20</sup> (9.59 g, 46.12 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) with the reaction flask immersed in a dry ice/acetone bath (-78°C). Once the addition was complete the deep blue suspension was stirred for 60 minutes and the reaction flask then allowed to warm up to room temperature. The resulting mixture was filtered through Celite and the red solution concentrated *in vacuo*. The resulting red oil was dissolved in hexane and filtered through Celite, in air, to remove of any traces of S<sub>4</sub>N<sub>4</sub>. The red filtrate was concentrated and then the oil exposed to air on a watch-glass overnight to give large orange needles of 1 (yield 2.36 g, 34.4 %). IR, <sup>1</sup>H NMR and mass spectral data were in accord with the literature values.<sup>21</sup>

[PPh<sub>4</sub>]<sub>2</sub>[Pd<sub>2</sub>Cl<sub>6</sub>] - A mixture of PdCl<sub>2</sub> (0.81 g, 4.6 mmol) and NaCl (0.53 g, 9.1 mmol) in distilled water (100 ml) was stirred at 70°C for 90 minutes. The resulting dark solution was treated with [PPh<sub>4</sub>]Cl (1.71 g, 4.6 mmol) dissolved in water (50 ml), giving a brown precipitate which was collected and recrystallised from CH<sub>2</sub>Cl<sub>2</sub>/toluene (yield 1.85 g, 73 %).

[PPh<sub>4</sub>]<sub>2</sub>[Pd<sub>2</sub>Br<sub>6</sub>] - A mixture of PdCl<sub>2</sub> (0.31 g, 1.8 mmol) and KBr (0.84 g, 7.1 mmol) in distilled/degassed water (100 ml) was stirred at 60°C for 90 minutes. The resulting wine-coloured solution was treated with [PPh<sub>4</sub>]Br (0.74 g, 1.8 mmol) dissolved in water (50 ml), giving a brown precipitate which was collected, in air, and then recrystallised from CH<sub>2</sub>Cl<sub>2</sub>/toluene (yield 1.02 g, 79 %).

[PPh<sub>4</sub>]<sub>2</sub>[Pd<sub>2</sub>I<sub>6</sub>] - A mixture of PdCl<sub>2</sub> (0.2 g, 1.1 mmol) and NaI (1.7 g, 11 mmol) in warm ethanol was stirred for 90 minutes and then it was allowed to cool down to room temperature. The excess of NaI was removed by filtration and the black filtrate treated

with  $[\text{PPh}_4]\text{I}$  (0.53 g, 1.1 mmol) to give a black precipitate which was collected and recrystallised from  $\text{CH}_2\text{Cl}_2/\text{toluene}$  (yield 0.2 g, 20 %).

#### 2.4.2 Reaction of $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_6]$ with $(\text{Me}_3\text{SiNSN})_2\text{S}$

A solution of  $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_6]$  (110 mg, 0.1 mmol) in  $\text{CH}_2\text{Cl}_2$  (150 ml) was treated with solid 1 (59 mg, 0.2 mmol), giving a brown solution which was stirred for 90 minutes. The volume of the solution was reduced to a few ml *in vacuo* and layered with  $\text{Et}_2\text{O}$ . Slow diffusion for 48 hours resulted in the growth of black material, as both well formed plates and a mass of micro-crystals, together with a very small crop of orange needles. These were separated from each other manually. IR spectroscopy (Table 2.5) showed the black plates and microcrystals to be  $[\text{PPh}_4][\text{PdCl}_2(\text{S}_2\text{N}_3)]$  (yield 45 mg, 36 % based on palladium; microanalysis Found C 45.4, H 3.1, N 6.2; Calc. C 46.3, H 3.2, N 6.7) and the orange crystals to be  $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_4(\text{S}_3\text{N}_2)]$ .

#### 2.4.3 Reaction of $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6]$ with $(\text{Me}_3\text{SiNSN})_2\text{S}$

A solution of  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6]$  (150 mg, 0.1 mmol) in  $\text{CH}_2\text{Cl}_2$  (150 ml) was treated with solid 1 (65 mg, 0.2 mmol), giving a dark red solution which was stirred for 90 minutes. The volume of the solution was reduced to a few ml *in vacuo* and layered with  $\text{Et}_2\text{O}$ . Slow diffusion for 48 hours resulted in the growth of three types of crystals: black three-dimensional prisms, brown plates and orange flakes. These were separated from each other manually. IR spectroscopy (Table 2.5) showed the orange and brown crystals to be  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_4(\text{S}_3\text{N}_2)]$  (yield *ca.* 5 mg) and  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6(\text{S}_2\text{N}_2)]$  (yield 20 mg, 13 % based on palladium) respectively. X-ray crystallography revealed the black crystals to be  $[\text{PPh}_4][\text{PdBr}_2(\text{S}_2\text{N}_3)]$  (yield 60 mg, 38 % based on palladium; Found C 40.2, H 2.7, N 5.3; Calc. C 40.5, H 2.8, N 5.9).

#### 2.4.4 Attempted reaction of $[\text{PPh}_4]_2[\text{Pd}_2\text{I}_6]$ with $(\text{Me}_3\text{SiNSN})_2\text{S}$

A solution of  $[\text{PPh}_4]_2[\text{Pd}_2\text{I}_6]$  (39 mg, 0.02 mmol) in  $\text{CH}_2\text{Cl}_2$  (150 ml) was treated with solid 1 (14 mg, 0.04 mmol), giving a black solution which was stirred for 90 minutes.

The volume of the solution was reduced to a few ml *in vacuo* and layered with Et<sub>2</sub>O. Slow diffusion for 4 days did not promote the growth of any crystalline material.

#### 2.4.5 Reaction of [PPh<sub>4</sub>][PdBr<sub>2</sub>(S<sub>2</sub>N<sub>3</sub>)] with dppe

A mixture of [PPh<sub>4</sub>][PdBr<sub>2</sub>(S<sub>2</sub>N<sub>3</sub>)] (20 mg, 0.03 mmol) and dppe (11 mg, 0.03 mmol) was dissolved in dry CDCl<sub>3</sub> (4 ml) giving a pale orange solution. The <sup>31</sup>P NMR spectrum of this solution showed, in addition to the [PPh<sub>4</sub>]<sup>+</sup> cation, the presence of [Pd(dppe)Br<sub>2</sub>] (δ 64.4 ppm) and [Pd(dppe)(S<sub>2</sub>N<sub>2</sub>)]<sup>32</sup> (δ<sub>A</sub> 55.1, δ<sub>B</sub> 48.5 ppm; <sup>2</sup>J(<sup>31</sup>P-<sup>31</sup>P) 26 Hz).

#### 2.4.6 Attempted photolytic activation of the reaction of *cis*-[PtCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] with (Me<sub>3</sub>SiNSN)<sub>2</sub>S

Photolysis was performed using a quartz medium-pressure, 125 W mercury-discharge lamp (Applied Photophysics) with output in the range 265-579 nm, together with a Schlenk-type reaction vessel which allowed the reaction to be performed under N<sub>2</sub>.

A mixture of **1** (80 mg, 0.3 mmol) and *cis*-[PtCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] (145 mg, 0.3 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (100 ml) was cooled in an ice bath and, with vigorous stirring, photolysed for 1 hour, during which time the colour of the solution changed from orange to dark red-brown. After photolysis, the solution progressively returned to the original orange colour. The solvent was removed *in vacuo* to give a brown solid. The <sup>31</sup>P NMR (CDCl<sub>3</sub>) showed only unreacted *cis*-[PtCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] (δ -16.36, <sup>1</sup>J(<sup>195</sup>Pt-<sup>31</sup>P) 3538 Hz).

#### 2.4.7 Reaction of [PtCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] with (Me<sub>3</sub>SiNSN)<sub>2</sub>S

A mixture of [PtCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] (40 mg, 0.05 mmol) and **1** (30 mg, 0.1 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (100 ml) to give a red solution which darkened within a few minutes to black. The reaction mixture was stirred for 3 days. The <sup>31</sup>P NMR (CDCl<sub>3</sub>) of the concentrated solution revealed the presence of [Pt(S<sub>2</sub>N<sub>2</sub>H)Cl(PMe<sub>2</sub>Ph)]<sup>11</sup> (δ -21.1 ppm, <sup>1</sup>J(<sup>195</sup>Pt-<sup>31</sup>P) 3412 Hz), an unknown compound (δ -22.1 ppm, <sup>1</sup>J(<sup>195</sup>Pt-<sup>31</sup>P) 3448 Hz) and species such as P(S)Me<sub>2</sub>Ph. Mass Spectrometry analysis (FAB+) of the black solid

obtained after removal of the solvent *in vacuo* only showed the presence of  $[\text{Pt}(\text{S}_2\text{N}_2\text{H})\text{Cl}(\text{PMe}_2\text{Ph})]$  and no peaks attributable to the unknown compound were found. This solid was dissolved in  $\text{CH}_2\text{Cl}_2$  (5 ml) and placed on a Bio-Beads gel-permeation column. Elution with  $\text{CH}_2\text{Cl}_2$  resulted in the separation of three bands. The first band was brown and was followed by a deep green band and an orange band.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ) of all three bands only showed  $\text{P}(\text{S})\text{Me}_2\text{Ph}$ . Slow diffusion of hexane into the concentrated crude reaction mixture did not give rise to any crystalline material.

#### 2.4.8 Reaction of $[\text{Pt}(\text{PPh}_3)_3]$ with $(\text{Me}_3\text{SiNSN})_2\text{S}$

A solution of 1 (30 mg, 0.1 mmol) in toluene (10 ml) was added to a solution of  $[\text{Pt}(\text{PPh}_3)_3]$  (100 mg, 0.1 mmol) in the same solvent (50 ml) to give a green solution, which turned pale brown within 10 minutes. After stirring for 1 hour the solvent was removed *in vacuo* to yield a brown solid. Addition of  $\text{CH}_2\text{Cl}_2$  to the solid resulted in a suspension of a red solid in a yellow solution, which was filtered. IR showed the red solid to be  $[\text{Pt}(\text{S}_2\text{N}_2)(\text{PPh}_3)]_2$ <sup>14</sup> (yield 8 mg, 14 %). The volume of the yellow filtrate was reduced to 5 ml *in vacuo* and a yellow solid precipitated by addition of hexane (150 ml), leaving only  $\text{PPh}_3$  (as shown by  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )) in solution. IR and  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ) measurements revealed the yellow solid to be  $[\text{Pt}(\text{S}_2\text{N}_2)(\text{PPh}_3)_2]$ <sup>14</sup> (yield 48 mg, 58 %) ( $\delta_{\text{A}}$  11.5 ppm,  $\delta_{\text{B}}$  24.1 ppm;  $^1J_{\text{A}}(^{195}\text{Pt}-^{31}\text{P}_{\text{A}})$  2995 Hz,  $^1J_{\text{B}}(^{195}\text{Pt}-^{31}\text{P}_{\text{B}})$  2825 Hz).

Essentially the same products were formed when the reaction was performed at a 2:1 1:Pt ratio.

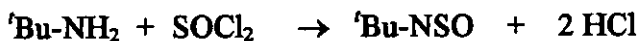


## CHAPTER 3. CHEMISTRY OF ('BuNSN)<sub>2</sub>S

### 3.1 Introduction

The preparation of ('BuNSN)<sub>2</sub>S **3**, *i.e.* the 'Bu analogue of (Me<sub>3</sub>SiNSN)<sub>2</sub>S, can be achieved by means of a three step process which is outlined in Scheme 3.1.<sup>34</sup>

Scheme 3.1



The X-ray structure of ('BuNSN)<sub>2</sub>S shows that the central S-N bonds are considerably longer (1.65-1.70 Å) than the outer ones (1.50-1.56 Å).<sup>35</sup> Both sets of bond distances are typical of single and double sulphur-nitrogen bonds respectively. The 'Bu groups are in a *trans* conformation relative to the nearest double N-S bonds (Fig. 3.1).

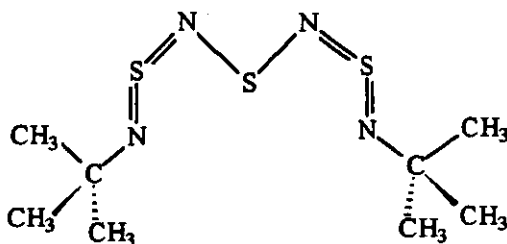


Figure 3.1 *The structure of ('BuNSN)<sub>2</sub>S*

No reactions of **3** with metal species have been reported, even though it has been known for a number of years. We can, however, gain some insight into its potential chemistry by analogy with that of ('BuN)<sub>2</sub>S.<sup>36</sup> Reactions of ('BuN)<sub>2</sub>S with metal centres involve:

- (a) co-ordination of the neutral ligand or,  
 (b) linkage of the fragments resulted after cleavage of the diimine.

(a) Co-ordination of neutral  $(^t\text{BuN})_2\text{S}$ . The compound  $(^t\text{BuN})_2\text{S}$  can act as a monodentate or bidentate ligand. In both cases the ligand is bound to the metal *via* nitrogen (Fig. 3.2). In  $(^t\text{BuN})_2\text{S}$  complexes several isomers can exist in solution as shown by  $^1\text{H}$  NMR studies.

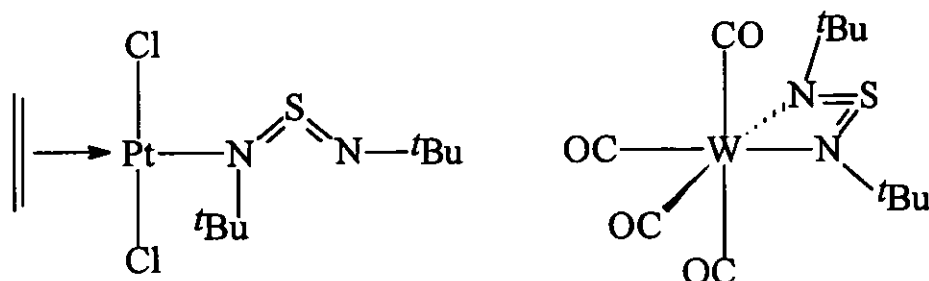


Figure 3.2 Co-ordination modes of  $(^t\text{BuN})_2\text{S}$ : monodentate,  $[\text{Pt}\{(^t\text{BuN})_2\text{S}\}(\text{C}_2\text{H}_4)\text{Cl}_2]$ , and bidentate,  $[\text{W}(\text{CO})_4\{(^t\text{BuN})_2\text{S}\}]$

(b) Fragmentation reactions. An example of this type of reaction occurs when  $(^t\text{BuN})_2\text{S}$  and  $(\text{II-Cp})_2\text{Ni}$  are refluxed in hexane to afford  $^t\text{BuN}(\text{II-CpNi})_3$ .<sup>37</sup> The cluster formed contains a  $^t\text{BuN}$  fragment bonded to all three Ni atoms (Fig. 3.3).

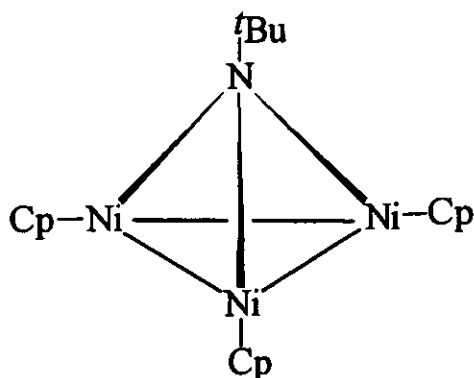


Figure 3.3 The molecular structure of  $^t\text{BuN}(\text{II-CpNi})_3$

This chapter deals with the preparation of (<sup>t</sup>BuNSN)<sub>2</sub>S along with the study of its reactivity towards a number of transition metals. The aim pursued was to compare its chemistry with that of its silyl analogue.

### 3.2 Results and Discussion

The reactivity of (<sup>t</sup>BuNSN)<sub>2</sub>S would be expected to be different to that of (Me<sub>3</sub>SiNSN)<sub>2</sub>S due to the distinct groups at both ends of the N-S chain. Specifically, in the case of the latter the reactive driving force provided by the elimination of, for example, Me<sub>3</sub>SiCl will be lacking in **3**. Thus, while a co-ordinated (Me<sub>3</sub>SiNSN)<sub>2</sub>S may be expected to react further (as in Fig. 2.10 and 2.12), (<sup>t</sup>BuNSN)<sub>2</sub>S is likely to be a far more robust ligand. We hoped that the lack of pathways for the loss of the <sup>t</sup>Bu groups would enhance the chances of isolating a complex with the (<sup>t</sup>BuNSN)<sub>2</sub>S ligand intact. There are two key incentives behind the work reported in this chapter:

- (a) no complexes containing a S<sub>3</sub>N<sub>4</sub> chain have been prepared to date. In addition,
- (b) the preparation of such a complex would clearly back up the mechanism suggested for the reaction between (Me<sub>3</sub>SiNSN)<sub>2</sub>S and [PPh<sub>4</sub>]<sub>2</sub>[Pd<sub>2</sub>X<sub>6</sub>] (X=Cl or Br), (see Chapter 2).

#### 3.2.1 Preparation of (<sup>t</sup>BuNSN)<sub>2</sub>S

Compound **3** may be prepared by a literature method (See Scheme 3.1).<sup>34</sup> However, it was found in this work that the synthesis of <sup>t</sup>Bu-NSO and <sup>t</sup>Bu-NSN-SiMe<sub>3</sub>, which involve distillation, can be improved by choosing Et<sub>2</sub>O as a solvent instead of n-hexane. It is observed that when n-hexane is employed the separation obtained when distilling is worse than when using Et<sub>2</sub>O because of the higher boiling point of the former.

It was also found that compound **3** can be obtained in a semicrystalline and highly pure form as follows: the oily red crude solid is placed in a flask and immersed in a dry ice/acetone bath, then it is washed with n-hexane to leave pure **3** as an orange solid.

### 3.2.2 Reaction of [Pt(PPh<sub>3</sub>)<sub>3</sub>] with (tBuNSN)<sub>2</sub>S

We have found that the compound (tBuNSN)<sub>2</sub>S reacts with [Pt(PPh<sub>3</sub>)<sub>3</sub>] in toluene to afford *cis*-[Pt(PPh<sub>3</sub>)<sub>2</sub>(NSO)<sub>2</sub>], P(S)Ph<sub>3</sub>, P(O)Ph<sub>3</sub>, free PPh<sub>3</sub> and an unknown phosphine platinum complex, characterised by a typical AX splitting pattern, as shown by <sup>31</sup>P NMR spectroscopy. The bis-thionylimino complex can be isolated as orange crystals and its identity confirmed by microanalysis.

The prominent feature of the reaction is the formation of a novel phosphine complex whose <sup>31</sup>P NMR (CDCl<sub>3</sub>) spectrum is, (δ<sub>A</sub> 9.49 ppm, δ<sub>X</sub> 18.03 ppm; <sup>1</sup>J<sub>A</sub>(<sup>195</sup>Pt-<sup>31</sup>P<sub>A</sub>) 3201 Hz, <sup>1</sup>J<sub>X</sub>(<sup>195</sup>Pt-<sup>31</sup>P<sub>X</sub>) 3481 Hz, <sup>2</sup>J(<sup>31</sup>P<sub>A</sub>-<sup>31</sup>P<sub>X</sub>) 24 Hz). The splitting pattern can be used to throw some light on its nature. There are two inequivalent phosphorus atoms as indicated by the resonances at 9.49 and 18.03 ppm. As a result of its inequivalence they couple to each other with a <sup>2</sup>J(<sup>31</sup>P<sub>A</sub>-<sup>31</sup>P<sub>X</sub>) coupling constant of 24 Hz, which is typical of PPh<sub>3</sub> compounds of Pt(II).<sup>32</sup> Finally, the phosphorus atoms are also coupled to the <sup>195</sup>Pt nuclei, which are 33% abundant. As a result of this each resonance is split into a doublet with the ratio of the size of the <sup>195</sup>Pt satellites to the central resonances being (33/2):66, *i.e.* 1:4. The novel complex is air sensitive and decomposes as soon as the reaction mixture is exposed to air. Regrettably, it could not be isolated.

Another remarkable point is the formation of a NSO complex, despite the reaction being performed under strictly anaerobic conditions. Considering that the purity of the starting materials was double checked, it is thought unlikely that they were the source of oxygen into the system.

According to the above experimental observations what may occur is that an extremely air or water sensitive species is formed in the early stages of the reaction. It may be that this species degrades to give the NSO complex and the unknown AX complex also. However, there is no positive evidence to support the existence of that hypothetical unstable compound. It is tempting to link this initial product to the AX spectrum. This certainly fits in with the observation that the latter readily decomposes in air. It should be

noted, however, that  $^{31}\text{P}$  NMR measurements, in an oxygen free atmosphere, reveal the presence of both the NSO complex and the AX complex.

### 3.2.3 Reaction of $[\text{PPh}_4]_2[\text{Pd}_2\text{X}_6]$ ( $\text{X}=\text{Cl}$ or $\text{Br}$ ) with $(^t\text{BuNSN})_2\text{S}$

The first observation worth noting is that none of the N-S complexes formed when  $(\text{Me}_3\text{SiNSN})_2\text{S}$  reacts with  $[\text{PPh}_4]_2[\text{Pd}_2\text{X}_6]$  (Chapter 2) seem to be generated when  $(^t\text{BuNSN})_2\text{S}$  is used instead of its silyl analogue. The same crystallisation method, which was successfully used in Chapter 2, did not promote the growth of any crystalline material on this occasion. The latter observation would be consistent with the formation of a complex in which  $(^t\text{BuNSN})_2\text{S}$  was bound to the metal, since the  $^t\text{Bu}$  groups present in the ligand would impart a high solubility to the complex as a whole. In fact, that is the sort of complex expected to be formed because the ligand cannot undergo facile loss of the  $^t\text{Bu}$  groups to give rise to a cyclometallathiazene.

$^1\text{H}$  NMR studies of the reaction give definitive proof that  $(^t\text{BuNSN})_2\text{S}$  does not behave as  $(\text{Me}_3\text{SiNSN})_2\text{S}$ . The evidence comes in the form of the signals observed (Table 3.1), none of which can be assigned to  $^t\text{Bu-Cl}$ ,  $^t\text{Bu-Br}$  or  $^t\text{Bu-}^t\text{Bu}$ . These three species are analogous to the ones generated by degradation of  $(\text{Me}_3\text{SiNSN})_2\text{S}$ .

$[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_6] + (^t\text{BuNSN})_2\text{S}$	$[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6] + (^t\text{BuNSN})_2\text{S}$
1.43 ppm, singlet	1.43 ppm, singlet
	1.51 ppm, singlet

Table 3.1  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) data recorded 60 min after mixing  $(^t\text{BuNSN})_2\text{S}$  with  $[\text{PPh}_4]_2[\text{Pd}_2\text{X}_6]$

The resonance at 1.43 ppm is due to the free ligand. Thus, it appears that  $(^t\text{BuNSN})_2\text{S}$  does not react with  $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_6]$ . In the case of  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6]$ , it can be seen that there is a singlet at 1.51 ppm together with another one assignable to the free ligand. Both singlets are of equal intensity. This indicates that the reaction proceeds slowly

since 60 min after mixing only approximately half of the free ligand has undergone reaction. In a tentative approach, it could be argued that the resonance at 1.51 ppm arises from a co-ordinated ligand in which the <sup>t</sup>Bu groups are in equivalent magnetic environments. It has been reported that complexation of (<sup>t</sup>BuN)<sub>2</sub>S to a metal is always accompanied with a shift of the <sup>t</sup>Bu resonances to low field.<sup>38</sup> Interestingly, this is in agreement with the assignment of the singlet at 1.51 ppm to a hypothetical (<sup>t</sup>BuNSN)<sub>2</sub>S complex. The previous discussion is by no means definitive since the proposed complex, if real, only can be detected by <sup>1</sup>H NMR and to date it has not been isolated.

The lack of any evidence of complexation of (<sup>t</sup>BuNSN)<sub>2</sub>S with [Pd<sub>2</sub>Cl<sub>6</sub>]<sup>2-</sup> appears to be at odds with the mechanism given for the analogous reaction of (Me<sub>3</sub>SiNSN)<sub>2</sub>S (Chapter 2). In the aforementioned mechanism, initial co-ordination of (Me<sub>3</sub>SiNSN)<sub>2</sub>S to palladium is suggested to account for the range of products obtained. The complex formed is said to be short lived as it cannot be detected by <sup>1</sup>H NMR spectroscopy. One might expect similar behaviour to be observed by (<sup>t</sup>BuNSN)<sub>2</sub>S, since attachment to the metal should occur by the N-S chain which is identical in both ligands. For some reason, however, this does not appear to be the case. This observation opens up another possibility. The nature of the R group could be important and Figure 2.10 may be wrong. The compound Me<sub>3</sub>SiCl could be eliminated at the very beginning to form a Pd-N bond, then the dimer could split up (Fig. 3.4).

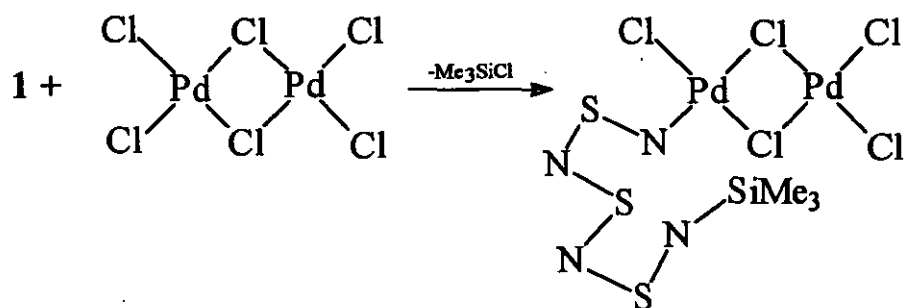


Figure 3.4 *Alternative intermediate to that given in Figure 2.10*

### 3.3 Experimental

#### 3.3.1 Preparation of Starting Materials

The dimers  $[\text{PPh}_4]_2[\text{Pd}_2\text{X}_6]$  ( $\text{X}=\text{Cl}$  or  $\text{Br}$ ) were prepared as noted in Chapter 2.

##### 3.3.1.1 Preparation of $(\text{BuNSN})_2\text{S}$

The precursors  $\text{Bu-NSO}$  and  $\text{Bu-NSN-SiMe}_3$  were prepared by a literature method,<sup>34</sup> substituting n-hexane for  $\text{Et}_2\text{O}$  as a solvent (See Results and Discussion).

$(\text{BuNSN})_2\text{S}$  3- A solution of freshly distilled  $\text{SCl}_2$  (2.04 g, 19.79 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 ml) was added *via* canula to a stirred solution of  $\text{Bu-NSN-SiMe}_3$  (7.52 g, 39.59 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 ml) with the reaction flask immersed in a dry ice/acetone bath ( $-78^\circ\text{C}$ ). Once the addition was complete the flask was allowed to warm up and the deep red solution stirred for 48 h. The solution was diluted with  $\text{CH}_2\text{Cl}_2$  (50 ml) and filtered through Celite, in air. The red filtrate was concentrated *in vacuo* to give a oily red crude solid. The crude material was placed in a flask and immersed in a dry ice/acetone bath ( $-78^\circ\text{C}$ ). It was washed with n-hexane to leave an orange solid. Yield of 3 1.875 g, 8.90 %.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 1.44 ppm, melting point  $86^\circ\text{C}$ .

#### 3.3.2 Reaction of $[\text{Pt}(\text{PPh}_3)_3]$ with $(\text{BuNSN})_2\text{S}$

A solution of 3 (24 mg, 0.09 mmol) in toluene (20 ml) was added *via* canula to a solution of  $[\text{Pt}(\text{PPh}_3)_3]$  (90 mg, 0.09 mmol) in toluene (20 ml). The resulting solution was stirred for 5 h, during which time it darkened and then lightened in colour. The solvent was removed *in vacuo* to give an orange solid.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , oxygen free) measurements revealed the presence of *cis*- $[\text{Pt}(\text{PPh}_3)_2(\text{NSO})_2]$ <sup>39</sup> ( $\delta$  8.8 ppm;  $^1J(^{195}\text{Pt}-^{31}\text{P})$  3190 Hz),  $\text{P}(\text{S})\text{Ph}_3$  ( $\delta$  43 ppm),  $\text{P}(\text{O})\text{Ph}_3$  ( $\delta$  28 ppm), free  $\text{PPh}_3$  ( $\delta$  -5 ppm), and an unknown phosphine platinum complex ( $\delta_{\text{A}}$  9.49 ppm,  $\delta_{\text{X}}$  18.03 ppm;  $^1J_{\text{A}}(^{195}\text{Pt}-^{31}\text{P}_{\text{A}})$  3201 Hz,  $^1J_{\text{X}}(^{195}\text{Pt}-^{31}\text{P}_{\text{X}})$  3481 Hz,  $^2J(^{31}\text{P}_{\text{A}}-^{31}\text{P}_{\text{X}})$  24 Hz). The compound *cis*- $[\text{Pt}(\text{PPh}_3)_2(\text{NSO})_2]$  was isolated as an orange crystalline solid by slow diffusion of Pet/Ether (60/80) into the NMR sample tube and its identity confirmed by microanalysis (Found C 50.13, H 3.48, N

3.55; Calc. C 51.23, H 3.55, N 3.32). All attempts to crystallise the novel phosphine complex failed.

### 3.3.3 Reaction of $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6]$ with $(t\text{-BuNSN})_2\text{S}$

Solid 3 (19 mg, 0.07 mmol) was added to a solution of  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6]$  (50 mg, 0.03 mmol) in  $\text{CH}_2\text{Cl}_2$  (50 ml). The resulting solution was stirred for 3 h. Removal of the solvent *in vacuo* led to an orange solid.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) spectroscopy revealed the presence of unreacted 3 ( $\delta$  1.43 ppm) and an unknown compound ( $\delta$  1.51 ppm). All attempts to crystallise the unknown compound failed.

The dimer  $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_6]$  did not react with compound 3 as shown by  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ) spectroscopy.



## CHAPTER 4. CHEMISTRY OF $\text{Se}(\text{NSO})_2$

### 4.1 Introduction

Undoubtedly, one of the main problems associated with the preparation of new Se-N compounds has been the lack of suitable stable precursors that can be prepared in good yields. For example, preparations of Se-N compounds have often been limited to reactions involving the use of the explosive  $\text{Se}_4\text{N}_4$ .

The last five years have, however, witnessed the synthesis of potentially important new selenium reagents such as  $\text{Se}(\text{NSO})_2$  and  $\text{Se}[\text{N}(\text{SiMe}_3)_2]_2$ .<sup>40,41</sup> Both are obtained by routes using  $\text{Se}_2\text{Cl}_2$  as the selenium source; the former by reaction with  $\text{Me}_3\text{SiNSO}$ , the latter by using  $\text{Li}[\text{N}(\text{SiMe}_3)_2]$  (Fig. 4.1).

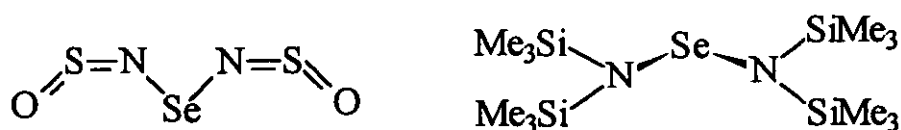


Figure 4.1 The structures of  $\text{Se}(\text{NSO})_2$  and  $\text{Se}[\text{N}(\text{SiMe}_3)_2]_2$

The presence of  $\text{SiMe}_3$  groups bonded to the nitrogen atoms in  $\text{Se}[\text{N}(\text{SiMe}_3)_2]_2$  should allow this compound to act as a source of the  $\text{NSeN}$  fragment by simple substitution reactions. The versatility of this reagent for the preparation of Se-N compounds has been studied (Fig. 4.2).<sup>42</sup>

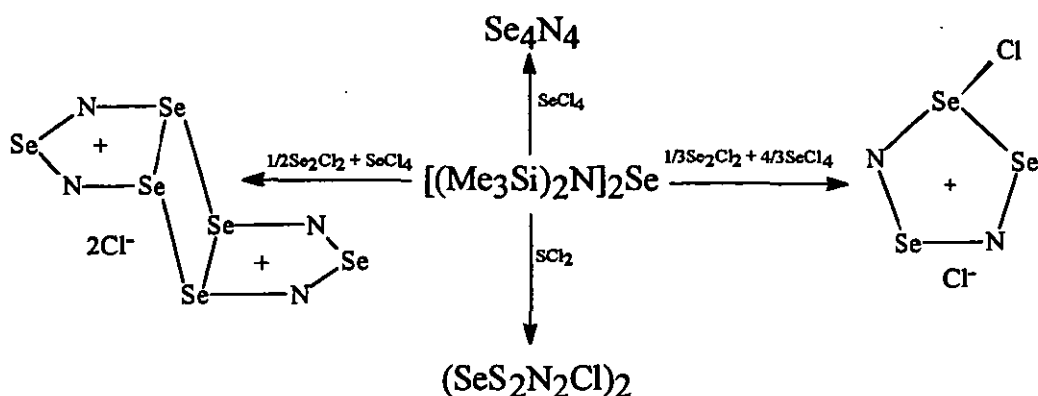


Figure 4.2 Use of  $\text{Se}[\text{N}(\text{SiMe}_3)_2]_2$  as a reagent for the preparation of Se-N compounds

The compound  $\text{Se}(\text{NSO})_2$  has also been the subject of intensive study.<sup>40</sup> It reacts with  $\text{AsF}_5$  in a 1:1 molar ratio to afford salts of the dimeric cation  $[(\text{SSe}_2\text{N}_2)_2]^{2+}$ ; if an excess of  $\text{AsF}_5$  is used then the stable dication  $[\text{Se}_2\text{N}_2\text{S}]^{2+}$  is formed. Reaction of  $\text{Se}(\text{NSO})_2$  with  $\text{SbCl}_5$  generates the chlorinated five-membered ring  $[\text{ClSe}_2\text{N}_2\text{S}]^+$  whilst the covalent dichloro compound  $\text{Cl}_2\text{Se}_2\text{N}_2\text{S}$  results when  $\text{POCl}_3$  is used instead (Fig. 4.3).

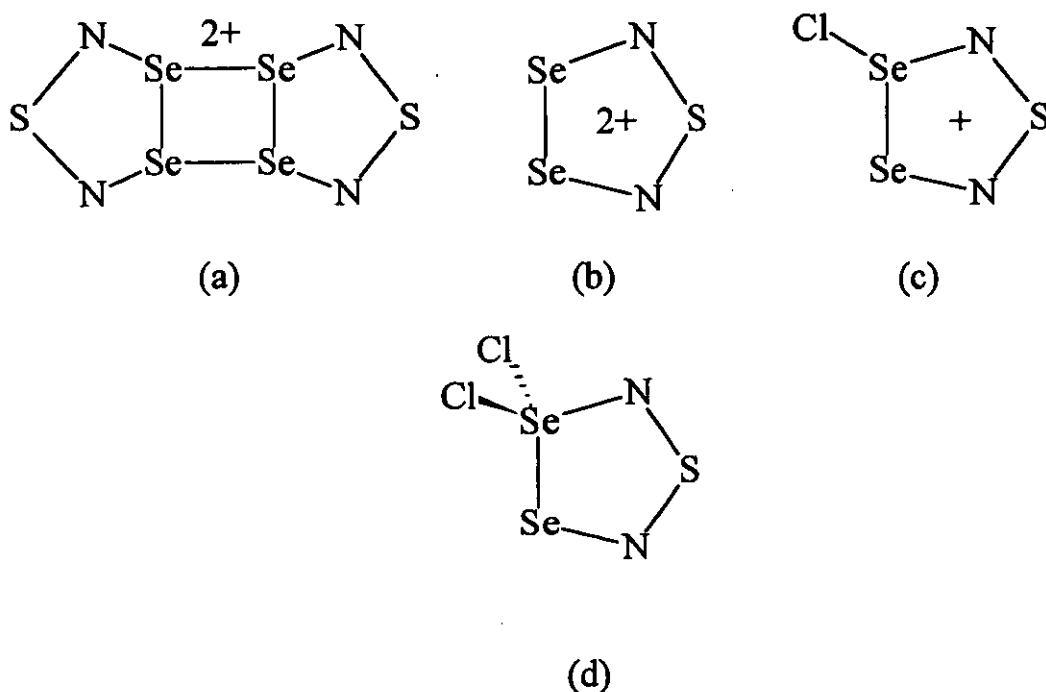


Figure 4.3 Structures of (a)  $[(\text{SSe}_2\text{N}_2)_2]^{2+}$ , (b)  $[\text{Se}_2\text{N}_2\text{S}]^{2+}$ , (c)  $[\text{ClSe}_2\text{N}_2\text{S}]^+$  and (d)  $\text{Cl}_2\text{Se}_2\text{N}_2\text{S}$

Another important facet of the chemistry of  $\text{Se}(\text{NSO})_2$  is its ability to undergo facile loss of  $\text{SO}_2$  making it a potent source of the  $\text{SSeN}_2$  moiety. Haas *et al.* reported the isolation of the adduct  $\text{SeSN}_2\cdot\text{TiCl}_4$ <sup>40</sup> when  $\text{Se}(\text{NSO})_2$  reacts with  $\text{TiCl}_4$  (Fig. 4.4).

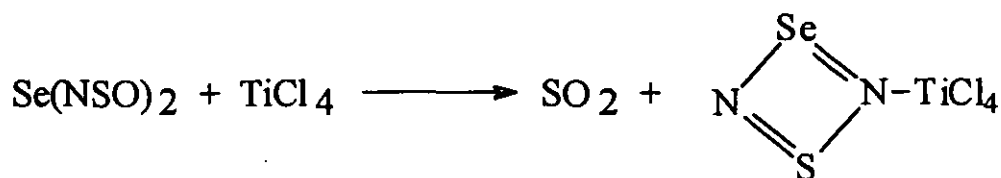


Figure 4.4 Products of the reaction of  $\text{Se(NSO)}_2$  with  $\text{TiCl}_4$

This result suggests that there is great scope for  $\text{Se(NSO)}_2$  to give rise to novel sulphur-selenium-nitrogen metal complexes. In this chapter we have undertaken a preliminary study of the reactivity of  $\text{Se(NSO)}_2$  with a range of metal centres.

## 4.2 Results and Discussion

### 4.2.1 Introduction

The use of  $\text{S(NSO)}_2$  as a source of the  $\text{S}_2\text{N}_2$  unit in the form of the  $(\text{S}_2\text{N}_2)^{2-}$  ligand, as part of a cyclometallathiazene, or as neutral  $\text{S}_2\text{N}_2$  adduct has been reported (Fig. 4.5).<sup>43, 44</sup>

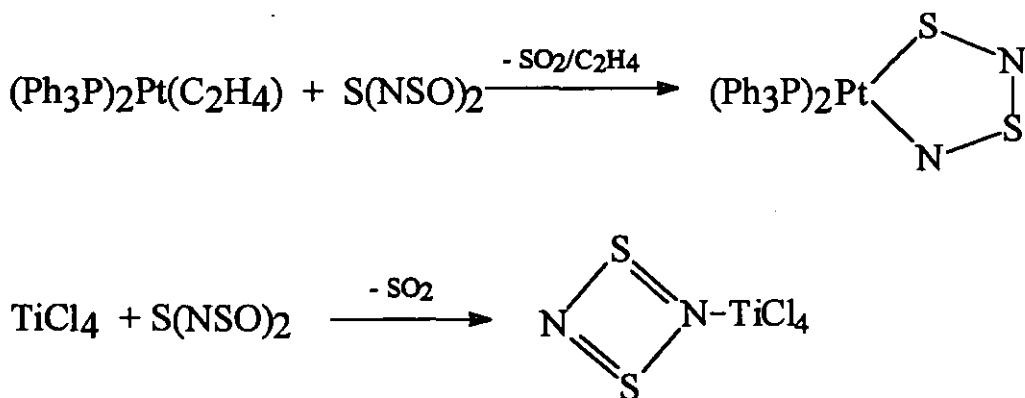


Figure 4.5 The use of  $\text{S(NSO)}_2$  as a source of the  $\text{S}_2\text{N}_2$  unit

The ability of  $\text{S(NSO)}_2$  to act as a precursor to the above sulphur-nitrogen-metal species prompted us to undertake a comparison of the reactivity of  $\text{Se(NSO)}_2$  with that of its S analogue. Specifically, we hoped that by analogy with the above  $\text{Pt}(0)$  reaction,  $\text{Se(NSO)}_2$  could act as source of complexes containing the  $(\text{SSeN}_2)^{2-}$  ligand.<sup>45</sup> Unlike the other known examples of such complexes, all of which show metal-Se bonding, the disposition of the Se atom in  $\text{Se(NSO)}_2$  suggests that such a reaction

could be expected to generate the first example of the ligand  $(\text{SSeN}_2)^{2-}$  linked to the metal through the S and N atoms (Fig. 4.6).

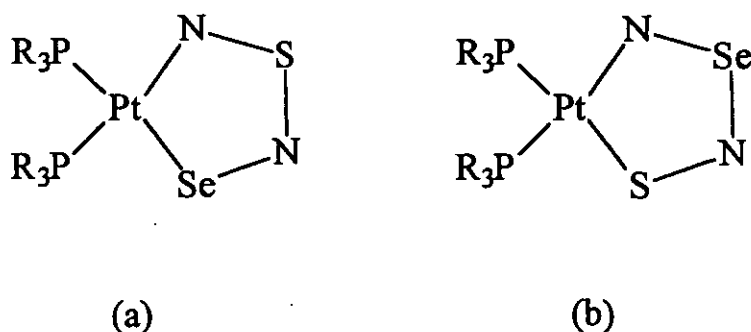


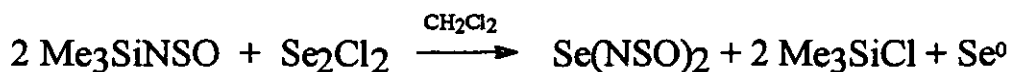
Figure 4.6 Structures of (a) a known complex containing the  $(\text{SSeN}_2)^{2-}$  ligand and (b) target complex

In addition, we have studied the chemical behaviour of  $\text{Se}(\text{NSO})_2$  in its reactions with  $[\text{PPh}_4]_2[\text{Pd}_2\text{X}_6]$  ( $\text{X}=\text{Cl}$  or  $\text{Br}$ ).

#### 4.2.2 Preparation of $\text{Se}(\text{NSO})_2$

Bis(sulfonylamido) selenium may be prepared from  $\text{Se}_2\text{Cl}_2$  and  $\text{Me}_3\text{SiNSO}$  according to Equation 4.1.<sup>40</sup>

Equation 4.1



As can be seen from Equation 4.1,  $\text{Se}_2\text{Cl}_2$  reacts effectively as  $\text{SeCl}_2$ . This is not surprising as there is evidence from  $^{77}\text{Se}$  NMR and Raman studies that  $\text{Se}_2\text{Cl}_2$  is in equilibrium with  $\text{SeCl}_2$  and  $\text{Se}_n\text{Cl}_2$  ( $n>2$ ), indicating relatively labile  $\text{Se}-\text{Cl}$  bonds for these species in solution.<sup>46</sup>

The purification of the crude material involves sublimation of  $\text{Se}(\text{NSO})_2$  onto a cold finger. The sublimation vessel must not be warmed up since, if this occurs, a substance of unknown nature sublimes instead of  $\text{Se}(\text{NSO})_2$ . This substance

decomposes, it passes from yellow to red colour, when the temperature of the cold finger rises after removing the dry ice/acetone mixture.

The preparation reported in literature does not give any detail about how long the sublimation must be held for. Our yield recorded (7%), after sublimating the crude solid for 5 h, is much lower than that given in the literature (69%). The yield could be improved by sublimating the crude for longer than 5 h. In fact, a second crop of  $\text{Se(NSO)}_2$  (yield 9%) can be obtained from the residues left in the vessel once the first crop is collected (see Experimental Section).

#### 4.2.3 Reactions of $\text{S(NSO)}_2$ and $\text{Se(NSO)}_2$ with $[\text{Pt}(\text{PPh}_3)_3]$

A yellow solid may be isolated from the reaction of  $\text{S(NSO)}_2$  with  $[\text{Pt}(\text{PPh}_3)_3]$  in toluene. The  $^{31}\text{P}$  NMR spectrum of this solid reveals the presence of four major chemical species (Fig. 4.7).

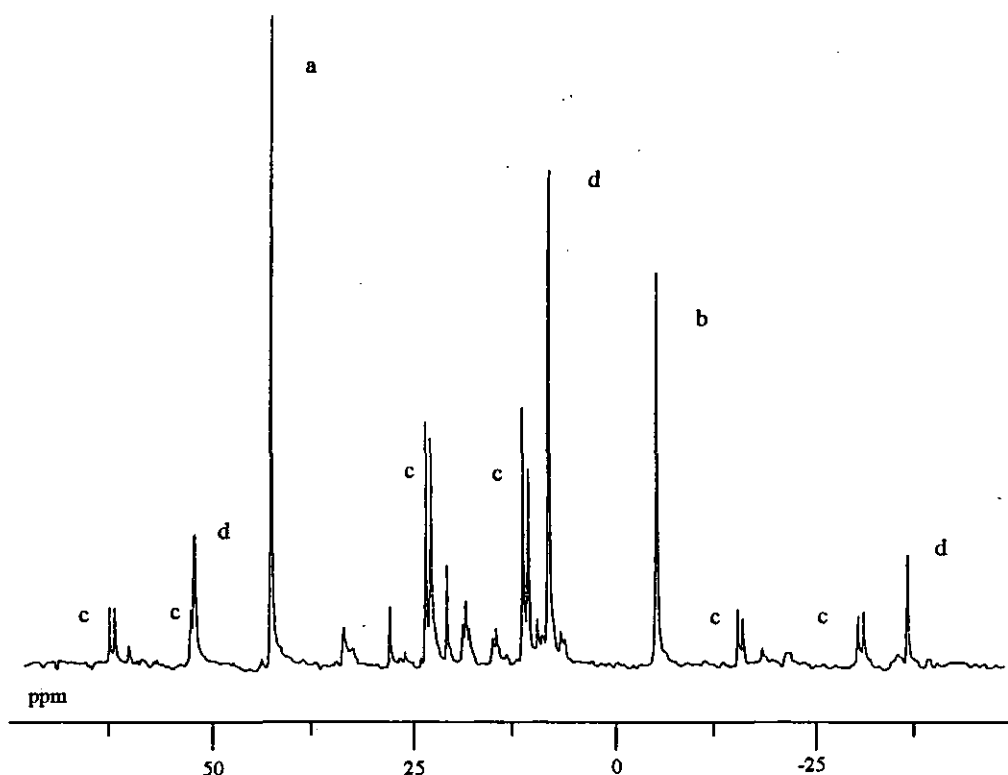


Figure 4.7  $^{31}\text{P}$  NMR spectrum of the crude material obtained when reacting  $\text{S(NSO)}_2$  with  $[\text{Pt}(\text{PPh}_3)_3]$ . The labels a, b, c and d indicate  $\text{P(S)Ph}_3$ ,  $\text{PPh}_3$ ,  $[\text{Pt}(\text{S}_2\text{N}_2)(\text{PPh}_3)_2]$  and  $\text{cis-}[\text{Pt(NSO)}_2(\text{PPh}_3)_2]$  respectively

Apart from  $\text{P(S)Ph}_3$  and free  $\text{PPh}_3$ , the spectrum consists of a pair of doublets with associated  $^{195}\text{Pt}$  satellites assigned to  $[\text{Pt}(\text{S}_2\text{N}_2)(\text{PPh}_3)_2]$  and a singlet flanked by its respective  $^{195}\text{Pt}$  satellites due to *cis*- $[\text{Pt}(\text{NSO})_2(\text{PPh}_3)_2]$  (Fig. 4.8).

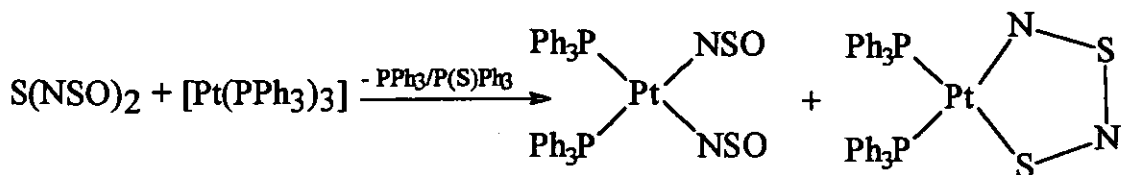


Figure 4.8 Products of the reaction of  $\text{S(NSO)}_2$  with  $[\text{Pt}(\text{PPh}_3)_3]$

*T. Chivers et al.* report that reaction between  $\text{S(NSO)}_2$  and  $[\text{Pt}(\text{PPh}_3)_2\text{C}_2\text{H}_4]$  leads to the formation of  $[\text{Pt}(\text{S}_2\text{N}_2)(\text{PPh}_3)_2]$ . They note that an “impurity” of unknown nature is also formed.<sup>43</sup> The observation that  $[\text{Pt}(\text{S}_2\text{N}_2)(\text{PPh}_3)_2]$  and  $[\text{Pt}(\text{NSO})_2(\text{PPh}_3)_2]$  are the complexes formed by reacting  $\text{S(NSO)}_2$  with  $[\text{Pt}(\text{PPh}_3)_3]$  suggests that the “impurity” mentioned by *T. Chivers et al.* is actually the same bis-thionylimino complex noted above. Therefore, both Pt(0) reagents react similarly with  $\text{S(NSO)}_2$ .

Figure 4.10 shows the  $^{31}\text{P}$  NMR spectrum of the crude product of the reaction between  $\text{Se(NSO)}_2$  and  $[\text{Pt}(\text{PPh}_3)_3]$ . A striking feature of this spectrum, particularly when compare to Figure 4.7, is its simplicity. Two major species are present:  $\text{P(Se)Ph}_3$  and *cis*- $[\text{Pt}(\text{NSO})_2(\text{PPh}_3)_2]$  (Fig. 4.9).

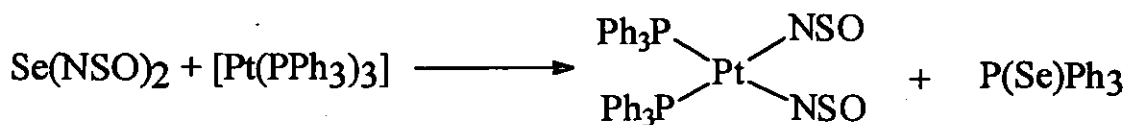


Figure 4.9 Products of the reaction of  $\text{Se(NSO)}_2$  with  $[\text{Pt}(\text{PPh}_3)_3]$

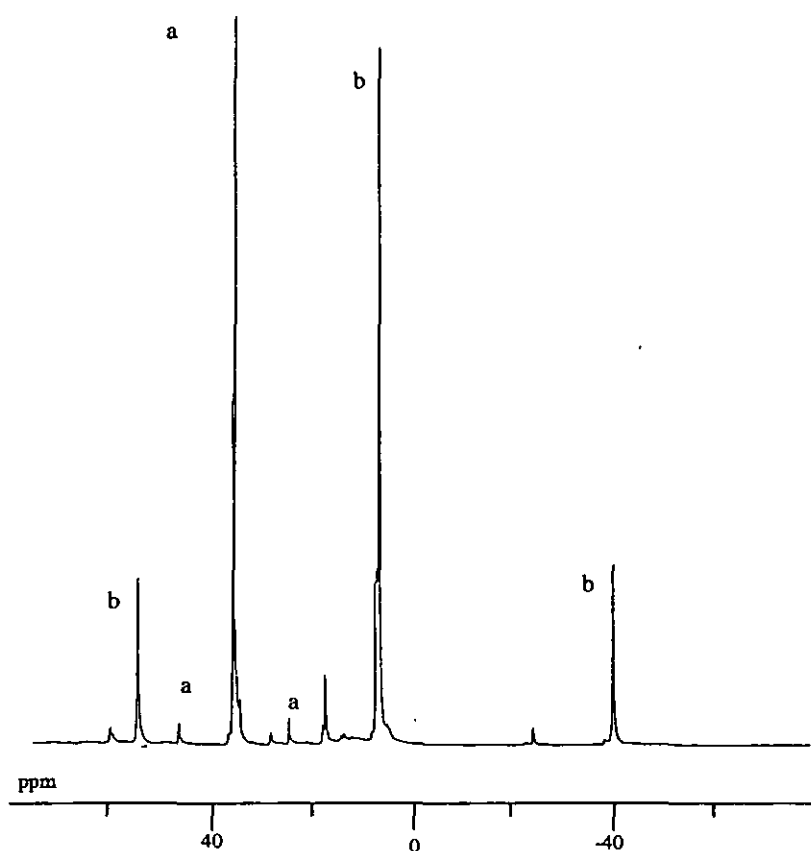


Figure 4.10  $^{31}\text{P}$  NMR spectrum of the crude material obtained when reacting  $\text{Se}(\text{NSO})_2$  with  $[\text{Pt}(\text{PPh}_3)_3]$ . The labels *a* and *b* indicate  $\text{P}(\text{Se})\text{Ph}_3$  and *cis*- $[\text{Pt}(\text{NSO})_2(\text{PPh}_3)_2]$  respectively

An approximation of the bonding arrangements in the acyclic S-N oxide  $\text{S}(\text{NSO})_2$  and in  $\text{MS}_2\text{N}_2$  rings is shown in Figure 4.11. It must be noted that in Figure 4.11, the bonding arrangement shown for  $\text{S}(\text{NSO})_2$  is probably an accurate reflection of the electron density. However, the position of “double bonds” in  $\text{M}(\text{N}_2\text{S}_2)$  mainly reflects the difference in bond lengths present.

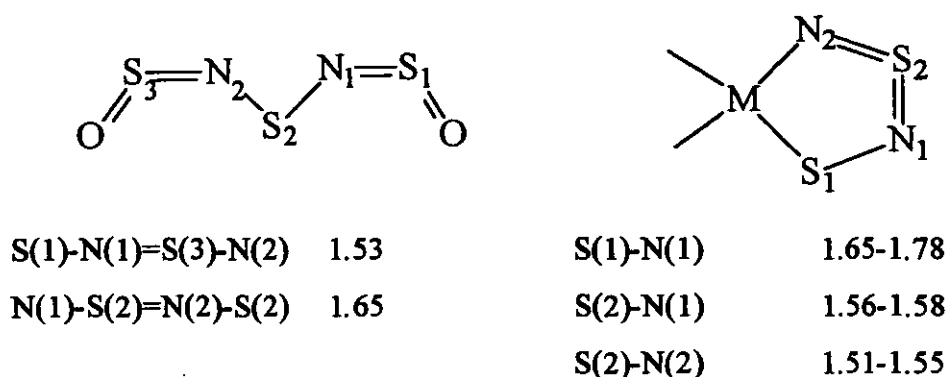


Figure 4.11 Bonding arrangement and bond lengths<sup>9</sup> (Å) in  $S(NSO)_2$  and  $M(N_2S_2)$

According to the position of the “double bonds” in Figure 4.11, if the attachment of the  $S_2N_2^{2-}$  unit to the metal when  $S(NSO)_2$  reacts with  $[Pt(PPh_3)_3]$  proceeds through the loss of  $SO_2$ , without cleavage in the SNSN chain, a rearrangement of the electron density within the chain must occur.

If  $Se(NSO)_2$  followed the above route in its reaction with  $[Pt(PPh_3)_3]$  the Se atom should pass from Se(II) to Se(IV), with double bonds to nitrogen. This is unlikely to happen since it is known that compounds in which Se is bonded to two N through double bonds are rare and unstable. Such a compound is  $Me_3Si-N=Se=N-SiMe_3$  which is extremely air sensitive and only stable below  $-48\text{ }^\circ\text{C}$ .<sup>47</sup> This observation may account for the lack of formation of the expected  $(SSeN_2)^{2-}$ .

#### 4.2.4 Reaction of $Se(NSO)_2$ with $[PPh_4]_2[Pd_2X_6]$ (X=Br or Cl)

Treatment of  $S(NSO)_2$  with  $[PPh_4]_2[Pd_2Cl_6]$  results in the formation of  $[PPh_4]_2[Pd_2Cl_6(S_2N_2)]$  which may be crystallised from the reaction mixture and characterised by IR. Although this reaction is not efficient compared to the other known routes,<sup>12</sup> it does show that there is, in principle, a route to the insertion of a neutral  $SeSN_2$  moiety by simply using  $Se(NSO)_2$  instead of  $S(NSO)_2$ .

If  $Se(NSO)_2$  and  $[PPh_4]_2[Pd_2Br_6]$ , in a molar ratio of 1:1, are stirred together in  $CH_2Cl_2$  for 24 h and the concentrated solution layered with  $Et_2O$ , sawtoothed edge red crystals are obtained together with considerable amounts of unreacted  $[PPh_4]_2[Pd_2Br_6]$ ,



the identity of the latter is confirmed by microanalysis. X-ray and microanalysis (C, H, N, S\*) performed on the red crystals reveal them to be the novel species  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6(\text{Se}_2\text{N}_2)]$  (Fig. 4.12, Table 4.1.a and 4.1.b). This compound is the bromo analogous to the recently prepared  $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_6(\text{Se}_2\text{N}_2)]$ .<sup>48</sup> Thus  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6(\text{Se}_2\text{N}_2)]$  is the second example reported of a complex containing a bidentate neutral  $\text{Se}_2\text{N}_2$  unit.

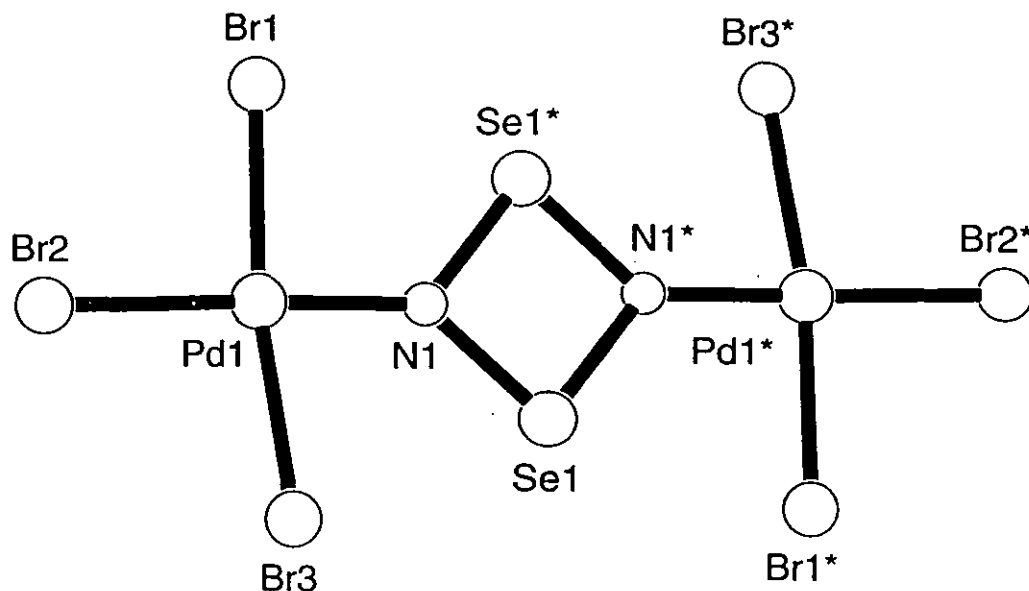


Figure 4.12 X-ray structure of the anion in  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6(\text{Se}_2\text{N}_2)]$

Pd-Br(1)	2.422(2)	Pd-Br(2)	2.393(2)
Pd-Br(3)	2.430(2)	Pd-N(1)	1.871(9)
N(1)-Se(1)	1.819(8)	N(1)-Se*(1)	1.916(10)
Non-bonded distances:			
Br(1)-Se*(1)	3.13	Br(3)-Se(1)	3.17
Se(1)-Se*(1)	2.73	N(1)-N*(1)	2.55

Table 4.1.a Selected bond lengths (Å) for  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6(\text{Se}_2\text{N}_2)]$

\* Sulphur microanalysis gave an observed value of 0 % which is consistent with the proposed structure of the anion

Br(1)-Pd-Br(2)	94.03(7)	Br(1)-Pd-Br(3)	171.31(8)
Br(2)-Pd-Br(3)	94.17(7)	Br(1)-Pd-N(1)	87.6(3)
Br(3)-Pd-N(1)	84.3(3)	Pd-N(1)-Se(1)	136.3(5)
Pd-N(1)-Se <sup>*</sup> (1)	129.2(4)	Se(1)-N(1)-Se <sup>*</sup> (1)	94.0(4)
N(1)-Se(1)-N <sup>*</sup> (1)	86.0(4)		

Table 4.1.b *Selected angles (°) for [PPh<sub>4</sub>]<sub>2</sub>[Pd<sub>2</sub>Br<sub>6</sub>(Se<sub>2</sub>N<sub>2</sub>)]*

The X-ray structure of [PPh<sub>4</sub>]<sub>2</sub>[Pd<sub>2</sub>Br<sub>6</sub>(Se<sub>2</sub>N<sub>2</sub>)] shows a neutral Se<sub>2</sub>N<sub>2</sub> unit which is co-ordinated *via* both nitrogen, in a centrosymmetric arrangement, to PdCl<sub>3</sub><sup>-</sup> units. The anion is virtually planar with the maximum deviation from planarity for Br(2) of 0.08 Å. The Pd-Br distances are in the range 2.393(2)-2.430(2) Å, the shortest being for Pd-Br *trans* to nitrogen. The Pd-Br(1) and Pd-Br(3) bonds are both bent towards the selenium atoms of the Se<sub>2</sub>N<sub>2</sub> ring, which is indicative of an electrostatic interaction between Se and Br. This effect has been noted many times for S<sub>2</sub>N<sub>2</sub> adducts.<sup>49</sup> However, unlike for S<sub>2</sub>N<sub>2</sub> adducts, the Br(1)-Pd-N(1) and Br(3)-Pd-N(1) angles are not equivalent, the latter angle is reduced with respect to the former.

The average Se-N bond length is 1.86 Å, which is longer than that in Se<sub>4</sub>N<sub>4</sub> (1.78 Å).<sup>50</sup> These bond lengths in [PPh<sub>4</sub>]<sub>2</sub>[Pd<sub>2</sub>Br<sub>6</sub>(Se<sub>2</sub>N<sub>2</sub>)] are not equivalent, reflecting a slight degree of asymmetry exhibited by the molecule as a whole. It appears that the different degree of interaction between Br(1)-Se<sup>\*</sup>(1) and Br(3)-Se(1), manifested in the unequal angles Br(1)-Pd-N(1) and Br(3)-Pd-N(1), produces the difference in the N(1)-Se<sup>\*</sup>(1) and N(1)-Se(1) distances. This asymmetry in the Se<sub>2</sub>N<sub>2</sub> ring also occurs in [PdCl<sub>6</sub>(Se<sub>2</sub>N<sub>2</sub>)]<sup>2-</sup> and it is in sharp contrast to the homogeneity of the S-N bonds in S<sub>2</sub>N<sub>2</sub> adducts.

A short interanion contact, Cl(3)-Cl<sup>\*</sup>(3), in the packing arrangement of [PPh<sub>4</sub>]<sub>2</sub>[Pd<sub>2</sub>Cl<sub>6</sub>(Se<sub>2</sub>N<sub>2</sub>)] was suggested as the source of asymmetry in the anion.<sup>48</sup> However, a view of the packing arrangement of [PPh<sub>4</sub>]<sub>2</sub>[Pd<sub>2</sub>Br<sub>6</sub>(Se<sub>2</sub>N<sub>2</sub>)] does not reveal any interaction between neighbouring anions. Thus, it seems that the asymmetry

in the  $\text{Se}_2\text{N}_2$  unit, in both adducts, is intrinsic to its nature and does not arise because of a particular disposition of the anions in the crystal packing.

The loss of symmetry when passing from  $\text{S}_2\text{N}_2$  to  $\text{Se}_2\text{N}_2$  adducts may be a trend for heavy chalcogens (Se and Te). An example of such an effect for a compound containing a  $\text{Te}_2\text{N}_2$  ring can be found in  $\text{Te}_4\text{N}_2\text{Cl}_8 \cdot (\text{AsF}_6)_2 \cdot 2\text{SO}_2$  (Fig. 4.13).<sup>51</sup>

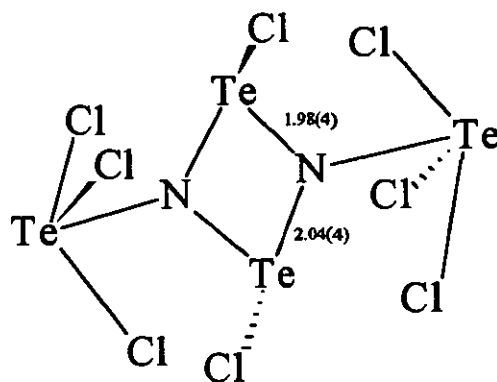


Figure 4.13 Structure of the cation  $\text{Te}_4\text{N}_2\text{Cl}_8^{2+}$ . Bond distances are in (Å)

If the reaction between  $\text{Se}(\text{NSO})_2$  and  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6]$  is carried out with a large excess of the former then all the solid collected, crystalline or semicrystalline analyses as  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6(\text{Se}_2\text{N}_2)]$ . The fact that a large excess of  $\text{Se}(\text{NSO})_2$  is needed to force the formation of  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6(\text{Se}_2\text{N}_2)]$  clearly shows that the reaction is not straightforward.

The compound we aimed to prepare, by reacting  $\text{Se}(\text{NSO})_2$  with  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6]$ , was actually  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6(\text{SeSN}_2)]$ . However, its formation even as an intermediate is unlikely. It would have not reacted further to give the observed species,  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6(\text{Se}_2\text{N}_2)]$ .

Reaction of  $\text{Se}(\text{NSO})_2$  with  $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_6]$  (molar ratio 1:1 or 2:1), following the procedure outlined above, does not give rise to crystals amenable to X-ray analysis. Microanalysis (C, H and N) performed on the solid collected shows an appreciable amount of nitrogen. However, this N content does not match with either the values calculated for  $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_6(\text{Se}_2\text{N}_2)]$  or  $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_6(\text{SeSN}_2)]$ . This result could

indicate that the solid collected contains some unreacted  $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_6]$  or that the product is actually not an expected compound.

The preparation and characterisation of  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6(\text{Se}_2\text{N}_2)]$  and  $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_6(\text{Se}_2\text{N}_2)]$  give definitive evidence of the existence of  $\text{Se}_2\text{N}_2$ , although in the form of a palladium adduct. Before the synthesis of these two adducts,  $\text{Se}_2\text{N}_2$  had only been detected, by mass spectroscopy, in the vapor phase of pyrolysed  $\text{Se}_4\text{N}_4$ . The interest in the two new  $\text{Se}_2\text{N}_2$  adducts lies in that they could be used to give rise to free  $\text{Se}_2\text{N}_2$  which then could polymerise to produce  $(\text{SeN})_x$ . It must be borne in mind that all attempts to prepare  $(\text{SeN})_x$  by similar methods to those used to build  $(\text{SN})_x$  chains have failed.<sup>52</sup>

The preparation reported for  $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_6(\text{Se}_2\text{N}_2)]$  involves the use of highly explosive  $\text{Se}_4\text{N}_4$ . However, the route to  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6(\text{Se}_2\text{N}_2)]$  makes use of  $\text{Se}(\text{NSO})_2$  which is a far safer reagent than  $\text{Se}_4\text{N}_4$ , although air sensitive.

#### 4.2.4.1 Infrared Study of $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6(\text{Se}_2\text{N}_2)]$

One disadvantage of the presence of  $[\text{PPh}_4]^+$  in  $[\text{PPh}_4]_2[\text{Pd}_2\text{X}_6(\text{Se}_2\text{N}_2)]$  ( $\text{X}=\text{Cl}$  or  $\text{Br}$ ) is that it has a number of very strong bands in the IR spectrum and thus obscures important features of the spectrum of the anion, in particular Se-N vibrations. This problem can be avoided by using a cation such as  $[\text{nBu}_4\text{N}]^+$  which gives rise to fewer bands than  $[\text{PPh}_4]^+$ .

The band at  $777\text{ cm}^{-1}$ , assigned to a Se-N vibration, in the IR spectrum of  $[\text{nBu}_4\text{N}]_2[\text{Pd}_2\text{Cl}_6(\text{Se}_2\text{N}_2)]$  is masked by strong cation vibrations in  $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_6(\text{Se}_2\text{N}_2)]$ . A metal-halogen stretch at  $334\text{ cm}^{-1}$  is observed in the IR spectra of both compounds

The preparation of the salt  $[\text{nBu}_4\text{N}]_2[\text{Pd}_2\text{Br}_6(\text{Se}_2\text{N}_2)]$  could not be achieved. Despite of this, a study of the lowest part of the IR spectrum ( $500\text{--}250\text{ cm}^{-1}$ , using CsI disks) of  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6(\text{Se}_2\text{N}_2)]$  permits us to draw some conclusions. Thus two bands of similar intensity at  $313$  and  $259\text{ cm}^{-1}$  attributable to Pd-Br vibrations are

observed. These two values can be used to discriminate between  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6(\text{Se}_2\text{N}_2)]$  and unreacted  $[\text{PPh}_4]_2[\text{Pd}_2\text{Br}_6]$ , since the latter only gives rise to one band at  $256\text{ cm}^{-1}$ .

### 4.3 Experimental

All reactions involving the use of the air-sensitive  $\text{Se}(\text{NSO})_2$  were carried out in a glove-box.

#### 4.3.1 Preparation of Starting Materials

The palladium dimers  $[\text{PPh}_4]_2[\text{Pd}_2\text{X}_6]$  ( $\text{X}=\text{Cl}, \text{Br}$ ) were prepared as described in Chapter 2.

##### 4.3.1.1 Preparation of $\text{Se}(\text{NSO})_2$

A solution of  $\text{Me}_3\text{SiNSO}$  (3.07 g, 22.80 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 ml) was added *via* cannula to a stirred solution of  $\text{Se}_2\text{Cl}_2$  (2.61 g, 11.40 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 ml) to give a purple solution and a dark precipitate. After 24 h the black crude material left after removing the solvent *in vacuo*, was placed in a sublimation vessel fixed with a cold finger (dry ice/acetone). The compound  $\text{Se}(\text{NSO})_2$  sublimated onto the cold finger as a yellow film together with  $\text{Se}^0$  (0.1 mbar for 5 h; vessel immersed in a water bath). At this stage the sublimation apparatus, being still under vacuum, was transferred into a glove-box. The  $\text{Se}(\text{NSO})_2$  was washed off with  $\text{CH}_2\text{Cl}_2$  and the yellow solution placed on a watch-glass. As  $\text{CH}_2\text{Cl}_2$  evaporates off yellow crystals of  $\text{Se}(\text{NSO})_2$  were formed. A second crop of  $\text{Se}(\text{NSO})_2$  was obtained by reassembling the apparatus and following the method described above. The total amount collected of  $\text{Se}(\text{NSO})_2$  was 375 mg (yield 16%). IR and melting point measurements were in accord with literature values.<sup>40</sup>

##### 4.3.2 Reaction of $[\text{Pt}(\text{PPh}_3)_3]$ with $\text{S}(\text{NSO})_2$

The compound  $\text{S}(\text{NSO})_2$  (14 mg, 0.09 mmol) was added with stirring to a solution of  $[\text{Pt}(\text{PPh}_3)_3]$  (90 mg, 0.09 mmol) in toluene (60 ml). The reaction mixture was stirred overnight. Solvent was removed from the reaction mixture under vacuum to give a yellow solid.  $^{31}\text{P}$  NMR (in  $\text{CDCl}_3$ ) measurements revealed the presence of

*cis*-[Pt(NSO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]<sup>39</sup> (δ 8.8 ppm; <sup>1</sup>J(<sup>195</sup>Pt-<sup>31</sup>P) 3190 Hz), [Pt(S<sub>2</sub>N<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>]<sup>14</sup> (δ<sub>A</sub> 11.5 ppm, δ<sub>X</sub> 24.1 ppm; <sup>1</sup>J<sub>A</sub>(<sup>195</sup>Pt-<sup>31</sup>P<sub>A</sub>) 2995 Hz, <sup>1</sup>J<sub>X</sub>(<sup>195</sup>Pt-<sup>31</sup>P<sub>X</sub>) 2825 Hz) together with P(S)Ph<sub>3</sub> and PPh<sub>3</sub>.

#### 4.3.3 Reaction of [Pt(PPh<sub>3</sub>)<sub>3</sub>] with Se(NSO)<sub>2</sub>

The compound Se(NSO)<sub>2</sub> (15 mg, 0.07 mmol) was added with stirring to a solution of [Pt(PPh<sub>3</sub>)<sub>3</sub>] (72 mg, 0.07 mmol) in toluene (60 ml) to give a suspension. The suspension was stirred overnight. Solvent was removed from the reaction mixture under vacuum to give a yellow solid. <sup>31</sup>P NMR (in CDCl<sub>3</sub>) measurements revealed the presence of *cis*-[Pt(NSO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]<sup>39</sup> (δ 8.8 ppm; <sup>1</sup>J(<sup>195</sup>Pt-<sup>31</sup>P) 3190 Hz), and P(Se)Ph<sub>3</sub> (δ 35.38 ppm; <sup>1</sup>J(<sup>77</sup>Se-<sup>31</sup>P) 730 Hz). The crude solid was dissolved in CDCl<sub>3</sub> (1 ml) and layered with Et<sub>2</sub>O to give yellow crystals of *cis*-[Pt(NSO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]-CDCl<sub>3</sub> (Found C 47.73, H 3.01, N 3.07; Calc. C 46.08, H 3.11, N 2.90).

#### 4.3.4 Reaction of Se(NSO)<sub>2</sub> with [PPh<sub>4</sub>]<sub>2</sub>[Pd<sub>2</sub>Br<sub>6</sub>]

Solid Se(NSO)<sub>2</sub> (35 mg, 0.17 mmol) was added to a solution of [PPh<sub>4</sub>]<sub>2</sub>[Pd<sub>2</sub>Br<sub>6</sub>] (36 mg, 0.02 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 ml) and the mixture stirred overnight. The solution was reduced in volume to 2 ml and layered with Et<sub>2</sub>O. After 48 h, sawtoothed edge red crystals (*ca.* 2 mg) were formed together with a non crystalline solid (13 mg). X-ray crystallography and microanalysis revealed the red crystals to be [PPh<sub>4</sub>]<sub>2</sub>[Pd<sub>2</sub>Br<sub>6</sub>(Se<sub>2</sub>N<sub>2</sub>)] (Found C 36.62, H 2.19, N 1.74, S 0.00; Calc. for [PPh<sub>4</sub>]<sub>2</sub>[Pd<sub>2</sub>Br<sub>6</sub>(Se<sub>2</sub>N<sub>2</sub>)]-CH<sub>2</sub>Cl<sub>2</sub>, C 35.83, H 2.55, N 1.70, S 0.00); the negative ion FAB spectrum revealed a group of peaks centred on *m/z* 534 due to [PdBr<sub>3</sub>(Se<sub>2</sub>N<sub>2</sub>)H]<sup>-</sup>. The non crystalline solid also resulted to be [PPh<sub>4</sub>]<sub>2</sub>[Pd<sub>2</sub>Br<sub>6</sub>(Se<sub>2</sub>N<sub>2</sub>)] as confirmed by microanalysis. Total yield 15 mg, 37 % based upon Pd.

When the reaction was performed in a 1:1 or 2:1 ratio (Se(NSO)<sub>2</sub>: [PPh<sub>4</sub>]<sub>2</sub>[Pd<sub>2</sub>Br<sub>6</sub>]) most of the [PPh<sub>4</sub>]<sub>2</sub>[Pd<sub>2</sub>Br<sub>6</sub>] remained unreacted as shown by microanalysis.

#### 4.3.5 Reaction of Se(NSO)<sub>2</sub> with [PPh<sub>4</sub>]<sub>2</sub>[Pd<sub>2</sub>Cl<sub>6</sub>]

Solid Se(NSO)<sub>2</sub> (37 mg, 0.18 mmol) was added to a solution of [PPh<sub>4</sub>]<sub>2</sub>[Pd<sub>2</sub>Cl<sub>6</sub>] (100 mg, 0.09 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 ml) and the mixture stirred

overnight. Slow diffusion of  $\text{Et}_2\text{O}$  into the concentrated crude reaction mixture resulted in the precipitation of a solid whose elemental analysis was C 46.75, H 3.23, N 0.72. The nature of this solid could not be determined.

## APPENDIX - CRYSTAL STRUCTURE DATA

Compound	[PPh <sub>4</sub> ][PdBr <sub>2</sub> (S <sub>2</sub> N <sub>3</sub> )]	[PPh <sub>4</sub> ] <sub>2</sub> [Pd <sub>2</sub> Br <sub>4</sub> (S <sub>3</sub> N <sub>2</sub> )]	[PPh <sub>4</sub> ] <sub>2</sub> [Pd <sub>2</sub> Br <sub>6</sub> (Se <sub>2</sub> N <sub>2</sub> )]
Empirical Formula	C <sub>24</sub> H <sub>20</sub> Br <sub>2</sub> N <sub>3</sub> PPdS <sub>2</sub>	C <sub>48</sub> H <sub>40</sub> Br <sub>4</sub> N <sub>2</sub> P <sub>2</sub> Pd <sub>2</sub> S <sub>3</sub>	C <sub>48</sub> H <sub>40</sub> Br <sub>6</sub> N <sub>2</sub> P <sub>2</sub> Pd <sub>2</sub> Se <sub>2</sub>
Formula Weight	711.74	1359.42	1556.95
Crystal Color, Habit	dark needle	orange needle	red, block
Crystal Dimensions	0.08x0.1x0.3mm	0.09x0.11x0.23 mm	0.10x0.10x0.10 mm
Crystal System	monoclinic	monoclinic	orthorhombic
Space Group	P2 <sub>1</sub> /n	P2 <sub>1</sub> /n	Pbca(#61)
Unit cell Dimensions (Å)	a=13.294(2) b=14.138(2) c=13.972(2)	a=10.445(4) b=12.966(4) c=41.403(4)	a=18.200(7) b=20.653(8) c=13.496(10)
Volume (Å <sup>3</sup> )	2581.4(6)	5593(2)	5072(3)
Z value	4	4	4
D <sub>calc</sub> (g cm <sup>-3</sup> )	1.83	1.61	2.038
μ (Cu-Kα) (cm <sup>-1</sup> )	116.6	103.74	137.67
Radiation	λ=1.54178 Å	λ=1.54178 Å	λ=1.54178 Å
F <sub>000</sub>	1392	2656	2968
Diffractionmeter	Rigaku AFC7S	Rigaku AFC7S	Rigaku AFC7S
2θ <sub>max</sub>	110°	110°	120.1°
No. of Reflections	3405	6354	4231
Corrections	Lorentz-polarization Absorption (trans. factors: 0.65 - 0.99)	Lorentz-polarization Absorption (trans. factors: 0.62 - 1.00)	Lorentz-polarization Absorption (trans. factors: 0.61 - 1.00)



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