Preparation and coordination chemistry of novel derivatised sulfimides

ABSTRACT

PREPARATION AND COORDINATION CHEMISTRY OF NOVEL DERIVATISED SULFIMIDES

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Keywords: Sulfimides, coordination chemistry, hydrogen bonding, palladium, platinum, bidentate ligands.

Treatment of [1,4-(PhS)$_2$C$_6$H$_4$] and [1,2-(PhS)$_2$C$_6$H$_4$] with the appropriate amount of O-mesitylenesulfonylhydroxylamine (MSH) yields the corresponding protonated sulfimides, both of which may be deprotonated with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to give the hydrated free sulfimides [1,4-(PhS{NH$_2$})$_2$C$_6$H$_4$] and [1,2-(PhS{NH$_2$})C$_6$H$_4$PhS]. It would seem that both products display the ability to give two distinct types of material, anhydrous and hydrated forms. The hydrated type [1,4-(PhS{NH$_2$})$_2$C$_6$H$_4$].2H$_2$O has been found by crystallography to form an extended array system; whereas the crystal structure of the dehydrate exhibits extra structural "rigidity" brought about by having two hydrogen–bonded sulfimide units per molecule. The ligand [1,2-(PhS{NH$_2$})C$_6$H$_4$PhS] also exhibits two distinct types of formation, one a dehydrate (exhibited as an oil) and the other a hydrated type (present as a crystalline solid).

Coordination chemistry was successfully attempted using, in the first instance the *bis*-sulfimide [1,4-(PhS{NH$_2$})$_2$C$_6$H$_4$] and reacting it with [Pd$_2$Br$_6$][PPh$_4$]$_2$ to give [Br$_2$PdN(H)S(Ph)C$_6$H$_4$S(Ph)N(H)]$_2$. X-ray crystallography reveals an interesting structural arrangement where, within a cyclic structure, the ligand acts as a bridge between two palladium atoms. The full potential of the ligand [1,2-(PhS{NH$_2$})C$_6$H$_4$PhS] is observed in its reaction with [Pd(PhCN)$_2$Cl$_2$] to give [Pd(PhSC$_6$H$_4$S(Ph)SPh(NH)Cl$_2$] - the first example of a bidentate sulfimide ligand. In contrast [Pt(MeCN)$_2$Cl$_2$] reacts with [1,2-(PhS{NH$_2$})C$_6$H$_4$PhS] to give the five membered metallocycle [Pt(PhSC$_6$H$_4$S(Ph)NC(Me)NH)Cl$_2$] - an example of a metal-activated organonitrile complex.

For my Mum and Dad

'We are all in the gutter, but some of us are looking at the stars'

Oscar Wilde, Lady Windermere's Fan, 1892, Act III

Acknowledgements

ABBREVIATIONS

°	degree of angles
Å	Ångström
bp	boiling point
BuLi	*n*-butyl lithium
°C	degrees Celsius
cm^{-1}	wavenumber
δ	chemical shift
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCM	dichloromethane
DMA	*N,N*-dimethylacetimide
DMF	*N,N*-dimethylformamide
DMSO	dimethylsulfoxide
DMSO-d$_6$	dimethylsulfoxide (deuteriated)
Dppe	1,2-bis(diphenylphosphine)ethane
eq	equivalent
Et	ethyl
EtOH	ethanol
FAB	fast atom bombardment
h	hour(s)
g	gram(s)
IR	infra red
J	coupling constant

m	molar
Me	methyl
MeCN	acetonitrile
MeOH	methanol
MHz	megahertz
min	minute(s)
mmol	millimole(s)
ml	millilitre(s)
m.p.	melting point
NaOH	sodium hydroxide
NBS	*N*-bromosuccinimide
NMM	*N*-methyl morpholine
NMR	nuclear magnetic resonance
Nu	nucleophile
Ph	phenyl
ppm	parts per million
psi	pounds per square inch
R	alkyl
rt	room temperature
s.m.	starting material
S_N2	nucleophilic substitution (bimolecular)
THF	tetrahydrofuran
TLC	thin layer chromatography

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Chapter one

Introduction

1.0 Introduction

Organosulfur chemistry has been a major area of investigation over the past few decades and of particular interest is the field of tricoordinate sulfur compounds. They have enormous potential for use in applications such as agrochemicals, medicinals, solvents, detergents and other industrial materials. Much of the research has focussed on sulfoxides and many new reagents have been developed for use in new types of organic syntheses. Of the many organosulfur species, the attention has been mainly centred on the carbon atom with the major types of reactions studied being substitution, elimination, addition and rearrangements. Meanwhile the reactions that take place around the sulfur atom are substitution, oxidation and reduction, while much more of a minor feature are elimination, addition and rearrangements.
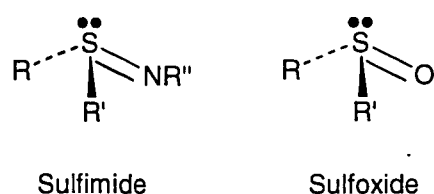
Figure 1: Sulfimides – isoelectronic with sulfoxides

Sulfimides are isoelectronic with sulfoxides and have been found to be similar in many of their reactions and properties (**figure 1**). Sulfimides, or sulfilimines as they are also known, have been studied for many years. The first reported sulfimide to be synthesised was reported when chloramine-T was added to mustard gas by a chemist named Raper in 1917.[1] It was not until a later date that this reaction was clarified and a method of synthesising tosylated sulfimides was introduced. This reaction was

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performed by Mann and Pope who reacted chloramine-T with diethyl sulfide in methanol at room temperature.[2] This procedure is still the basis of many modern routes to the synthesis of sulfimides (**scheme 1**).[3]

$$ \underset{Et}{\overset{Et}{>}}S \quad + \quad Na^+ \; Cl\;\overline{N}Ts \quad \xrightarrow{\text{- NaCl}} \quad \underset{Et}{\overset{Et}{>}}S-NTs $$
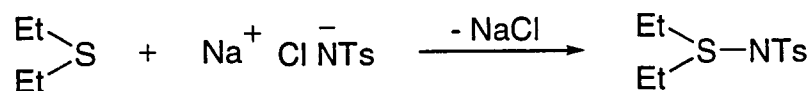
Scheme 1: Mann – Pope reaction of diethyl sulfide with chloramine-T

From the 1960's onwards groups such as Gilchrist and Moody *et al* [4] and Oae and Furukawa *et al* [5] have studied, and synthesised, a wide variety of sulfimides and the general chemistry that can be performed on them.   The use of other reagents, specifically mesitylenesulfonylhydroxylamine (MSH) **1** and hydroxylamine O-sulfonic acid (HSA), can be used for the synthesis of sulfimides as reported by Tamura *et al* (**figure 2**).[6]

1
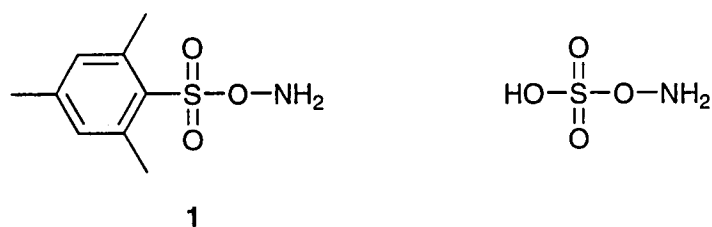
Figure 2: Structures of O-mesitylenesulfonylhydroxylamine (MSH) 1 and

hydroxylamine O-sulfonic acid (HSA)

It should be noted that **1** is used in preference to the aminating agent hydroxylamine O-sulfonic acid (HSA), whose formula is similar to that of **1** except for the absence of

the mesitylene group which is replaced by a single hydrogen atom (**figure 2**). The use of **1** is preferred due to its simple procedure, mild reaction conditions, solubility in most organic solvents and its ability to aminate a wider range of starting materials.

This strong aminating agent has been applied very successfully to synthesise many complexes, such as the unstable dialkyl sulfimides, that had proved difficult by other methods. It can also be used to aminate a range of functional groups creating compounds such as N-imines and N-aminoazonium salts (**figure 3**).[7] These compounds have proved useful as synthetic intermediates within the realm of heterocyclic chemistry. The nucleophilicity of the imino or amino nitrogen, the electrophilicity of the heteroaromatic ring and the dipolar character permit them to react in a number of ways, dependent on the nature of the heteroaromatic ring, substituents, the reagent and the reaction conditions.

N-imine   N-aminoazonium salt
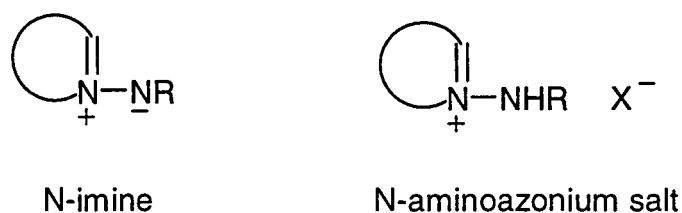
Figure 3: General structure of N-imines and N-aminoazonium salts

In the 1970's and 1980's a great effort was made in ascertaining the general chemistry of such compounds, this was stimulated by the fact that sulfimide derivatives display a range of antimicrobial, anti-tumour and pesticidal activities.[5] The versatility of these compounds proceeded to invoke interest, as in 1998 patents in the areas of pesticides and photographical material were submitted. Several publications in the past few

years have reported on their uses in the formation of chiral epoxides,[8] the generation of chiral sulfimides, [9,10] photolytically induced Stevens rearrangements in tosylated sulfimides,[11] the use of chiral sulfimides as a nitrene sources,[12] and in the formation of their selenium analogues, the selenimides.[13]

1.1 General properties of sulfimides

The interest generated by the sulfimide family of compounds is the fact that they are isoelectronic with sulfoxides and sulfonium ylides (**figure 4**).

Sulfimide   Sulfoxide   Sulfonium ylide   Sulfonium salt
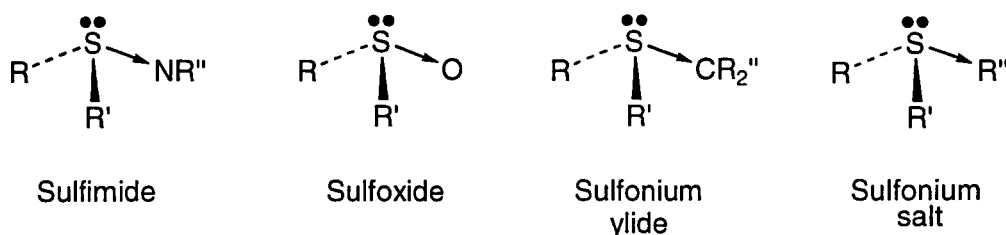
Figure 4: Similarity of sulfimides with corresponding sulfonium ylides

All of the properties are similar, as indeed are the reactions, including the fact that sulfimides possess a chiral centre - only if both substituent groups are different. This can be shown by X-ray crystallography where the pyramidal structure may be resolved to give two enantiomers.[5] Sulfimides can also undergo pyramidal inversion, without bond rupture, at temperatures below 200°C and optically active sulfimides racemise at temperatures of around 80°C. Therefore chiral sulfimides can be used to predict the final stereochemistry of products, an area which is of much interest in the field of asymmetric synthesis.[9,10] Another interesting difference to sulfoxides is their ability to have an extra bonding site available on the nitrogen atom and hence they can

therefore be derivatised. Sulfimides with only a hydrogen atom attached to the nitrogen are considered to be free sulfimides, whereas when any other group is attached they are known as N-substituted sulfimide compounds.

The subject of the nature of the S-N bonding in sulfimides has been a matter of controversy, with some researchers believing it to be a double bond (**figure 5**). This however is highly unlikely due to the basic character of the terminal imino group of the sulfimide, the longer bond length of the S-N linkage and the smaller stretching frequency it possesses. It is also thought that the S-N bond may not be a simple single bond but a *dp-π* type double bond, formed by a 2*p* orbital of nitrogen and a 3*d* orbital of sulfur. The structural conformation of either a double or single bonded structure is dependent on the nature of the substituents R, R' and X. The structure of similar phosphonium ylides shows the contribution of *3d-2pπ* bonding is quite significant.[14] Further research has shown that the stabilisation of carbanions by a α-sulfur atom is due to the strong polarisability of the α-sulfur group and not due to *3d-2pπ* bonding.[15,16] It is now the thought of many that the bond length lies somewhere in between that of a single and double bond, hence the conclusion that it is actually a semi-polar bond. This being so, the sulfur-nitrogen linkage can be regarded as being similar to the bonding between N-O atoms in amine oxide compounds.

The UV spectrum also suggests a semi-polar S-N bond by showing that it is not capable of conjugation with a benzene ring.[5] The terminal imino group is more nucleophilic than that of the sulfinyl oxygen of sulfoxides and the S-N bond is also weaker due to additional π-bond formation.
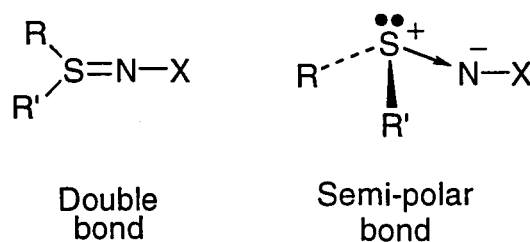
Figure 5: Representations of the S=N bonding in sulfimides

If the S-N bond length is considered to be a semi-polar single bond, then the average bond length is estimated using Pauling's values to lie somewhere between 1.76 Å for a single S-N bond and 1.52 Å for a double S-N bond. The positive charge in the semi-polar S-N bond is found to lie around the sulfur atom leaving the negative charge lying close to the nitrogen atom. N-unsubsituted dialkyl sulfimides are very unstable and readily undergo decomposition at room temp to give sulfides or sulfoxides in the presence of moisture. Dialkyl sulfides are more nucleophilic than diaryl or aryl alkyl sulfides. The basicity of free diaryl sulfimides have pKa values in the region of 7-9 and are quite similar to primary alkyl amines. Thus free sulfimides have proved to be very good nucleophiles, which react with many electrophilic reagents in common organic reactions.

Infrared spectra prove to be useful in the determination of sulfimide compounds with the stretching frequency of the S-N bond being in the range of 800-1150cm^{-1}. This is dependent on the substituents present on the terminal sulfimide nitrogen, but not dependent on any substituents present on the sulfur atom, even increasing or decreasing ring size of substituents has no effect. The stretching frequency of the S-O bond in sulfoxides is higher than the corresponding S-N bond in sulfimides. This

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suggests that the S-O bond is stronger than the S-N bond; a trend in keeping with the relative thermal stabilities of these compounds.[17]

The strong electron donor property of sulfimides can be seen by the reaction of N-benzoyldimethylsulfimide with Pd(II) and Pt(II) salts yielding a crystalline product. The complex is not bound by the carbonyl oxygen atom but by the imino nitrogen atom of the sulfimide.[18,19] It has been found that the methyl-N-p-tosylsulfilimino group is as electron withdrawing as the cyano group or methanesulfonyl group and more electron withdrawing than the methanesulfinyl group.[20]

1.2 Research in the area of sulfimide chemistry – past and present

The interest in sulfimide chemistry has been rapidly growing and many papers are still being published on their current uses in organic chemistry.[21,22] The organic reactions include many common synthetic procedures, such as to react free diphenylsulfimide with electrophilic alkenes in a Michael type addition reaction.[23] Recent publications have reported a novel desulfurisation process for light oil, based on the removal of N-tosylsulfimides produced by the reaction of sulfur containing compounds with chloramine-T.[24,25] These sulfimides have been reported to possess antimicrobial, diuretic and hypotensive properties on tumor growth and activity as anti-depressants and stimulants of the central nervous system.[26] The argument to use these recovered sulfimide by-products for use as medicinal supplies is also stated in the publication.

Research has developed only recently as to sulfimides uses in the field of inorganic chemistry. The coordination chemistry of sulfoxides provided inspiration, not only in the bonding they can exhibit (O-bound, S-bound and even bridging), but also in terms

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of the importance of such products.[27] An example of this is the use of optically active sulfoxides in current research for the production of compounds, which are stereo-specific.[28]

The first full characterisation of a metal sulfimide complex came with the isolation of $[UCl_2(Ph_2SNH)Cp^*_2]$ [29] (although in 1976 Toriuchi *et al* noted other complexes that were more poorly characterised).[19] All other research in this area has been achieved by Kelly *et al* who has shown the affinity that sulfimide compounds have towards metal centres. The research had mainly focussed on the ligand S,S-diphenylsulfimide and the way that it reacts with a variety of metal complexes.

The product of the reaction of Ph_2SNH **2** with the halogen bridged palladium species $[PPh_4]_2[Pd_2Br_6]$ proved to be a homoleptic complex with four ligands, all bound by nitrogen to the palladium atom in a square planar geometry.[30] In contrast the N-substituted sulfimide $Ph_2SNCH_2CH_2CN$ reacts with the aforementioned palladium species to give either $[PPh_4][PdBr_3(Ph_2SNCH_2CH_2CN)]$ or *trans-*$[PdBr_2(Ph_2SNCH_2CH_2CN)_2]$ depending on the ratio used. Even in the presence of excess ligand a homoleptic species does not form indicating that reaction routes are very dependent upon the nature of substituents on the nitrogen (**figure 6**). In this work however all sulfimides we will use will be *free* sulfimides.
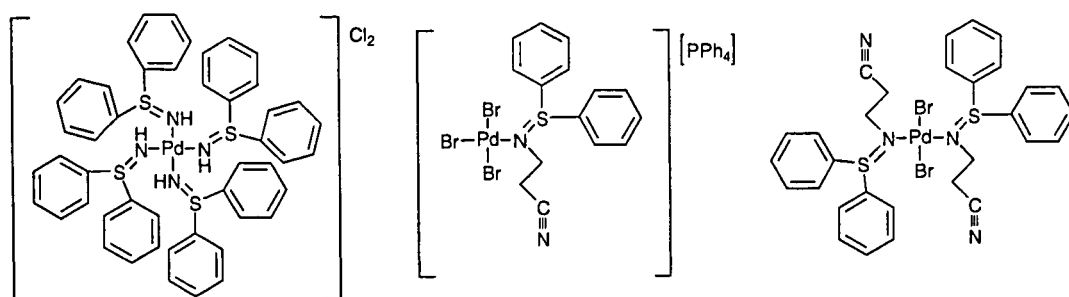
Figure 6: Palladium complexes using free and N-substituted sulfimide ligands

A unique reaction occurs with copper(II) chloride performed in acetonitrile, as expected the 2:1 nitrogen bound *trans* product is formed, but unusually producing two geometrical isomers (allogons) depending upon crystallisation technique – one pseudo tetrahedral and one square planar (**figure 7**).[31,32] While it is common for late transition metal complexes to exhibit **either** square planar or tetrahedral geometries, it is much less common to find situations where both may be formed. While anionic copper(II) species such as $[CuCl_4]^{2-}$ are known to be able to exhibit such properties, the aforementioned complex appears to be the first example of such behaviour in a *neutral* copper(II) complex. Copper is a first row transition metal and is able to show these two geometrical isomers because the crystal field stabilisation energy is much reduced for first row transition metals than those in the second and third rows of the periodic table.

Pseudo tetrahedral   Square planar
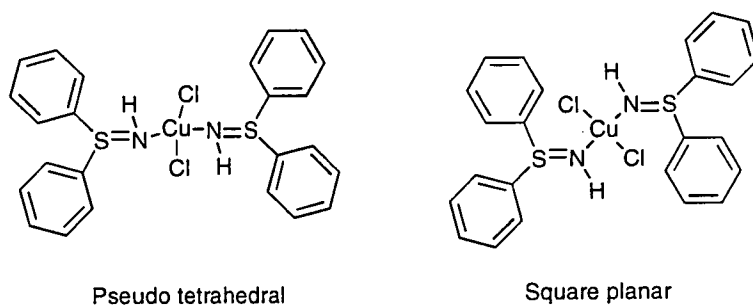
Figure 7: Unusual geometrical isomers displayed with neutral copper(II) species

When a 1:3 molar ratio of $CuBr_2$ and **2** are reacted a $[CuL_4][CuX_2L_2]X_2$ system is observed, along with the square planar isomer of the 2:1 *trans* nitrogen bound product. Both of these complexes are obtained when an excess of the ligand is used, whereas when a 2:1 ratio of ligand to $CuBr_2$ is used, only the pseudo tetrahedral *trans* product formed.

Another interesting oxo-centred product is formed when the copper(II) halides are reacted with **2** in air. The square planar structure exhibits strong hydrogen bonding interactions between the ligands and the counterions.

The cobalt complexes show an example of how the sulfimide can be utilised to give an octahedral structure when $CoCl_2$ is reacted in a 1:6 molar ratio with **2**. An example of the first homoleptic sulfimide complex is observed where each set of the three sulfimide N-H groups form hydrogen bonding pockets in which the chloride counterions sit (**figure 8**).[33]
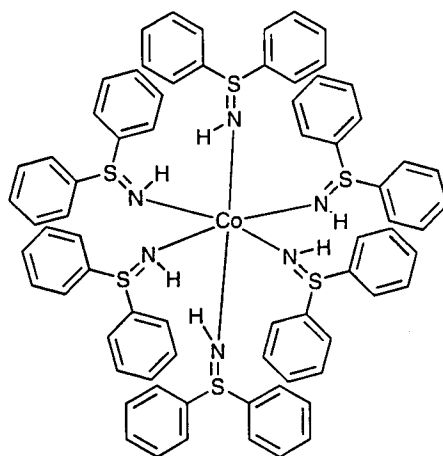
Figure 8: Six coordinate cobalt complex using Ph₂SNH

One would presume that the bulk of the phenyl groups would prevent a six coordinate complex but steric hinderance seems to play no part in the formation of this product.

The chemical versatility of organonitriles and their reactions play an important role in industry. Routes for the creation of C-C, C-N, C-O and C-S bonds in organic chemistry formed by the addition of nucleophiles,[34] electrophiles,[35] or asymmetric dipolar cycloadditions to the C≡N triple bond,[36,37,38] have been most sought after. The problems of lack of electrophilic activation of the nitriles can hinder the reactions, however this can be overcome by the use of metal ions, which in turn act as extremely strong activators towards nucleophilic attack.[39,40]

One of these interesting metal-activated organonitriles was created by Kelly *et al*, with the reaction of *bis*-acetonitrileplatinum(II)dichloride with **2** in a 1:2 molar ratio. This gave a bidentate complex with the sulfur atom of the ligand bound to the platinum metal centre, and where the nitrogen atom has undergone nucleophilic addition to the nitrile group. The result is the formation of five membered nitrile chelating product

with a nitrogen bound ligand and a chlorine atom around the platinum centre, along with a chlorine counterion (**figure 9**).[41]

This is a metal mediated addition reaction, as the free ligand **2** does not react with acetonitrile in solution without the presence of the metal complex. The products from these reactions were then utilised in order to free the new class of sulfimide/nitride ligand, which were then reacted further with several metal complexes. The nature of this reaction is also dependent on the metal used, as it has been proved that none of the sulfimide/nitrile addition product forms when using $Pd(MeCN)_2Cl_2$ or $Cu(MeCN)_2Cl_2$ starting materials.
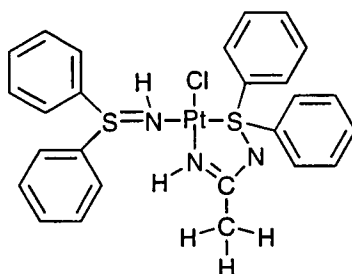
Figure 9: Product of platinum mediated addition of acetonitrile to 2

Previous research has also shown it is possible to coordinate four ligands around the platinum centre by the reaction of **2** with $[PPh_4]_2[PtCl_4]$. The difference in this reaction is that the expected nitrogen bound square planar product is formed where the N-H groups can co-operate in hydrogen bonding to the chloride counterions.

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1.3 Coordination chemistry using hemilabile ligands

A major characteristic of complexes containing hemilabile ligands is their ability to provide unoccupied coordination sites by cleavage of the labile metal-ligand bond. This formerly weakly bound donor atom can be easily displaced by a huge number of molecules with a slightly better coordination capability to the metal centre. These substitutions are usually reversible and the leaving group is still attached to the complex through the coordinated atom and therefore still in close proximity to the metal centre ready for re-coordination. This behaviour is known as the 'opening and closing mechanism' and is a typical feature of hemilabile ligands (scheme 2).
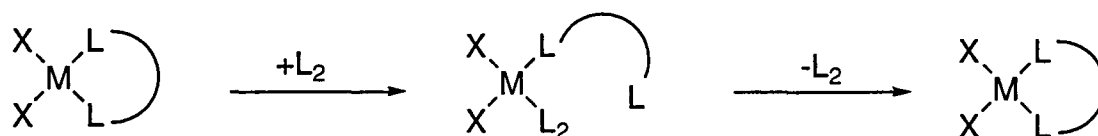
Scheme 2: Ring opening and closing mechanism of hemilabile ligands

Some examples of hemilabile ligands, where one atom is more strongly coordinating than the other are that of phosphorus-oxygen ligands.[42,43,44] The phosphorus ligand is a strong donor to metal centres, such as in the case of rhodium and iridium species, but oxygen forms a substantially weaker bond which can be readily replaced. This effect is due to hard/soft acid/base (HSAB) theory where the phosphorus atom is a softer base than the oxygen atom, and both iridium and rhodium are considered soft acids. The theory states that soft acids will form stronger bonds with soft bases and vice-versa. This example is analogous to sulfimide compounds where the nitrogen atom forms strong bonds with metal atoms and the sulfur is much more weakly bound to metal centres.

The greater stability of hemilabile ligands is known as the chelate effect. This is an entropy-induced effect; in general they form more stable analogues than their monodentate analogues. This chelate effect can be explained in terms of the favourable entropy for the chelation process. The probability of a different independent molecule coordinating to the metal complex becomes more unfavourable than if the already attached free end of the molecule, which is in the immediate vicinity to the metal, is in competition for the site at the metal centre. Another way of visualising the more favourable entropy change is to realise that a process in which the number of independent particles increases proceeds with an increase in entropy (the larger number of particles, the greater is the possible disorder).

There has also been increasing interest in the class of ligands known as pincers (**figure 10**). These pincer ligands are bound to the metal through either the nitrogen atoms of imines or the phosphine atom of phosphoamines.[45,46] In these examples we observe the increased stability of the ligand towards the metal centre and their ability to participate in catalytic reactions.

R= C or N
R'= N or P
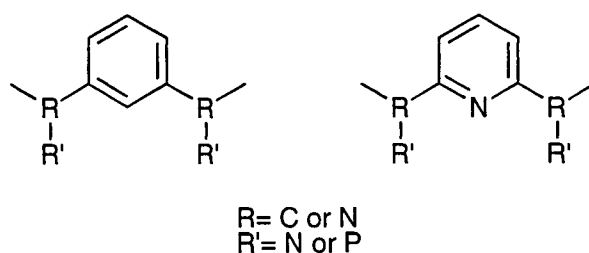
Figure 10: General structures of pincer ligands

For example pincer ligands can be used with many metal centres including platinum, palladium, iridium, rhodium, ruthenium to name a few. Most common are the P-C-P

ligands where we see phosphorus forming two bonds with the metal centre and the carbon of the ring is also bonded to the metal. These P-C-P iridium complexes can be used in the catalytic dehydrogenation reaction of aliphatic C-H bonds.[47] An interesting dendritic effect in homogeneous catalysis has been reported using an arylnickel(II) catalyst, with an N-C-N bonding framework. Here we see a metallodendrimer catalyst where catalytically active metal centres are connected to an inert carbosilane framework via a linker group.[48] Another N-C-N complex can be found to display a unique donor-bonding mode by intermolecularly chelating to bridge two lithium atoms.[49]

1.4 Conclusion, aims of this work

As a result of previous studies it is apparent that **2** acts as an excellent ligand towards a range of metal centres. In the light of this, and in view of the enhanced coordination ability brought about by the chelate effect an investigation into the possibility of preparing multidentate sulfimides was instigated. The following chapters will detail the different approaches we took to develop this idea.

1.5 References

[1] H.S.Raper, Report to British Chemical Warfare Dept., May, 1917

[2] F.G Mann and W.J.Pope. *J.Chem.Soc.*, 1922, **121**, 1052

[3] O.G.Vlasova, O.A.Rakitin and L.I.Khmelnitski, *Org.Prep.Proc.Int.*, 1994, **26**, 331

[4] T.L.Gilchrist and C.J.Moody, *Chem.Rev.*, 1977, **77**, 409

[5] S.Furukawa and S.Oae. Sulfilimines and related derivatives, ACS. Washington DC. 1983

[6] Y.Tamura, K.Sumoto, H.Matsushima, H.Taniguchi and M.Ikeda. *J.Org.Chem.*, 1973, **38**, 4324

[7] Y.Tamura and M.Ikeda, *Adv. in Heterocyc. Chem.*, **29**, 71

[8] P.C.Baird and P.C.Taylor, *J.Chem.Soc.Chem.Commun.*, 1995, 893

[9] H.Takada, Y.Nishibayasji, K.Ohe and S.Uemwa, *J.Chem.Soc.Chem.Commun.*, 1996, 931

[10] G.Celentano, S.Colonna, N.Gaggero and C.Richelmi, *J.Chem.Soc.Chem.Commun.*, 1998, 701

[11] H.Morita, H.Kamiyama, M.Kyotani, T.Fujii, T.Yoshimura, S.Ono and C.Shimasaki, *J.Chem.Soc.Chem.Commun.*, 1997, 1347

[12] A.D.M.Curtis, R.McCague, C.A.Ramsden and M.R.Raza, *J.Chem.Soc.Chem.Commun.*, 1999, 189

[13] H.Takada, M.Oda, Y.Miyake, K.Ohe and S.Vemura, *J.Chem.Soc.Chem.Commun.*, 1998, 1557

[14] R.H.Hoffmann, D.B.Boyd and S.Z.Goldberg, *J. Am. Chem. Soc.*, 1970, **92**, 3929

[15] A.Streitwieser and J.E.Williams, *J. Am. Chem. Soc.*, 1975, **97**, 191

[16] F.Bernadi, T.G.Csimadia, A.Mangini, H.B.Schlegel and S.Wolfe, *J. Am. Chem. Soc.*, 1975, **97**, 2209

[17] S.Oae, M.Fukumura and N.Furukawa, *Phosphorus Sulfur*, 1981, **10**, 153

[18] G.Matsubayashi, M.Toriuchi and T.Tanaka, *Chem.Lett.*, 1973, 985

[19] M.Toriuchi, G.Matsubayashi, H.Koezuka and T.Tanaka, *Inorg.Chim.Acta*, 1976, **17**, 253

[20] A.Kucsman and I.Kapovits, *Phosphorus Sulfur*, 1977, **3**, 13

[21] R.P.Claridge, R.W.Millar, J.P.B.Sandall and C.Thompson, *J.Chem.Research*, 1999, 520

[22] R.P.Claridge, R.W.Millar, J.P.B.Sandall and C.Thompson, *Tetrahedron*, 1999, **55**, 10243

[23] N.Furukawa and S.Oae, *Synthesis*, 1976, 30

[24] Y.Shiraishi, T.Naito, T.Hirai and I.Komasawa, *J.Chem.Soc. Chem. Commun.*, 2001, 1256

[25] Y.Shiraishi, T.Naito, T.Hirai and I.Komasawa, *Ind. Eng. Chem. Res.*, 2002, 4376

[26] B.M.Trost and L.S.Melvin, Jr., Sulfur Ylides, Academic Press, New York, 1975

[27] T.Tanase, T.Aiko and Y.Yamamoto, *J.Chem.Soc. Chem. Commun.*, 1996, 2341

[28] M.Otto, J.Parr and A.M.Z.Slawin, *Organometallics*, 1998, **17**, 4527 and references therein

[29] R.E.Cramer, K.A.N.S.Ariyaratne and J.W.Gilje, *Z. Anorg. Allg. Chem.*, 1995, **621**, 1856

[30] P.F.Kelly and A.M.Z.Slawin, *J.Chem.Soc.Chem.Commun.*, 1999, 1081

[31] P.F.Kelly, A.M.Z.Slawin and K.W.Waring, *J.Chem.Soc.Dalton Trans.*, 1997, 2853

[32] P.F.Kelly, S.-M.Man, A.M.Z.Slawin and K.W.Waring, *Polyhedron*, 1999, 3173

[33] P.F.Kelly, A.M.Z.Slawin and K.W.Waring, *Inorg.Chem.Commun.*, 1998, **1**, 249

[34] G.V.Boyd, The Chemistry of Amidines and Imidates, S.Patai, Z.Rappoport, Eds., Wiley: Chichester, 1991, Vol **2**, p 339

[35] I.D.Gridnev and N.A.Gridneva, *Usp. Khim (Russ. Chem. Rev.)*, 1995, **64**, 1091

[36] S.Karlsson and H.E.Hogberg, *Org. Prep. Proceed. Int.*, 2001, **33**, 103

[37] L.Raimondi and M.Benaglia, *Eur. J. Org. Chem.*, 2001, 1033

[38] K.V.Gothelf and K.A.Jørgensen, *J.Chem.Soc.Chem.Commun.*, 2000, 1449

[39] V.Y.Kukushkin and A.J.L Pombeiro, *Chem.Rev.*, 2002, **102**, 1771

[40] S.I.Murahashi and H.Takaya, *Acc.Chem.Res.*, 2000, **33**, 225

[41] P.F.Kelly, A.C.Macklin, A.M.Z.Slawin and K.W.Waring, *Polyhedron*, 2000, **19**, 2077-2081

[42] J.T.Groves and Y.Watanabe, *J. Am. Chem. Soc.*, 1986, **108**, 7834

[43] T.G.Traylor and R.Popovitz-Biro, *J. Am. Chem. Soc.*, 1988, **110**, 239

[44] T.C.Bruice, P.N.Balasubramanian, R.W.Lee and L.Smith Jr, *J. Am. Chem. Soc.*, 1988, **110**, 7890

[45] P.Dani, M.Albrecht, G.P.M.van Klink and G.van Koten, *Organometallics*, 2001, **19**, 4468-4476

[46] G.J.P.Britovsek, V.C.Gibson, S.Mastroianni, D.C.H.Oakes, C.Redshaw, G.A.Solan, A.J.P.White and D.J.Williams, *Eur. J. Inorg. Chem.*, 2001, 431-437

[47] M.Gupta, W.C.Kaska and C.M.Jensen, *J.Chem.Soc. Chem. Commun.*, 1997, 461

[48] A.W.Kleij, R.A.Gossage, R.J.M.Klein Gebbink, N.Brinkmann, E.J.Reijerse, U.Kragl, M.Lutz, A.L.Spek and G.van Koten, *J. Am. Chem. Soc.*, 2000, **122**, 12112

[49] R.Schlengermann, J.Sieler and S.Jelonek, E. Hey-Hawkins, *J.Chem.Soc. Chem. Commun.*, 1997, 197

Chapter two

Synthesis of bis-sulfimides and mixed sulfide/sulfimides
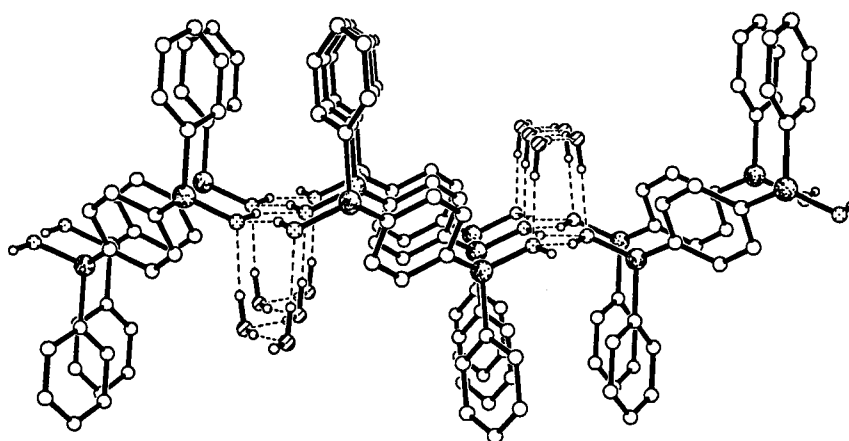
2.0 Synthesis of *bis*-sulfimides and mixed sulfide/sulfimides

2.1 O-Mesitylenesulfonylhydroxylamine (MSH)

MSH **1** is a very powerful aminating agent that has proved effective in the formation of sulfimides from the corresponding sulfides. The synthesis was performed almost *in situ* (meaning the product is actually isolated but is used extremely quickly), as it has been known to rapidly decompose to a black residue at room temperature when dealing with large quantities or when exposed to other chemicals.[1] The precursor was found to decompose after a few weeks but this was delayed by storing in the freezer under nitrogen.

During the course of this work it was found that the most consistent method for preparation of **1** consisted of adding perchloric acid to the precursor ethyl-O-mesitylenesulfonylacetohydroxamate **3** in dioxane at 0°C.[2,3] The perchloric acid was added very slowly and with thorough stirring as a white, thick precipitate appeared quite rapidly. Caution is advised at this point, as one must take care when adding perchloric acid to an organic reagent. When water was added only the crude white solid of **1** was found to precipitate and the other by-products were washed away by the addition of petroleum ether 60/80. The proposed S_N2 mechanism can be seen below (**scheme 3**). Nucleophilic attack of the perchloric acid at the imine carbon causes subsequent formation of **1** giving the ester and propyl-acetate as by-products.
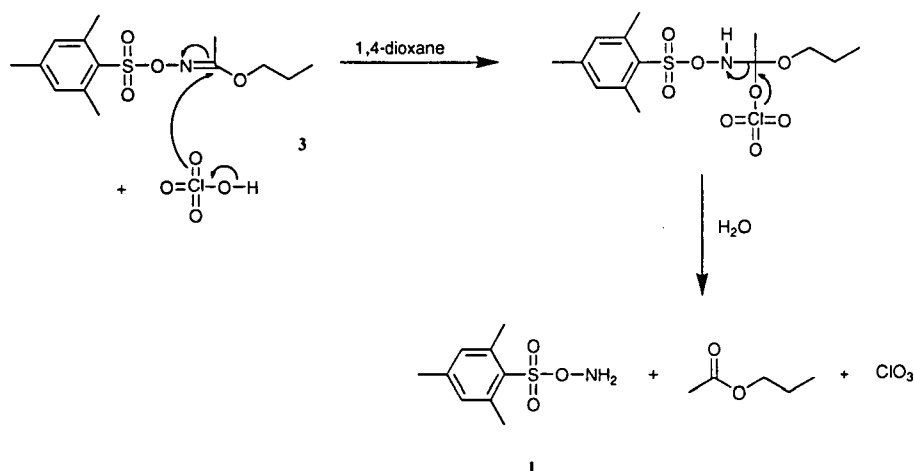
Scheme 3: Proposed mechanism for the synthesis of MSH 1

Water was found to be present in the final recrystallised product; this can have adverse effects on most reactions causing reduced yields and in some cases no reaction at all. A reduction in the amount of water present was overcome by extracting with Et_2O after the solid was washed with cold petroleum ether 60/80. If the subsequent reaction required completely dehydrated **1**, the white solid was placed under vacuum on the high vacuum line for several hours before use, this was found to solve the problem. This was a very quick and efficient reaction, which took only thirty minutes and produced yields of approximately 50%.

Other methods of synthesising **1**, such as treating the precursor with 50% H_2SO_4 and Et_2O, were attempted but with little success. This method was used in the first instance to avoid using perchloric acid due to the dangerous nature of this substance. The drawbacks were a low yield of **1** and a long preparation time compared to the standard method i.e. four hours compared to thirty minutes with the perchloric acid addition method.

2.2 Deprotonation reactions using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)

It has been found that free sulfimides have relatively high basicity with pKa values of around 7-9;[4] therefore it was thought a strong base would be required in order to bring about deprotonation. Various methods were tried such as using a dilute base such as sodium hydroxide solution.[5] This failed due to the increased polarity and hence increased basicity of the *bis*-sulfimide compared to that of Ph$_2$SNH **2**. Another method, reported in previous literature, includes passing the protonated compound through a column of ion exchange resin (amberlite IRA410).[6] This was partially successful and we did manage to isolate enough of the product to gain a mass spectra but the yield was so low that it was thought that another method was needed.

Attempts to use 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a deprotonating agent proved to be far more successful, although initial use of a 1:1 ratio was found to be insufficient to affect full deprotonation of the NH$_2{}^+$ unit in our new systems. Tests revealed that using a 3.5:1 ratio of DBU to the sulfimide was the correct amount to remove only one proton and thus leave the sulfimide unit intact.

2.3 Synthesis of [1,4-(PhS{NH$_2$})$_2$C$_6$H$_4$][mesSO$_2$]$_2$ 4

The protonated ligand [1,4-(PhS{NH$_2$})$_2$C$_6$H$_4$][mesSO$_3$]$_2$ **4** was chosen in the first instance as a starting point to extend the original ligand, **2**, by adding another SPh functional group. Previous attempts to synthesise this compound using chloramine-B and chloramine-T methods had provided limited results. This is probably due to the increased steric hinderance and basicity of the extra functional group or maybe due to the harsh conditions used during these methods (i.e. heating at 50°C in sulphuric acid for 30 minutes).[7]

The starting sulfide [1,4-(PhS)$_2$C$_6$H$_4$] **5** was easily synthesised from the readily available bromo starting material [1,4-C$_6$H$_4$Br$_2$] **6**. Both sulfur positions were aminated by placing two equivalents of **1** into the reaction mixture. One would expect the first sulfur position to be aminated quite quickly (due to the greater amount of **1** initially present) but it appears that the second sulfur also aminates after only 1 hour of stirring. The white precipitate was then filtered and washed with CH$_2$Cl$_2$ before being dried *in vacuo* to remove any excess water. A TLC of the solid performed on silica plates showed only one spot, this was used to indicate the purity of the compound.

The solid proved insoluble in anything less polar than methanol with all the usual solvents tried (i.e. dichloromethane, acetonitrile) thus indicating a very polar compound. Further recrystallisation of the crude product using MeOH/Et$_2$O produced a crystalline white solid (**scheme 4**).
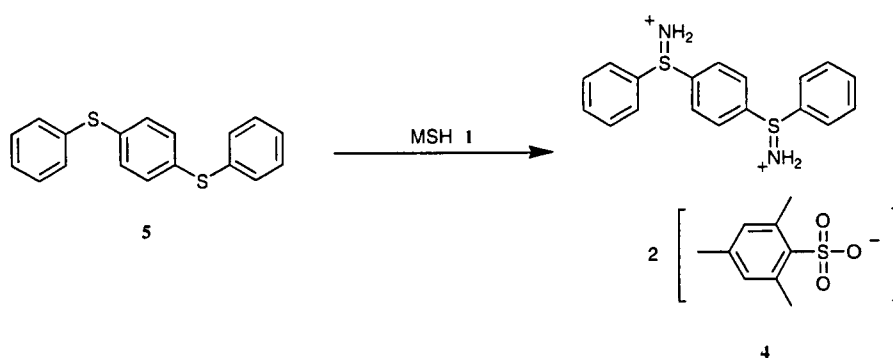
Scheme 4: Synthesis of [1,4-(PhS{NH$_2$})$_2$C$_6$H$_4$][mesSO$_2$]$_2$ 4

The infrared data shows the presence of the mesitylenesulfonate anion at 1190 cm^{-1} (due to S=O stretches) along with the aromatic and aliphatic stretches at 2971, 846

and 749 cm^{-1} respectively. The broad nature of the mesitylenesulfonate band prevents the S=N stretch from being observed. The ^{1}H NMR data for the product, performed in DMSO-d$_6$, shows a group of phenyl multiplets at 7.25-7.65 δppm integrating as 18H. The alkyl protons on the mesitylene sulfonyl anion are seen at 2.02 and 1.71 δppm integrating as 12H and 6H respectively. The mass spectrometry using fast atom bombardment (FAB) contains peaks attributable to the loss of 200 mass units (mesitylene sulfonyl anion) at [325] from the mass ion [525]. This is followed by the loss of 15 mass units (NH) at [310] due to the S-N bond cleavage. Microanalysis data proved effective in determining the purity of the molecule by being within strict parameters of the required values (a requirement of being within 0.5% of the calculated figure for percentage of carbon atoms).

2.4 Synthesis of [1,4-(PhSNH)$_2$C$_6$H$_4$] 7

In order to deprotonate 4, the solid was suspended in dichloromethane and a solution of DBU, also in dichloromethane, was added dropwise with constant stirring. The solution appeared clear half way through addition, and then when complete a solid was seen to precipitate. It was then filtered and washed with water to remove any of the DBU by-products (scheme 5). It should be mentioned at this stage that the product had formed a dihydrate after several washings with water.
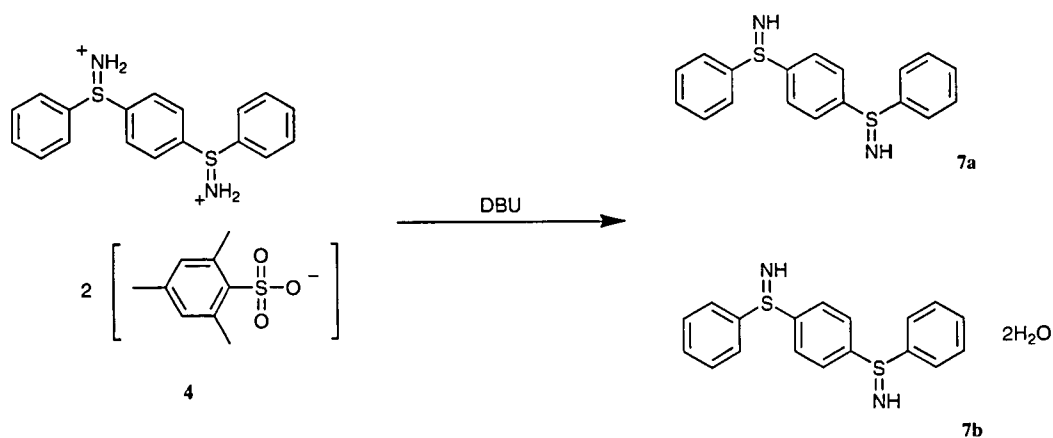
Scheme 5: Synthesis of [1,4-(PhSNH)$_2$C$_6$H$_4$] 7

The free *bis*-sulfimide **7** proved to be insoluble in most common solvents such as CH$_2$Cl$_2$ and acetonitrile due to its extremely polar nature. It did however dissolve with stirring in MeOH and was subsequently recrystallised by slow diffusion of Et$_2$O vapour into a MeOH solution giving two types of crystals: a needle and 3-D block form. These two types of crystal correspond to the dihydrate **7b** (**figure 11**) and the water-free form **7a** respectively (**figure 12**).
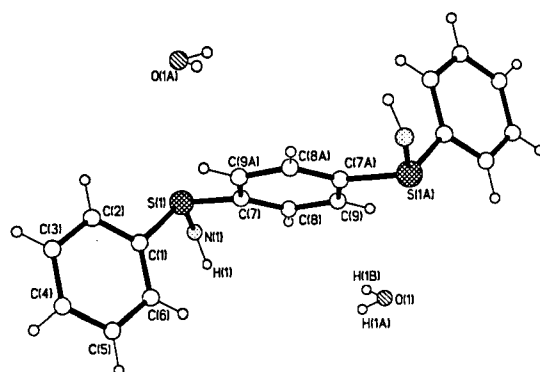
Figure 11: Crystal structure of dihydrate 7b. Selected bond lengths (Å) and angles (°): N(1)–S(1)–C(1) 111.86(15), N(1)–S(1)–C(7) 110.06(15), N(1)–S(1) 1.578(2)

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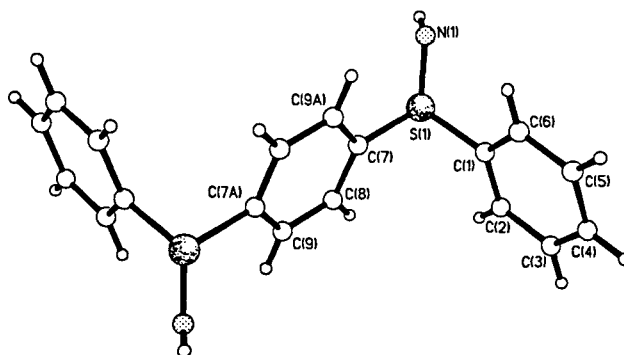
Figure 12: Crystal structure of anhydrous 7a. Selected bond lengths (Å) and angles (°): N(1)–S(1) 1.571(2), N(1)-H(1) 0.72(2), S(1)–N(1)-H(1) 112(4)

The hydrated type **7b** has been found by crystallography to form an extended array **(figure 13)**. In this case the presence of N-H...N, O-H...N and O-H...O interactions at both sulfimide units generates parallel ladder arrangements with waters above and below the plane of the nitrogens. The arrays now exhibit an extra dimensionality thanks to the linking phenyl units. The result is a 2-D sheet structure **(figure 14)**; this is also mirrored within the structure of the anhydrous analogue.
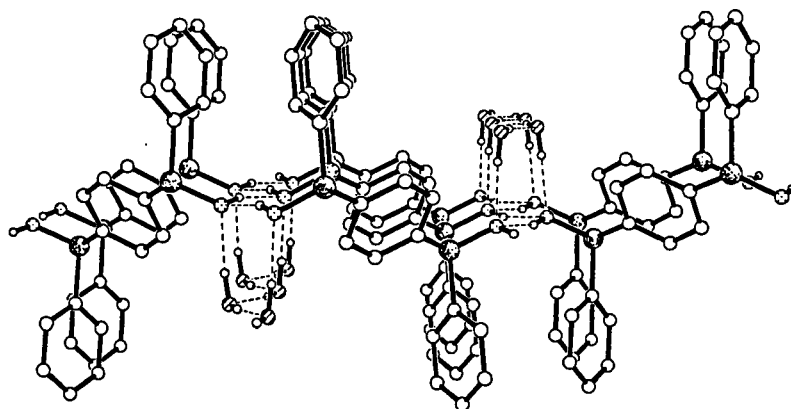
Figure 13: Crystal structure of 7b showing the extended array formation with H₂O Selected bond distances (Å) and angles (°): S(1)–N(1) 1.578(2), N(1)...H(1B) 1.99(4), H(1A)...O(10) 2.19(5); C(1)-S(1)-C(7) 98.72(14), C(1)-S(1)-N(1) 111.86(15), C(7)-S(1)-N(1) 110.06(15), S(1)-N(1)-H(1) 111(4).

Interestingly, in the latter case there appear to be no significant C-H...N interactions of the kind seen in **2**, but the material still remains a solid. This presumably stems from the extra structural "rigidity" brought about by having two hydrogen–bonding sulfimide units per molecule (**figure 15**) and the extra dimensionality this gives the system when compared to the *mono*sulfimide **2**.
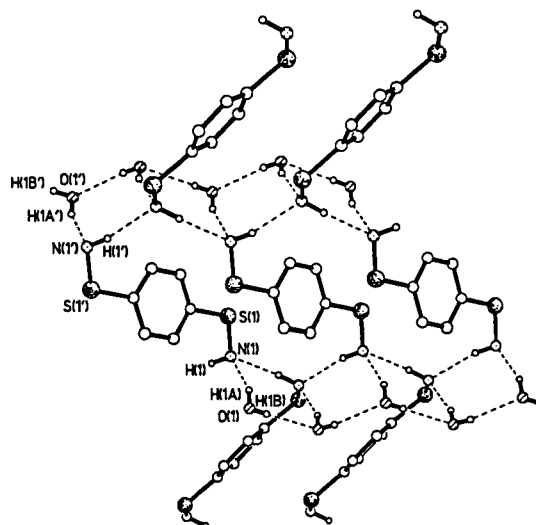
Figure 14: The X-ray crystal structure of 7b showing a side-on view of the array highlighting the kinked-ladder arrangements linked into a 2-D sheet (non-bridging phenyl groups omitted for clarity). Selected bond distances (Å) and angles (°): S(1)–N(1) 1.578(2), N(1)...H(1B) 1.99(4), H(1A)...O(10) 2.19(5); C(1)-S(1)-C(7) 98.72(14), C(1)-S(1)-N(1) 111.86(15), C(7)-S(1)-N(1) 110.06(15), S(1)-N(1)-H(1) 111(4).
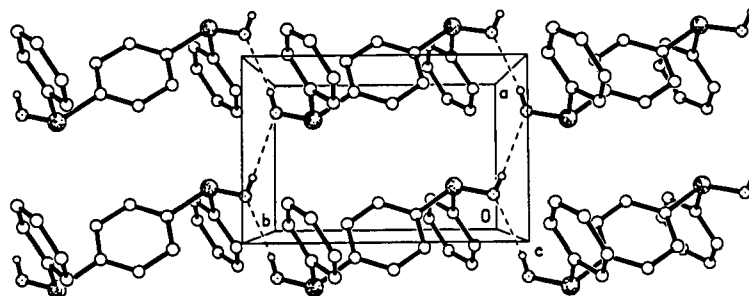
Figure 15: Crystal structure of 7a showing how the structure gains extra stability from the two sulfimide units. Selected bond lengths (Å) and angles (°): N(1)–S(1) 1.571(2), N(1)–H(1) 0.72(2), S(1)–N(1)–H(1) 112(4)

The key to the formation of the water-bearing arrays is undoubtedly the fact that the sulfimide nitrogens can act as H-bond donors via the N-H bond and as acceptors from two units: an O-H and a N-H. This presumably reflects both the fact that the nitrogens are relatively sterically unencumbered and that the ylid structure of the sulfimide unit puts negative charge on them. The resulting N_2O_2 rings, which are the building blocks of the kinked ladders of the arrays, are slightly distorted square planes. Thus within the N_2O_2 rings we see N-N, O-N and O-O distances of 3.1, 2.8 and 2.9Å respectively, N-N-O and N-O-O angles of 98.5° and 80.4° and a maximum deviation of 0.094 Å from the mean plane.

The S=N bond length is 1.57 Å which indicates that the linkage is nearer to a double bond arrangement when quoting the estimated literature value of 1.76 Å for a single bond and 1.52 Å for a double bond (according to Pauling's values of covalent bond radii of sulfur and nitrogen atoms).[8] This suggests the cationic charge should be localised on the sulfur atom and should exhibit substantial π-bonding character. The infrared data shows the presence of the N-H group with a stretch at 3111 cm^{-1} along with the S=N stretch at 929 cm^{-1}. Aromatic and aliphatic stretches are observed at 827, 753 and 687 cm^{-1} respectively. The ^{1}H NMR data for the structure performed in DMSO – d₆ shows a group of phenyl multiplets at 7.00-7.32 δppm integrating as 14H. The mass spectrometry using fast atom bombardment (FAB) contains peaks attributable to the mass ion at [325]. This is followed by the loss of 15 mass units (NH) at [310] due to the S-N bond cleavage. Further fragmentation results in the loss of 15 mass units (NH) at [294]. Microanalysis data proved effective in determining the purity of the molecule by being within strict parameters of the required values including the two waters of hydration.

2.5 Synthesis of [1,2-(PhS{NH₂})C₆H₄PhS][mesSO₂] 8

The importance of creating **8** hinges on its ability to freely form bidentate rings when bonding with metal species. The presence of both sulfide and sulfimide units in one does mean that it possesses the prerequisites to be a polydentate ligand. The corresponding 1,2-*bis* sulfimide does not however form; even in the presence of excess **1** only **8** forms. Its inability to do this is almost definitely attributable to the 1,2 *ortho* positions of the SPh units around the aromatic ring, thus contributing to an increase in steric hinderance.

The reaction proceeded as previously, where **1** was added to the *bis*-sulfide [1,2-(PhS)₂C₆H₄] **9**, but in this instance no precipitate was observed and the solution remained clear. The solution was dried *in vacuo* which produced a sticky white solid (**scheme 6**). Attempts at recrystallisation from both DCM/Et₂O and MeOH/Et₂O produced crystals. It should be noted that the product is soluble in dichloromethane undoubtedly due to the fact that it has only one aminated site; this makes it less polar than its *bis*-sulfimide counterpart **4**.
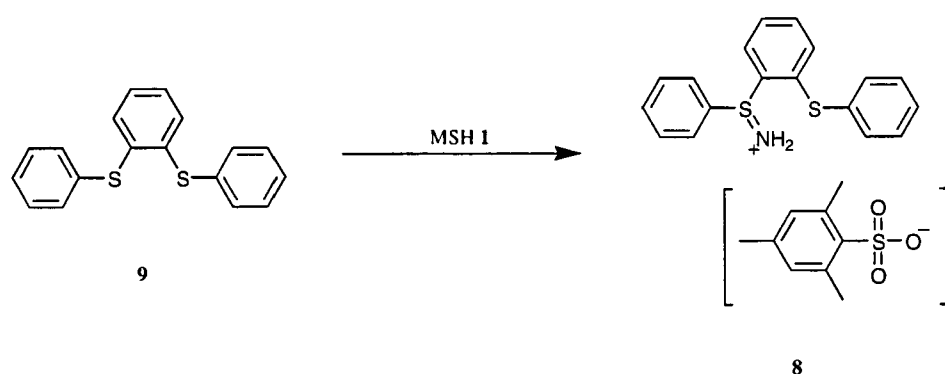
Scheme 6: Synthesis of [1,2-(PhS{NH₂})C₆H₄PhS][mesSO₂] 8

The infrared data shows the presence of the mesitylenesulfonate anion with a characteristic broad band at 1168 cm⁻¹ along with the aromatic and aliphatic stretches

at 2969, 751 and 678 cm^{-1} respectively. The NMR data for the structure performed in CDCl$_3$ shows a group of phenyl multiplets at 6.94-7.70 δppm integrating as 13H. By far the most interesting feature is the presence of a doublet of doublets at 8.50-8.54 δppm, which integrates to 1H (**figure 16**). A D$_2$O shake was performed on the solution in order to gauge whether this peak was attributable to the NH$_2^+$ protons. The peaks remained on the spectra, which indicates that this was indeed due to one of the aromatic protons next to the S=NH$_2^+$ functional group. It would seem that the S=NH$_2^+$ group is shifting the signal downfield, a feature that is not observed in **4**.

The close proximity of the aromatic proton to the NH$_2^+$ group must be the cause of this. Interestingly the NH$_2^+$ protons are observed as a broad band at 3.10 δppm, which subsequently disappears when the D$_2$O shake is performed on the solution (D$_2$O is added to the nmr solution after it has been analysed, then the sample is shaken to mix the two solutes, it is then analysed again, but this time any stretch that is due to N-H will disappear because it will have been replaced by N-D which doesn't show up in ^{1}H NMR). The alkyl protons on the mesitylenesulfonate anion can be seen at 2.55 and 2.20 δppm integrating as 6H and 3H respectively. These two signals also show an upfield shift when compared to that of **4**.
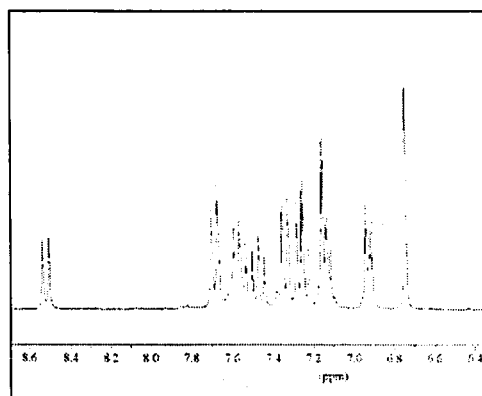
Figure 16: ^{1}H NMR spectra of **8** showing the aromatic region

The mass spectrometry data, using fast atom bombardment (FAB), only contains peaks attributable to the mass ion at [310]. This is followed by the loss of 16 mass units (NH_2^+) at [294] due to the S-N bond cleavage. Microanalysis data proved effective in determining the purity of the molecule by being within strict parameters of the required values. The melting point is 132-134°C, which is considerably lower than that of **4** (210-212°C). This can be explained by the reduced ionicity of **8** which contains only one $S=NH_2^+$ functional group.

2.6 Deprotonation of [1,2-(PhS{NH₂})C₆H₄PhS][mesSO₂] 8

It was not known whether the deprotonation of **8** would react in the same way as its *bis* counterpart **4**. The same procedure was followed of a 3.5:1 ratio of DBU to product, in a solution of dichloromethane, added dropwise with stirring (**scheme 7**). The stark difference was seen immediately as a precipitate failed to be produced, even after 30 minutes of stirring had elapsed. In the case of the **7**, an immediate precipitate formed when water was added to the solution, whereas an oil was observed on this occasion. After decanting the water layer the oil was dried by placing under vacuum

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overnight. The water solution was kept and an interesting discovery was made –
crystals had formed.
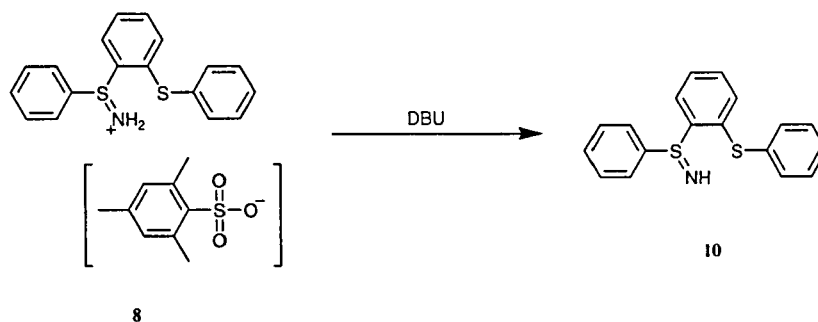
Scheme 7: Deprotonation of [1,2-(PhS{NH$_2$})C$_6$H$_4$PhS][mesSO$_2$] 8

Further analysis was obtained on both the oil and the crystals, it would seem that the
product displayed two distinct types of formation, one as an anhydrous oil **10a** and
one as a hydrated solid **10b**. The X-ray crystal structure of the needles, grown from
MeOH/H$_2$O, confirms the presence of both the sulfide and sulfimide groups (**figure
17**) and reveals an array structure (**figure 18**) analogous to that of **2**. It would appear
that the presence of the extra SPh unit mitigates against effective array formation in
the absence of water. It would also seem that the formation of C-H...N interactions as
in the case of **7** is now prevented by the steric bulk of the sulfide group. As in the
case of **7**, the S=N bond length of 1.59Å is still closer to the predicted double S=N of
1.52 Å, than to the S-N single bond of 1.76 Å.
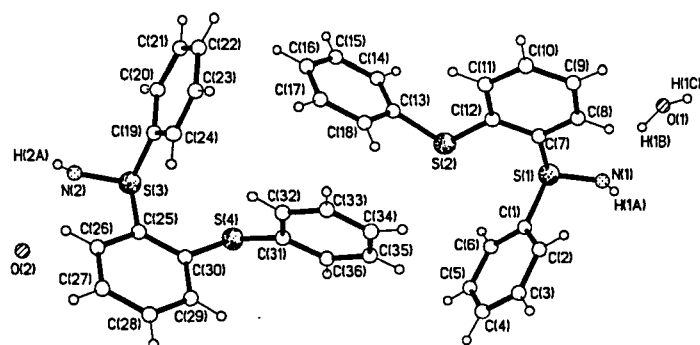
Figure 17: The crystal structure of 10b. Selected bond distances (Å) and angles (°): S(1)–N(1) 1.590(8), N(1)-H(1B) 2.00(7); C(1)-S(1)-C(7) 98.6(4), C(1)-S(1)-N(1) 109.8(4), C(7)-S(1)-N(1) 110.2(4), S(1)-N(1)-H(1A) 102.0(7), C(12)-S(2)-C(12) 105.7(4).
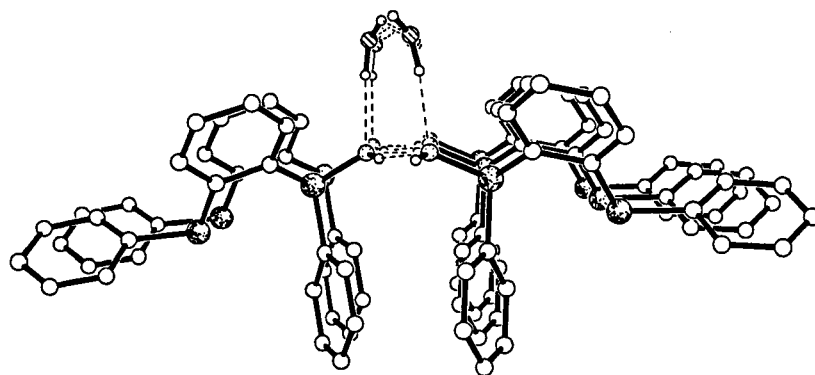
Figure 18: Crystal structure of monohydrated 10b showing the array formation with H_2O. An array builds from the O–H...N interaction shown (2.00(7)Å) and N–H...N interactions of 2.22(9) and 2.17(10)Å.

The infrared data shows the presence of the N-H group with a stretch at 3130 cm^{-1} along with the S=N stretch at 920 cm^{-1}. Aromatic and aliphatic stretches at 756 and

693 cm^{-1} respectively. The NMR data for the structure performed in CDCl$_3$ shows a group of phenyl multiplets at 7.53-7.65 δppm integrating as 13H. The doublet of doublets are still present but have shifted upfield from that of the protonated ligand **8** to 7.93-7.99 δppm (**figure 19**).
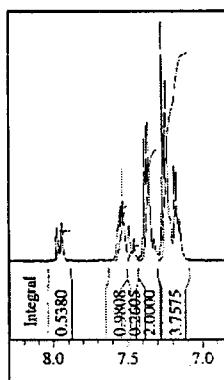
Figure 19: ^{1}H NMR spectra of 10 showing the aromatic region

Here we see by looking at the crystal structure (**figure 17**) just how close the proton on C(26) is to the sulfimide group hence causing the anomaly in the splitting pattern. Mass spectrometry using fast atom bombardment (FAB) contains peaks attributable to the mass ion at [310]. This is followed by the loss of 15 mass units (NH) at [294] due to the S-N bond cleavage. Microanalysis data proved effective in determining the purity of the molecule by being within strict parameters of the required values.

2.7 Synthesis of [1,4-(PhS{NH$_2$})C$_6$H$_4$PhS][mesSO$_2$] 11

The product from the reaction of **1** with **5** where only one of the sulfur atoms has been aminated can be seen in **scheme 8**. Care was taken to halt further amination of the second sulfur by keeping a higher concentration of **5** in solution and adding **1** slowly. The method was repeated using the same reaction conditions as previously mentioned,

with a clear solution present on completion. The final product was also worked up in a similar fashion to before yielding a sticky white solid, which we were unable to recrystallise from MeOH/Et$_2$O and CH$_2$Cl$_2$/Et$_2$O; it also proved to be soluble with polar solvents as in the case of the *mono*sulfimide counterpart **8**.
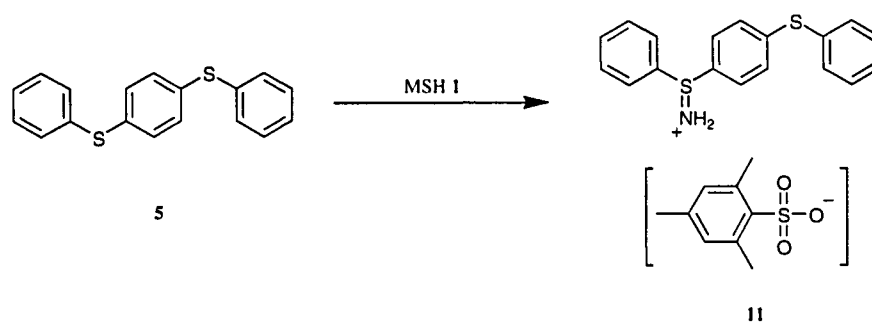
Scheme 8: Synthesis of [1,4-(PhS{NH$_2$})C$_6$H$_4$PhS][mesSO$_2$] 11

The infrared data shows the presence of the mesitylene sulfonyl anion at 1192 cm^{-1} along with the aromatic and aliphatic stretches at 2974, 816 and 750 cm^{-1} respectively. The ^{1}H NMR data for the product, performed in CDCl$_3$, shows a doublet at 7.98-8.02 δppm integrating as 1H (as seen in **8**), a group of phenyl multiplets at 7.19-7.67 δppm integrating as 13H. The phenyl protons on the mesitylenesulfonate anion can be seen as a doublet at 7.00-7.02 δppm integrating as 2H. The phenyl protons on the mesitylene sulfonyl anion can be seen as singlets at 2.43 and 2.14 integrating as 6H and 3H respectively. The mass spectrometry using fast atom bombardment (FAB) contains peaks attributable to the loss of 200 mass units (mesitylenesulfonate anion) at [310] from the mass ion [510]. This is followed by the loss of 15 mass units (NH) at [294] due to the S-N bond cleavage. Microanalysis data proved effective in

determining the purity of the molecule by being within strict parameters of the required values.

2.8 Deprotonation of [1,4-(PhS{NH₂})C₆H₄PhS][mesSO₂] 11

The same method of deprotonation using DBU was applied in this instance, once again on a 3.5:1 ratio (**scheme 9**). The protonated solid **11** was DCM soluble and therefore there were no solubility problems when performing the reaction. A white solid of the formula [1,4-(PhSNH)C₆H₄PhS] **12** was observed after washing with water. Recrystallisation of the product proved quite troublesome, as the usual routes were undertaken, such as CH_2Cl_2/Et_2O, $MeOH/Et_2O$ and $MeCN/Et_2O$, and proved unsuccessful. $MeOH/H_2O$ was tried and although the solid was found to be pure, no crystals had formed.
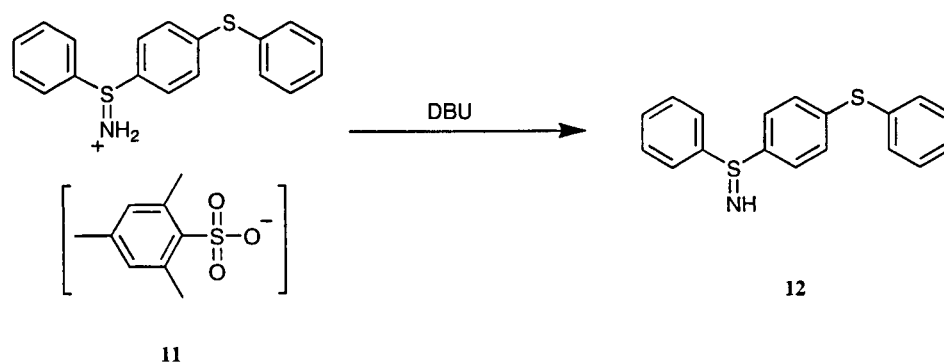
Scheme 9: Deprotonation of [1,4-(PhS{NH₂})C₆H₄PhS][mesSO₂] 11

The infrared data shows the presence of the N-H group with a stretch at 3235 cm⁻¹ along with the S=N stretch at 924 cm⁻¹. Aromatic stretches can also be seen at 819, 757 and 693 cm⁻¹ respectively. The ¹H NMR data for the structure performed in CDCl₃ shows a group of phenyl multiplets at 7.14-7.49 δppm integrating as 15H, but

interestingly in this case no doublet peaks are observed. The mass spectrometry using fast atom bombardment (FAB) contains peaks attributable to the mass ion at [310]. This is followed by the loss of 15 mass units (NH) at [294] due to the S-N bond cleavage.

2.9 Comparison of data

MSH **1** was the reagent of choice when aminating the *bis* and mixed sulfide systems **5** and **9**. It was found that DBU was a strong enough base even to deprotonate the most basic of our ligands **4**. Several comparisons can be made using these new classes of sulfimide ligands. The first observation is the capacity of the hydrated products to form extended hydrogen bonded arrays with the water molecules. The second point is the marked differences of the 1,4- *bis* and *mono* sulfimides **7** and **12**. On the one hand there is the insoluble, extremely polar dihydrated product of **7b**, whereas in **12** more soluble, less polar characteristics are observed. We can conclude that the addition of one more sulfimide unit has substantially changed the nature of the compound, from the ability to form crystals to the strength of the basicity.

When comparing the infrared data, we see from **table 1** that there are only slight differences in the S=N stretching frequencies. These are such marginal differences that we cannot make any assumptions that the extra S=NH group of **7** makes any difference to the frequency of the stretch in the infrared region. Indeed it has been found from previous research into sulfimide compounds, that only great differences are seen in the infrared spectra when N-bound constituents are changed.

Table 1: Comparison of infrared data

Compound	S=N bond Stretching frequency (cm^{-1})	N-H bond stretching frequency (cm^{-1})
[1,4-(PhSNH)$_2$C$_6$H$_4$] **7**	929	3111
[1,4-(PhS{NH})C$_6$H$_4$PhS] **12**	924	3235
[1,2-(PhS{NH})C$_6$H$_4$PhS] **10**	920	3128

Interestingly, the S=N stretches are not observed in the case of the protonated ligands due to the broad nature of the mesitylenesulfonate anion (*cf.* 1180 cm^{-1}). As previously mentioned the S=N stretches vary greatly on the substituents present on the terminal N-atoms and can be seen at wavenumbers between 800 cm^{-1} and as high as 1150 cm^{-1}. Having the anion attached to the nitrogen of the sulfimide group could also be the cause of an increase in this case. The differences of the N-H stretching frequencies between each compound are significant, with a characteristic broad stretch seen in each case.

The ^{1}H NMR spectra of the above compounds also exhibit differences in the frequencies of multiplet peaks in the aromatic region. The main difference is observed in the spectra of **10** where we see doublet of doublet peak downfield of the main aromatic multiplet. One can predict that this is due to having an S=NH group in close proximity to the proton of the bridging phenyl ring, but it may also be due to its *ortho* configuration, as this effect is not observed in the *para mono*-sulfimide **12**.

2.10 References

[1] F.D.King and D.R.M.Walton, *Synthesis*, 1975, 788

[2] Y.Tamura, K.Sumoto, H.Matsushima, H.Taniguchi and M.Ikeda. *J.Org.Chem.*, 1973, **38**, 4324

[3] N.Furukawa and S.Oae, *Synthesis*, 1976, 30

[4] N.Furukawa, T.Yoshimura, T.Omata and S Oae, *Chem.Ind.*, 1974, 702

[5] K.Tsujihara, N.Furukawa, K.Oae and S.Oae, *Bull.Chem.Soc.Jpn.*, 1969, **42**, 2631

[6] S.Furukawa and S.Oae. Sulfilimines and related derivatives, ACS. Washington DC. 1983

[7] O.G.Vlasova, O.A.Rakitin and L.I.Khmelnitski, *Org.Prep.Proc.Int.*, 1994, **26**, 331

[8] L.Pauling, The Nature of Chemical Bond, Cornell Univ. Press: Ithaca, New York, 1960, 3rd Ed., p224

Chapter three

Coordination chemistry using the bis-sulfimide and mixed sulfide/sulfimide ligands
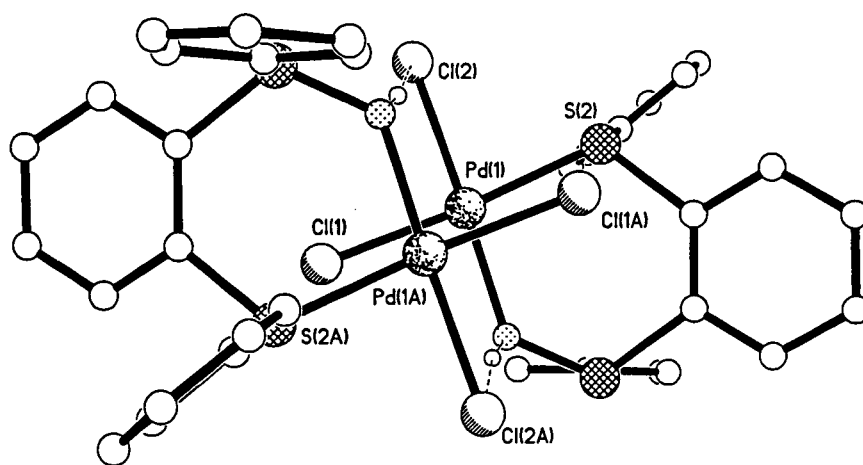
3.0 Coordination chemistry using the *bis*-sulfimide and mixed sulfide/sulfimide ligands

As discussed in previous chapters, many interesting and unique properties can be seen when using **2** as a coordinating ligand with a variety of metal complexes.[1,2,3] The objectives of our studies were to emulate some of these, as well as producing novel reactions, using our new species of sulfimides. The interest presided in whether the new sulfimides would bond to the metal species and perform in the same way as the original ligand **2**. Also of interest was the effect of the introduction of an extra, bulky S-Ph group and whether steric interference from this would hinder the formation of any newly produced complexes. The three sulfimides that were chosen also possessed the ability to act as bidentate ligands, either in a chelating or bridging fashion.

Much of our research will focus on reactions with palladium(II) and platinum(II) metal complexes. These occur in group 10 of the periodic table and mostly make d_8 square planar complexes on reaction. Sulfimide ligands lend themselves to form strong bonds with platinum and palladium atoms because of their soft nature. This can be seen in the strong coordinating ability of dimethylsulfoxide to platinum atoms. The nitrogen atom is considered to be a "harder" atom than sulfur due to the fact that it is a first row p-block element; this is opposed to sulfur, a second row p-block element, which can still form reasonably strong bonds with the two metal atoms. Therefore it is safe to say that our new class of sulfimide ligands are well suited for reactions with palladium(II) and platinum(II) complexes.

3.1 Reactions of [1,4-(PhSNH)₂C₆H₄].2H₂O - 7b with palladium complexes

The *bis*-sulfimide ligand **7b** proved very insoluble with the commonly used solvents CH₂Cl₂ and acetonitrile, this caused us several problems when trying to react them with metal complexes. It was decided that a number of reactions would be performed with a series of palladium complexes: [PPh₄]₂[Pd₂Br₆] **13**, [PPh₄]₂[Pd₂Cl₆] **14** and [PPh₄]₂[Pd₂I₆] **15**. The reactions were performed in CH₂Cl₂, and as the ligand **7b** was still slightly insoluble, they were left to react slowly with the complex for several days. [Br₂PdN(H)S(Ph)C₆H₄S(Ph)N(H)]₂ **16** was formed in reasonable yield as either a red microcrystalline product or a red powdered solid.
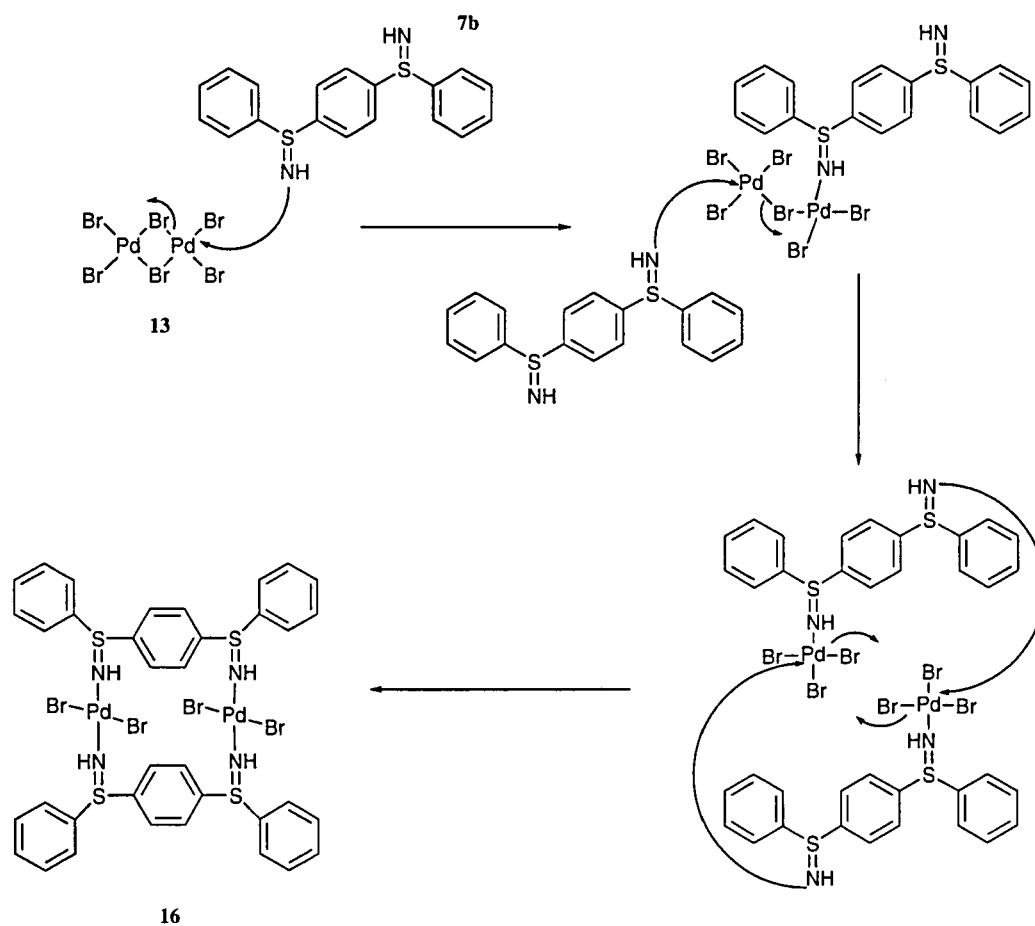
Scheme 10: Proposed mechanism for the formation of 16

The proposed mechanism for this reaction can be seen in **scheme 10**. We initially see the rupture of the bridging bromine bond from the palladium atom; this is caused by the nucleophilic attack of the nitrogen atom on the metal centre. This bond is broken due to its weaker nature compared with the terminal bromine atom. Next we see another molecule of **7b** attacking the other bridging bromine-palladium bond, causing the formation of two separate but identical palladium complexes. The result is a bridged palladium(II)complex which was found by X-ray crystallography, using a synchrotron source, to reveal an interesting crystal structure where the asymmetric unit comprises two half molecules on centres of symmetry (**figure 20**).
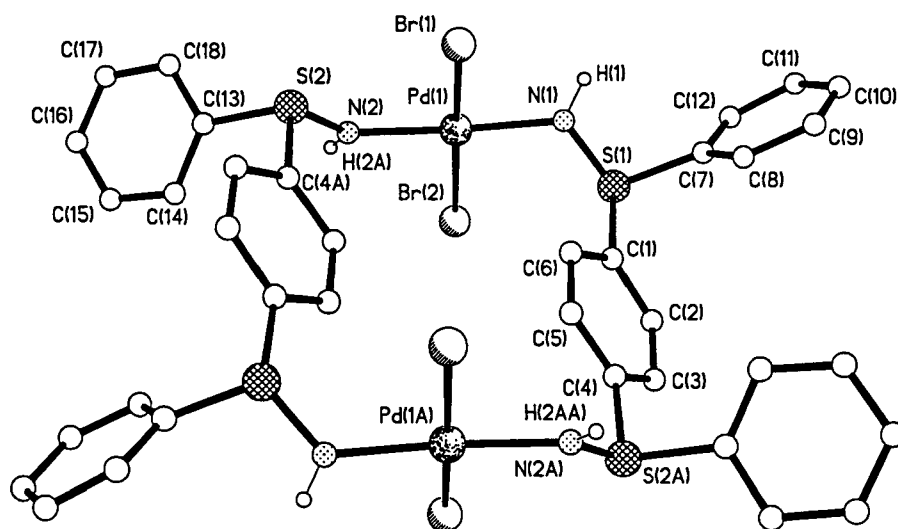
Figure 20: Crystal structure of complex 16. Selected bond distances (Å) and angles (°): Pd(1)–N(1) 2.020(5), Pd(1)–N(2) 2.025(5), N(1)–S(1) 1.622(5), N(2)–S(2) 1.618(5), N(3)–S(3) 1.590(6), N(4)–S(4) 1.583(6), N(1)–Pd(1)–N(2) 174.7(2), Br(2)–Pd(1)–Br(1) 170.91(3)

Here we see two palladium atoms bridged together by the *bis*-sulfimide ligands in a *trans* arrangement forming an overall binuclear 18-membered ring arrangement. A deviation from the linear angle of 180° of a perfect square planar structure can be justified by studying the data of the angles. A difference from the linear of up to 19° can be observed at the positions Br(3)–Pd(2)–Br(4) and Br(2)–Pd(1)–Br(1), where the angles are 173.02 and 170.91° respectively.

A difference in the S-N bond lengths is also observed where at N(1)–S(1) and N(2)–S(2) the bond lengths are 1.622 and 1.618 Å respectively and at positions N(3)–S(3) and N(4)–S(4) we see bond lengths of 1.590 and 1.583 Å respectively. This constitutes to an average difference of 0.02 Å, where one side of the structure is slightly different to the other. The constraints placed on the ligand in order to conform to the cyclic structural arrangement of the dimer would give a good reason for this anomaly.
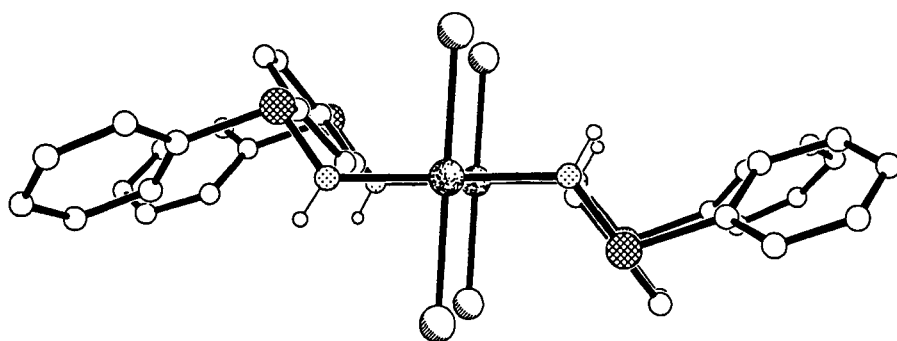
Figure 21: Side on view of the complex 16

The side on view of the crystal structure shown in **figure 21** best illustrates the positions of the Pd-Br, Pd-N, S-N and bridging phenyl units and how they relate to

each other in space. We see that the Pd-Br bonds are almost perpendicular to the Pd$_2$N$_4$ plane (N(2)-Pd(1)-Br(2) = 85.7°) while the S-N bonds of each of the ligands also project on either side of this plane (in what has been referred to as a "sofa bed" arrangement). The linking phenyl units of each ligand are parallel to each other and inclined at an angle of 52.8° to the Pd$_2$N$_4$ plane. Perhaps the most intriguing thing about the structure is that the positions of the sulfur atoms define an almost perfect square, with S(2)-S(1) = 6.325 Å, S(2)-S(1A) = 6.326 Å and S(1)-S(2)-S(1A) = 91.5°. As **figure 21** shows the bridging phenyls are offset relative to each other hence this precludes any π-π interactions. Unlike many of the complexes of **2** that have been previously investigated there appear to be no significant interactions between the N-H groups of the ligands and halide ligands of adjacent molecules.[4]

The only isolable material in this reaction appeared to be the complex **16**. The reaction produced a yield of 67% based upon palladium and when the reaction filtrate was treated with Et$_2$O more of the same material was obtained. The latter proceedure generated **16** as an orange solid which did not redissolve back into CH$_2$Cl$_2$. From this observation we can conclude that a small amount of another soluble complex of **7b** was present, however it proved difficult to speculate its form as attempts to isolate this resulted in the formation of **16**.

The reaction of the iodo analogue **15** with the ligand **7b** appeared to proceed in an identical manner to that of the bromo counterpart. Again the product was an insoluble orange/red material whose IR spectrum was found to be extremely similar to that of **16**. Taken together with microanalysis this allows us to formulate it as [Pd{1,4(PhS{NH})$_2$C$_6$H$_4$}I$_2$]$_2$ **17** with confidence. We have every reason to believe

that **17** has the same kind of binuclear structure as **16**, although we were unable to produce crystals suitable for X-ray crystallography.

Likewise [Pd{1,4(PhS{NH})$_2$C$_6$H$_4$}Cl$_2$]$_2$ **18** was formed in the analogous reaction with the chloro analogue **14**; The IR spectrum of this material is very similar to that of **16** and **17** and in this case we observe one Pd-Cl stretch at 346 cm^{-1} which is consistent with the *trans* halides. Microanalysis results in this case indicate that the dichloromethane solvate forms.

Due to the insolubility of **7b** in CH$_2$Cl$_2$ the reaction time observed for the formation of all these types of compounds is long (typically three days). The length of reaction time is key to the formation of the binuclear product; changing the solvent system has a dramatic effect upon the course of the reaction. Because compound **7b** is soluble in methanol, the addition of a solution of the ligand in methanol to a solution of **13** in CH$_2$Cl$_2$ was attempted, which resulted in an immediate reaction. An insoluble product was generated (with just [PPh$_4$]Br left in solution, as shown by IR) but in this case we observed a pale brown coloured solid rather than the bright orange red colour of **16**.

IR spectroscopy reveals the presence of bands due to the ligand **7b** but the key stretches, ν[N-H] and ν[N-S], are both stronger and broader than those in **16** and are shifted to 3220 and 897 cm^{-1} respectively. Microanalysis supports the formulation [Pd{1,4(PhS{NH})$_2$C$_6$H$_4$}Br$_2$] **19** but unlike **16** (which shows the peaks which may be predicted from the single crystal data) the X-ray powder pattern of this product shows no discernable peaks. We believe that this product to be an amorphous polymeric material rather than the binuclear structure of **16**.

Interestingly, it forms even when only one equivalent of **7b** is used in the reaction. In this case we would expect the compound [PPh$_4$]$_2$[(PdBr$_3$)$_2${(PhS{NH})$_2$C$_6$H$_4$}] to form in which the *bis*-sulfimide **7b** would link two [PdBr$_3$]$^-$ units. Instead we see the polymeric material generated, while the reaction filtrate can be shown to contain [PPh$_4$]Br and unreacted **13** by use of IR spectroscopy. It is reasonable to assume this reaction proceeds *via* a *trans*ient intermediate of the form [PdBr$_3${(PhSNH)$_2$C$_6$H$_4$}]$^-$ in which one of the nitrogen atoms of the ligand is bound to palladium. It would appear that the halide *trans* to N in this case is activated towards displacement by another nitrogen.

Similar results are observed for reactions involving [Pd$_2$Cl$_6$]$^{2-}$ and [Pd$_2$I$_6$]$^{2-}$, generating insoluble polymeric products which are very pale brown and dark brown respectively. The IR spectra of both products are analogous to that of the bromide product with broad v[N-H] (3211 and 3217 cm^{-1} for chloride and iodide respectively) and very broad v[N-S] peaks (centered on 897 cm^{-1} in both cases).

It would appear, therefore, that only when the reaction of **7b** with [Pd$_2$X$_6$]$^{2-}$ is slowed down by the use of CH$_2$Cl$_2$ as solvent is a molecular product seen; the use of methanol encourages the fast formation of a polymeric material. Note though that in some solvents the reaction does not proceed at all. For example, if the reactions are attempted in MeCN then after three days of stirring the mixture simply consists of a suspension of unreacted **7b** in the solution of the palladium starting material.

As for the structure of the polymeric complexes we can only speculate that they possess a linear polymeric arrangement made up of alternating PdX$_2$[(PhSNH)$_2$C$_6$H$_4$]

units. Of course other structual motifs could be envisaged and it may even be that the material contains a mixture of different oligomers (though we can be sure that none of the binuclear complex is present thanks to the IR and powder X-ray results); only single crystal X-ray crystallography would provide an unequivocal answer and we have yet to obtain crystalline samples. Once formed the material is totally insoluble in all solvents and techniques used to obtain single crystals of **19** are not amenable in this case thanks to the fast reaction time.

3.2 Reactions of [1,2-(PhSNH)C₆H₄PhS] 10a with various metal complexes

We have been successful in the coordination of **10a** using a variety of metal complexes; each reaction was used to gain knowledge of the unique properties of this ligand.

3.2.1 Reaction of [1,2-(PhSNH)C₆H₄PhS] 10a with [(MeCN)₂PtCl₂] 20

The five membered metallocyle [Pt(PhSC₆H₄S(Ph)NC(Me)NH)Cl₂] **21** was formed from the reaction of **10a** with **20** in reasonable yields. It can be seen that during the reaction the nucleophilic addition of the nitrogen to the nitrilic carbon has taken place. This is then followed by proton transfer and coordination of the sulfur *via* the loss of the remaining acetonitrile. This has been previously found in the case of reactions using **2** and it is thought that this only happens in the presence of platinum-nitrile complexes.[5] The bulky S-Ph unit present in this ligand has no steric effect and does not prevent the reaction from taking place.

The product was soluble with stirring in DCM and was subsequently recrystallised by slow diffusion of Et₂O vapour into a DCM solution to yield yellow crystals. The

product **21** was solved using X-ray crystallography (**figure 22**). In this reaction we observe one of the advantages the sulfimide compounds has over that of the isoelectronic sulfoxides - a free bonding space which is ready to accept other atoms, in this case the nitrile moiety.
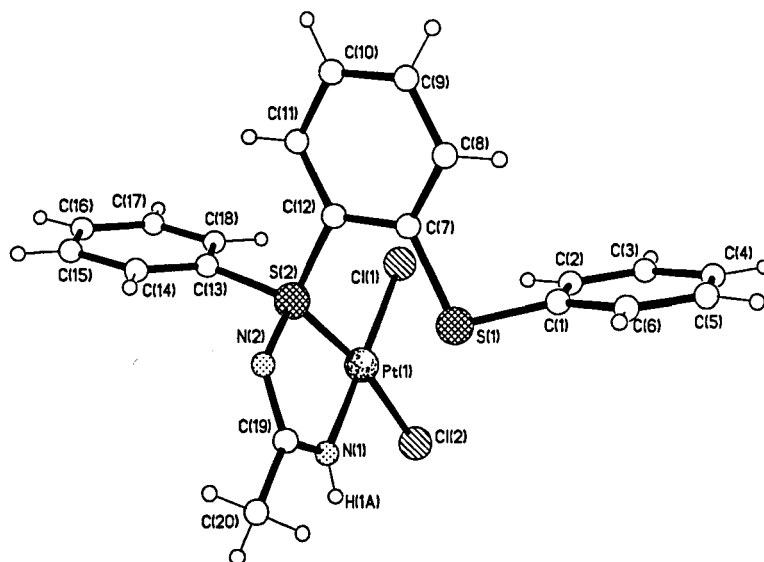
Figure 22: Crystal Structure of 21: Selected bond distances (Å) and angles (°):

Pt(1)–N(1) 1.992(4), Pt(1)–S(2) 2.1647(12), S(2)–N(2) 1.632(4), S(2)–Pt(1)–Cl(2)

170.00(5), N(1)–Pt(1)–Cl(1) 175.50(12).

The X-ray crystal structure reveals bond parameters within the metallocycle little different to those in the aforementioned reaction with **2**; of interest though are the relatively close Cl...N-H interactions (2.88 Å) between adjacent molecules which generate an extended array within which adjacent PtNCNS planes are angled at 51° to each other. We see a deviation from the perfect square planar structure, where the S-Pt-Cl angle and the N-Pt-Cl angle are no longer linear (170.0° and 175.5° respectively).

As **figure 22** shows the thioether unit of **10a** orientates itself in such a way as to leave the phenyl end unit as far away from the rest of the atoms of the molecule as possible. While steric considerations no doubt provide one driving force for the adoption this orientation, another interesting feature of the structure is the close interaction of the thioether sulfur atom with the platinum. As **figure 22** shows, this atom approaches the axial position of the platinum, resulting in a Pt–S distance of 3.446 Å. This distance is slightly longer than that observed in the previously reported complex [Pt($\underline{\text{NH}}$=SPh$_2$)$_2$\{$\underline{\text{NH}}$=C(Me)N=SPh$_2$\}$_2$][PF$_6$]$_2$; both values compare well with those observed in a number of recent examples of complexes exhibiting axial Pt–S interactions. For example, such interactions (in this case slightly shorter, at 3.3 Å or less) result in dimer formation within [ClCr(4-mpyt)$_4$Pt] (mpyt = 4-methylpyridine-2-thiolate).[6] The Cl(1)–Pt–S(1) angle (100.3°) also provides an indication of the presence of a significant Pt–S interaction.

The S-N bond length is found to be 1.632 Å, this is different to that of the un-coordinated ligand whose S-N bond length is 1.59Å, but is still deemed to be closer to a double bond than a single for these two atoms. As was expected the C(19)-N(1) bond length is significantly shorter than the C(19)-N(2) bond length (1.29 *cf.* 1.34 Å), this is attributable to the higher bond order due to one of them being a double bond and one a single bond. Thus we can say with an amount of trepidation that the bonding within the neutral ligand is N(H)=C(CH$_3$)N=S(C$_6$H$_5$SPh).

The infrared studies show a very strong, broad N-H stretch at 3062 cm^{-1}, a stretch can also be seen at 1522 cm^{-1} which corresponds to the C=N bond in the nitrile metallocycle. The presence of the S=N stretch is dramatically shifted, seen at

800 cm^{-1}, from that of the un-coordinated ligand at 919 cm^{-1}(thus indicating a much weaker S=N bond in the complex). The data obtained can be compared with that from the analogous reaction using **2**, where all of these features are observed.

The ^{13}C NMR data shows the C=N peak at 182.3 δppm and the peak attributable to CH$_3$-C is observed at 18 δppm. These can be compared to the peaks seen in the aforementioned reaction with **2** at 183.6 and 19 δppm, respectively. ^{195}Pt NMR was used to determine the presence of any other isomers or products in the reaction mixture. Only one peak is observed in CDCl$_3$ at δ −3087 ppm due to the product **21**.

When the solvent is changed to DMSO-d$_6$ and the ^{195}Pt NMR obtained, we see the presence of several peaks. This can be explained by the strong coordinating properties of the DMSO ligand towards platinum complexes. The DMSO must have displaced bonds within the metallocycle causing several by-products that are observed in the NMR spectra. The mass spectrometry data confirms the presence of the mass ion at [616] units followed a peak caused by fragmentation at [581] attributable to the loss of a chlorine atom.

3.2.2 Reaction of [1,2-(PhSNH)C$_6$H$_4$PhS] 10a with [(DMSO)$_2$PtCl$_2$] 22

The aim of this reaction was to attempt to show the possibility of bidentate binding properties of **10a** towards metal centres. [(DMSO)$_2$PtCl$_2$] **22** was reacted with **10a** in a 1:2 ratio in the hope that both the sulfur and nitrogen atoms would replace the two DMSO ligands. One could reason that the sulfur would indeed bind to the platinum atom due to its thiophillic nature. Sadly only one of the DMSO ligands was replaced to give [Pt(DMSO){1,2-(PhSNH)C$_6$H$_4$PhS}Cl$_2$] **24**, with the nitrogen of the sulfimide

bound to the platinum atom. This was confirmed using infrared and mass spectrometry data, the latter showing peaks due to the mass ion at [652] units followed by a peak at [617] attributable to the loss of a chlorine atom.

3.2.3 Reaction of [1,2-(PhSNH)C₆H₄PhS] 10a with [dppePtCl₂] 24

The main reasoning behind this reaction is that the rigidity and the strong binding capacity that the dppe ligand exhibits towards platinum centres would increase the chances of binding the sulfur atom of the sulfide to the platinum. Therefore **24** was the metal complex of choice along with the addition of several different species of counter ions. These included compounds such as NH₄BF₄, TlPF₆, AgBF₄ and AgSbF₆, the main aim of their use was to assist in the crystallisation of the final product. The best results were obtained by having [SbF₆]⁻ as the counter ion with the formation of AgCl₍ₛ₎ as a by-product, the proposed mechanism is shown below (**scheme 11**).
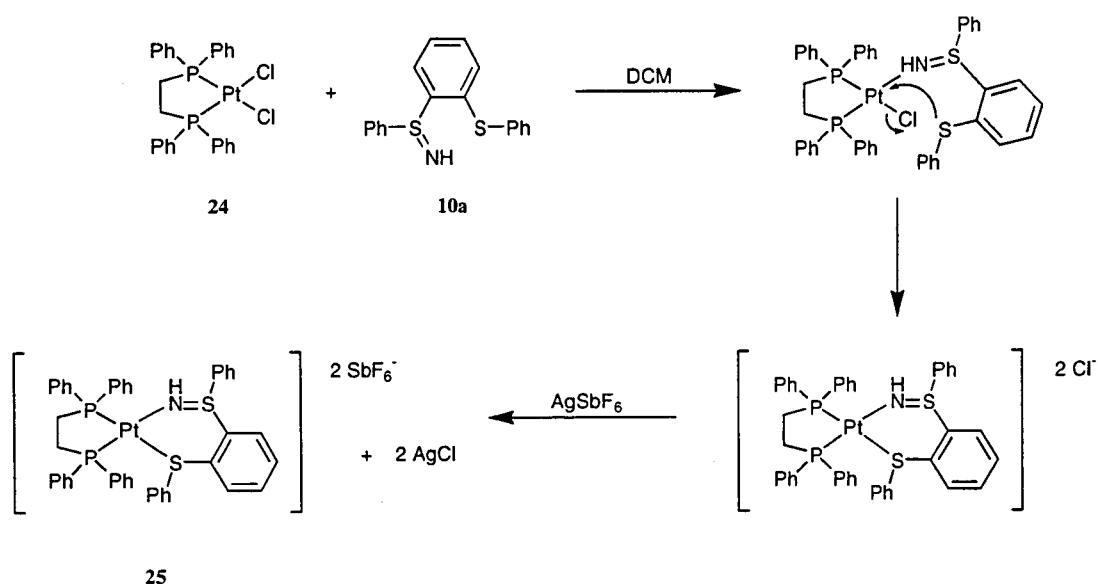
Scheme 11: Proposed mechanism for formation of [Pt(dppe){1,2-(PhSNH)C₆H₄PhS}][2Cl] 25

Infrared data shows peaks at 1107 and 825 cm^{-1} both due to the [SbF$_6$]$^-$ counter ion, the N-H and S=N stretches of the sulfimide can be seen at 3057 and 930 cm^{-1} respectively. The mass spectrometry data proved useful by showing peaks at [1137], due to the mass ion, followed by fragmentation with a peak at [901] attributable to the loss of SbF$_6$$^-$ counter ion. ^{31}P NMR data displays two different peaks at 50.17 and 40.11 δppm, with four other peaks attributable to platinum satellites seen at 96.99, 82.07, 3.60 and -1.60 δppm respectively. The product was soluble with stirring in DCM and was subsequently recrystallised by slow diffusion of Et$_2$O vapour into a DCM solution, this gave a clear microcrystalline material that proved too small to diffract using X-ray crystallography.

3.2.4 Platinum (IV) reactions using mixed sulfide/sulfimide ligands 10a and 12

The interest in the conversions of nitriles at metal centres stems from the possibilities of their uses in areas such as: (i) the use of the nitriles as synthons to prepare new compounds that cannot be readily prepared by usual organic methods. (ii) They could provide the environmentally friendly metal catalysed hydrolytic transformation of RCN species to amides, e.g. of significant interest to pharmaceutical industry. (iii) They could be useful in the synthesis of diverse imino complexes *via* nucleophilic addition, e.g. these compounds exhibit unusual antitumor properties.

In association with Professor V Y Kukushkin and co-workers we have performed several platinum (IV) mediated nitrile-sulfimide coupling reactions using our ligands. These reactions proceeded smoothly at room temperature and formed the corresponding heterodiazadiene compounds of the type [PtCl$_4${NH=C(R)N=SR'Ph}$_2$] where R = Me, Et, CH$_2$Ph, Ph and R' = [1,2-(PhSNH)C$_6$H$_4$PhS] **10** or [1,4-

(PhSNH)C₆H₄PhS] **12**.   This is in contrast to the above reaction with the platinum(II)

species where the formation of chelate products are observed (**scheme 12**).

It has been discovered that the reaction of *trans* [PtCl₄(RCN)₂] with **2** led exclusively

to *trans* [PtCl₄{NH=C(R)N=SPh₂}₂] **26**, meanwhile the reaction of *cis/trans* mixtures

of [PtCl₄(RCN)₂] with **2** led to *cis/trans* mixtures of [PtCl₄{*E*-NH=C(R)N=SPh₂}₂].

Kukushkin *et al* have shown through the use of theoretical calculations at both

HF//HF and MP2//HF levels that the *trans* isomer is of a higher stability than the *cis*

isomer.

R = Me, Et, CH₂Ph, Ph
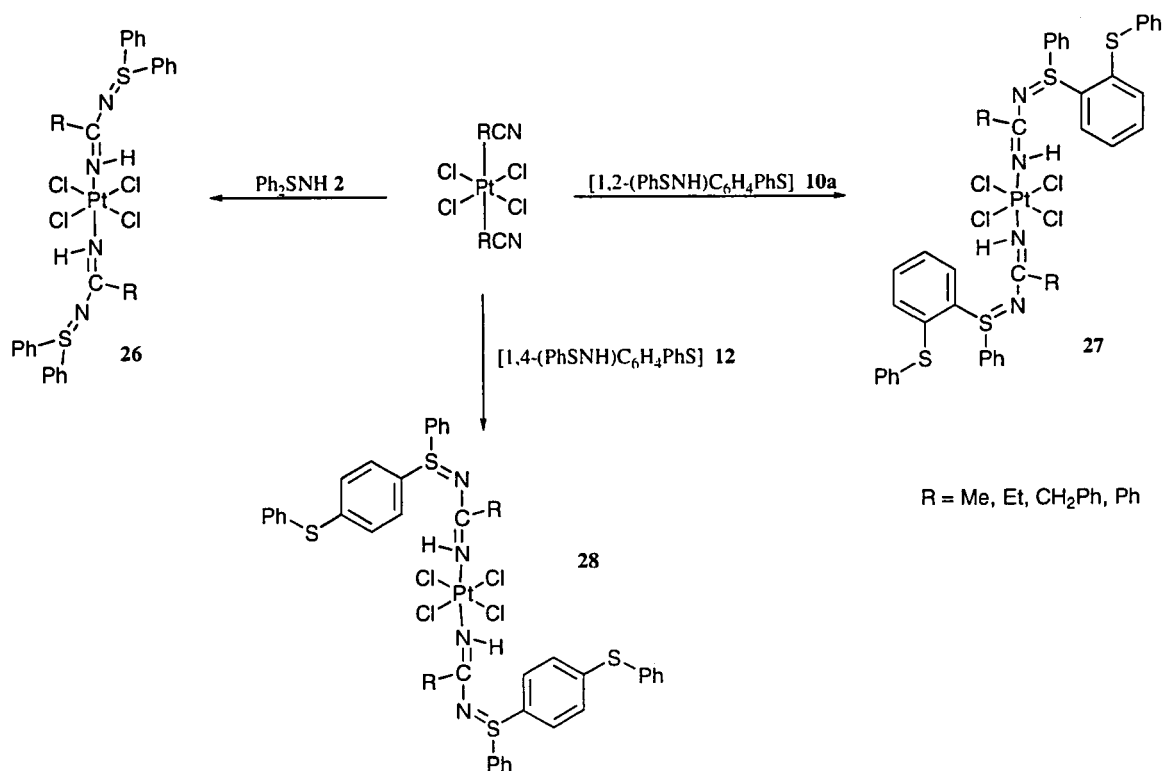
Scheme 12: Pt(IV) complexes of sulfimide ligands

Acid catalysed hydrolysis of these compounds gave a crystalline material on treatment with HCl, which proved to be the amidine Pt(IV) complex of the formula [PtCl₄{NH=C(NH₂)R}₂] along with diphenyl sulfoxide (**scheme 13**). *Mono*chloro and dichloro diphenyl sulfides, formed as secondary products on deoxygenation of Ph₂SO with HCl were also detected in the reaction mixture.
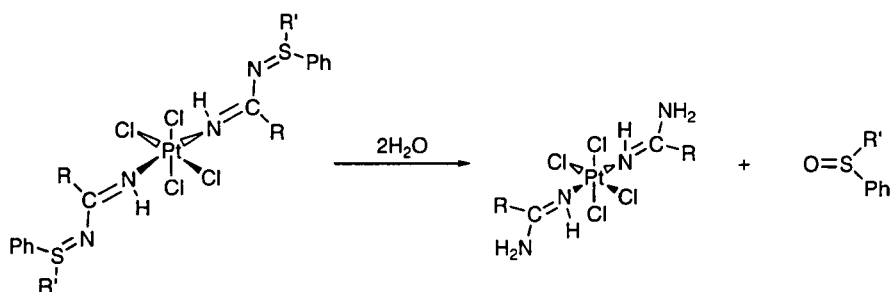
Scheme 13: Acid catalysed hydrolysis of the heterodiazadiene complexes

The heterodiazadiene ligands are liberated by the use of dppe, which acts in two ways, one as a reducing agent and the other as a substituting group in order to release the heterodiazadienes from the platinum centre (**scheme 14**). This constitutes a novel route to the isolation of these rare types of compounds.
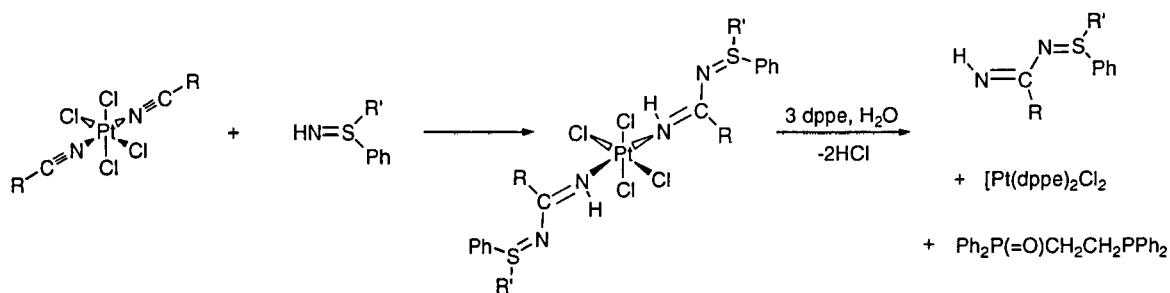
Scheme 14: The liberation of heterodiazadiene ligands using dppe

3.2.5 Reaction of [1,2-(PhSNH)C₆H₄PhS] 10a with [(PhCN)PdCl₂] 29

The 1:1 reaction of **10a** with **29** gave interesting results. A precipitate was present after addition of the ligand **10a**, which then redissolved with stirring, and when left to stand overnight the formation of red/orange crystals occurred. The crystal structure shows that the ligand has bonded to the palladium metal at the sulfur and the nitrogen sites of the sulfimide forming the structure [Pd(PhSC₆H₄S(Ph)SPh(NH)Cl₂] **30** (**figure 23**). This shows the first example of how **10a** can be used as a bidentate ligand.
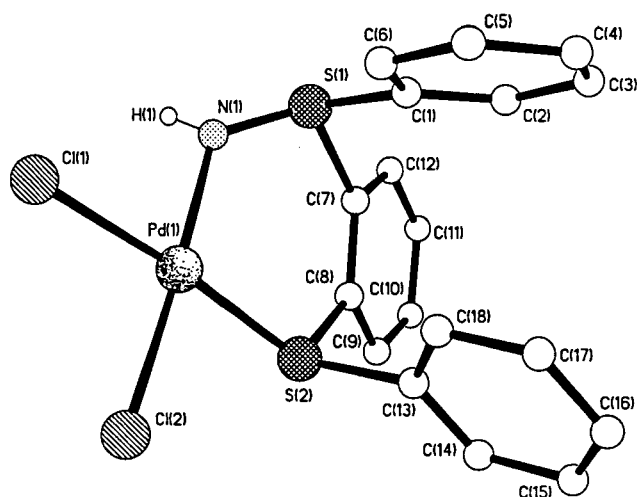
Figure 23: Crystal structure of 30. Selected bond distances (Å) and angles (°): S(2)–Pd(1) 2.267(6), S(1)–N(1) 1.597(18), N(1)–Pd(1) 2.019(18), N(1)–Pd(1)–Cl(1) 85.58(6), S(2)–Pd(1)–Cl(1) 165.25(2), N(1)–Pd(1)–Cl(2) 166.40(6), S(2)–Pd(1)–Cl(2) 84.24(2), N(1)–Pd(1)–S(2) 98.00(6), S(1)–N(1)–Pd(1) 127.27(11).

The six membered metallocycle shows significant deviation from planarity where the two sulfurs appear 0.282 Å (S1) and 0.216 Å (S2) above the mean plane of the six atoms, this constitutes a rare example of a XNSCCS ring. A search of the Cambridge

Structural Database reveals only eight examples where such an arrangement is observed (**figure 24**).[7,8] As **figure 24** shows, the only examples (**a** and **b**) in which atom X is a metal contain a tridentate ligand.[9] The rest consist of the two examples shown wherein X is a nitrogen atom (**c** and **d**) together with four examples in which this atom is carbon (including the one shown, **e**).[10,11,12,13,14,15]
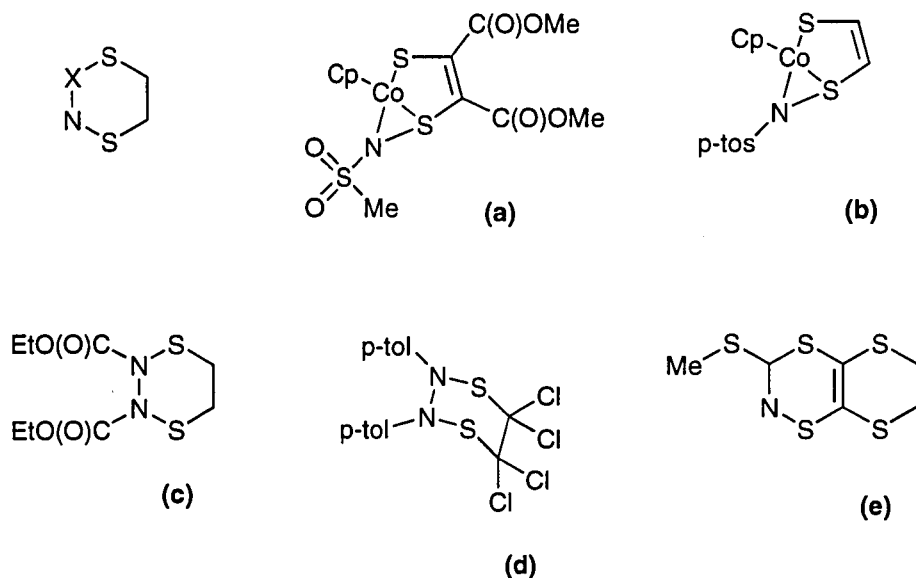
Figure 24: Previous examples of species exhibiting the XSCCSN cyclic unit observed in structure 30

Perhaps the most intriguing feature of the structure of **30** is the fact that the molecules arrange themselves into dimers (**figure 25**). These units are held together by hydrogen-bonding between the N-H groups and chlorides of opposite molecules. The contact between molecules is close, with a Pd-Pd distance of 3.512 Å. Interestingly, this value is almost exactly the same as the closest Pd-Pd interactions in $[Pd(S_2N_2H)(PMe_2Ph)_2][BF_4]$ which also has Pd attached to a sulfur and to an N-H unit on an S-N bond.[16] In that case a 1-D structure was formed by an infinite array of the cations; in the case of **30** this cannot take place. The orientation of the non-bridging

phenyl groups prevents the close approach of any further molecules. The lengths of the two Pd-Cl bonds within the molecule differ from each other by 0.02 Å, with the chlorine *trans* to the sulfur being shorter than the chlorine atom *trans* to the nitrogen (2.30 Å *cf.* 2.32 Å respectively). This is in contrast to hard soft/acid base theory, where we would expect the Pd-Cl bond length trans to the nitrogen atom to be longer than the Pd-Cl bond trans to the sulfur; and due to nitrogen being a harder base than sulfur. This indicates that the sulfur atom is more weakly bound to the soft acid of the palladium metal centre than the nitrogen atom.
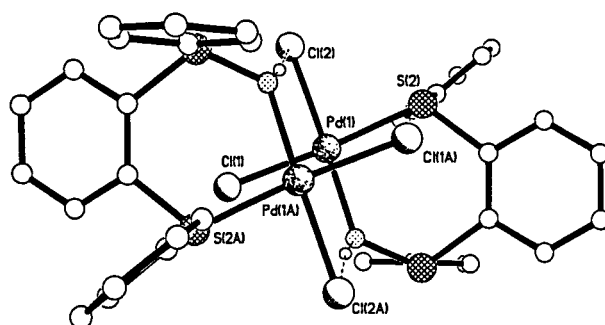
Figure 25: The formation of dimers within the overall structure of 30.

Intradimer distances (Å) and angles (°): Pd(1)-Pd(1A) 2.492, S(2)-Cl(1A) 2.406,

N(1)-Cl(2A) 2.447(2), N(1)-H(1)-Cl(2A) 143.0(2).

That the thio-ether group of **10a** should coordinate to a metal centre is of no great surprise, given that the coordination chemistry of such units is extensive. In general, however, such ligands are relatively weakly bound and indeed can often act as easily substituted leaving groups. Of the two coordination sites in **30** one would thus expect the Pd-S bond to be broken by an incoming ligand and this can be demonstrated by the reaction of **30** with triphenylphosphine (PPh$_3$).

Slow addition of solid PPh$_3$ to a stirred solution of **30** in CH$_2$Cl$_2$ resulted in lightening of the colour of the solution; removal of the solvent *in vacuo* followed by trituration with petroleum ether resulted in a yellow solid [Pd(PPh$_3$){(PhS)C$_6$H$_4$(PhSNH)}Cl$_2$] **31**. The ^{31}P NMR spectrum of this solid (CDCl$_3$) consists of a singlet at 27.7 δppm while the IR spectrum confirms the presence of bands typically associated with both sulfimide units (911 cm^{-1}) and with phospines (1096 cm^{-1}). Slow diffusion of ether into a CH$_2$Cl$_2$ solution of the product resulted in the formation of orange crystals for which X-ray crystallography revealed the structure shown in **figure 26**. As **figure 26** shows, **31** consists of a palladium centre coordinated to a PPh$_3$ and to [1,2-(PhSNH)C$_6$H$_4$PhS] (acting in this case as a *mono*dentate N-bound ligand) bound in *trans* fashion. Two *trans* chloride ligands make up the rest of the coordination sphere.

Figure 26: The X-ray crystal structure of 31. Selected bond distances (Å) and angles (°): N(1)–S(1) 1.602(6), Pd(1)–N(1) 2.094(6), Pd(1)–P(1) 2.2120(13), N(1)–Pd(1)–Cl(2) 84.46(17), P(1)–Pd(1)–Cl(2) 94.07(6), N(1)–Pd(1)–P(1) 168.21(17)
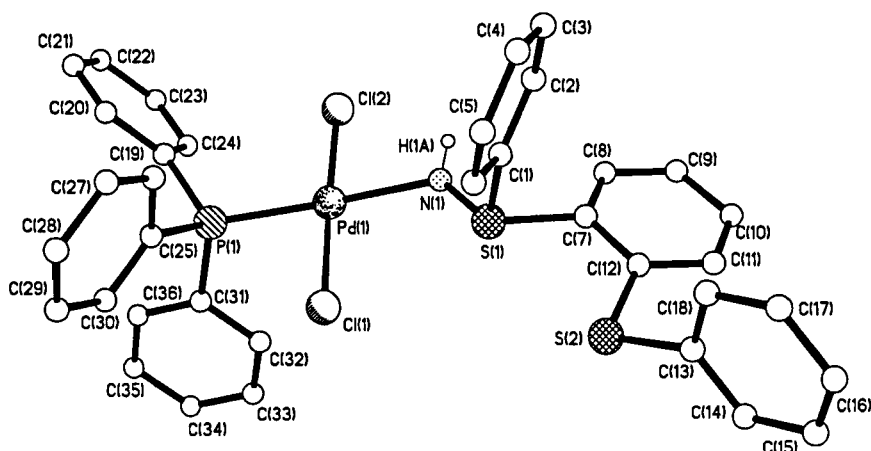
The course of the reaction of **30** with PPh$_3$ thus involves two steps - the substitution of the phosphine into the Pd-S bond, followed by isomerisation to the observed *trans*

arrangement. Presumably the latter effect is brought about by the significant steric interactions that would be present between the six phenyl groups in the initially formed *cis* intermediate. The ^{31}P chemical shift of the phosphine group is consistent with it being *trans* to an N-H unit.

Addition of the phosphine to **30** had to be very slow in order to obtain pure **31**. If this was not carefully observed then variable amounts of a yellow coloured, far less soluble product was obtained. Microanalysis indicates that this product is of the structure PdCl$_2$(PPh$_3$)$_2$ **32** and in such cases it is revealed in the ^{31}P NMR spectrum of the product by a peak at 23.4 ppm. The ability of PPh$_3$ to break the Pd-N bond as well as the Pd-S bond of the starting material **30** can be confirmed by addition of one molar equivalent of the phosphine to **30**. This results in the immediate precipitation of the sparingly soluble **31**.

3.2.6 2:1 reaction of [1,2-(PhSNH)C$_6$H$_4$PhS] 10a with [(PhCN)$_2$PdCl$_2$] 29

In the presence of two molar equivalents of **29** we see the formation of nitrogen bound sulfimide complex [Pd{(PhS)C$_6$H$_4$(PhSNH)}$_2$Cl$_2$] **33** in reasonable yields. The product was soluble with stirring in DCM and subsequently recrystallised by slow diffusion of Et$_2$O vapour into a DCM solution to give clear microcrystalline material that was solved using X-ray crystallography (**figure 27**).
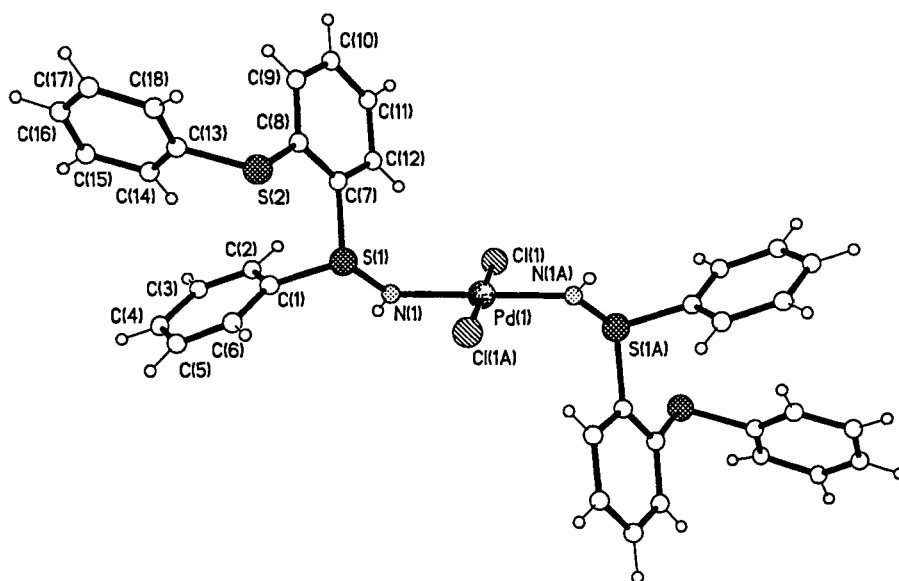
Figure 27: X-ray crystal structure of 33. Selected bond distances (Å) and angles (°): N-S 1.607, Pd-N 2.024, Pd-Cl 2.289, Cl-Pd-N 92.2 and 87.8, N-Pd-N, Cl-Pd-Cl 170 by symmetry, Pd-N-S 118.6

Infrared data shows peaks at 3052 and 898 cm^{-1} both due to the N-H and S=N stretches of the sulfimide respectively. The mass spectrometry data proved useful by showing peaks at [761] and [723], due to the fragmentation patterns and hence attributable to the loss of the two chlorine atoms respectively. A further peak is observed at [600] units this is due to the further loss of a [PhSNH] fragment along with a further loss of 187 mass units, at [413], due to the other half of the ligand (Ph$_2$S). It is quite common for **10a** to break up into this pattern and can be seen in the original spectra of the ligand. X-ray crystallography (**figure 27**) reveals a square planar structure, where the ligands are nitrogen bound to the palladium atom in a *trans* configuration. The data reveals a truly symmetrical structure with N-Pd-N and Cl-Pd-Cl bond angles of 180° and equidistant Pd-N bond lengths of 2.027 Å.

3.2.7 Heck reaction using [Pd{(PhS)C₆H₄(PhSNH)}Cl₂] 30 as the catalyst

Richard Heck in the early 1970's discovered a palladium-catalysed reaction in which the carbon group of a haloalkene or haloarene is substituted for a hydrogen on the carbon-carbon double bond (a vinylic hydrogen) of an alkene.[17] This reaction, known as the Heck reaction, is particularly valuable in synthetic organic chemistry because it is the only general method yet discovered for this type of substitution.

The form of the palladium catalyst most commonly added to the reaction medium is palladium(II) acetate, Pd(OAc)₂. This compound and others of the same oxidation state are better termed precatalysts because the catalytically active form of the metal is a complex of the zero-valent metal, Pd(0), formed in situ by reduction of Pd(II) to Pd(0). The complex is usually formed by reaction with added ligands (L) to give the actual catalyst, Pd(0)L₂. This catalyst then reacts with the organic halide to begin the catalytic cycle. Complex 30 was found to be of suitable character for use as a catalyst in the Heck reaction. The Heck reaction was used, in this instance, to produce *trans* stilbene 34 from the starting materials of phenyl iodide 35 and styrene 36, along with the palladium complex 30 to aid the reaction in catalytic amounts.

Stage 1: In situ generation of Pd(0) species

Scheme 15: Formation of the palladium(0) species 37
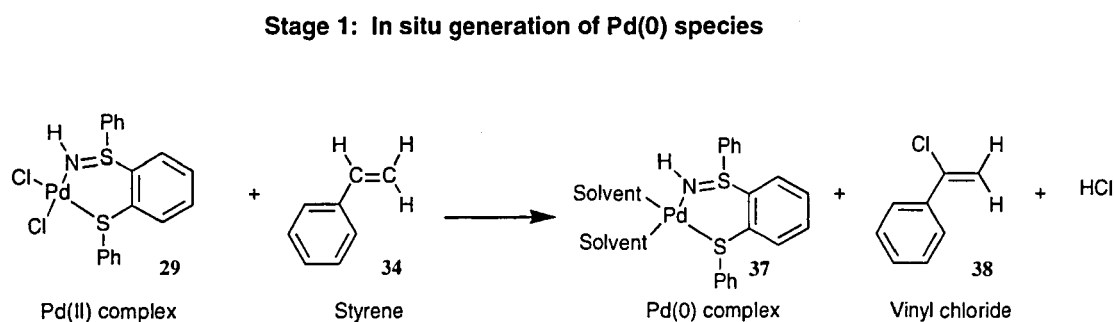
As seen in **Scheme 15**, stage 1 involves the two electron reduction of Pd(II) **30** to Pd(0) **37** which is brought about by the olefin **34** and produces a vinyl chloride **38** and HCl. Because the catalyst is present in such tiny amounts, only an insignificant amount of **36** is lost to this reaction.

We can observe from the catalytic cycle of the heck reaction (**scheme 16**) a series of steps are involved. Step 1 sees the oxidative addition of the haloarene **35** to the Pd(0) complex **37**, which in turn gives a tetracoordinated Pd(0) complex **39** containing both the R and X groups bonded to the palladium atom. In step 2 we see the syn addition of styrene **36** and PdL_2X which gives an intermediate **40**, which undergoes internal rotation about the central carbon-carbon single bond in Step 3 to place H and PdL_2X syn to each other **41**. Syn-elimination of H and PdL_2X in Step 4 gives *trans* stilbene **34** and the acid $HPdL_2X$ **42**. Reductive elimination of HX induced by the base gives the conjugate acid of base B and regenerates the $Pd(0)L_2$ catalyst **37** in step 5.
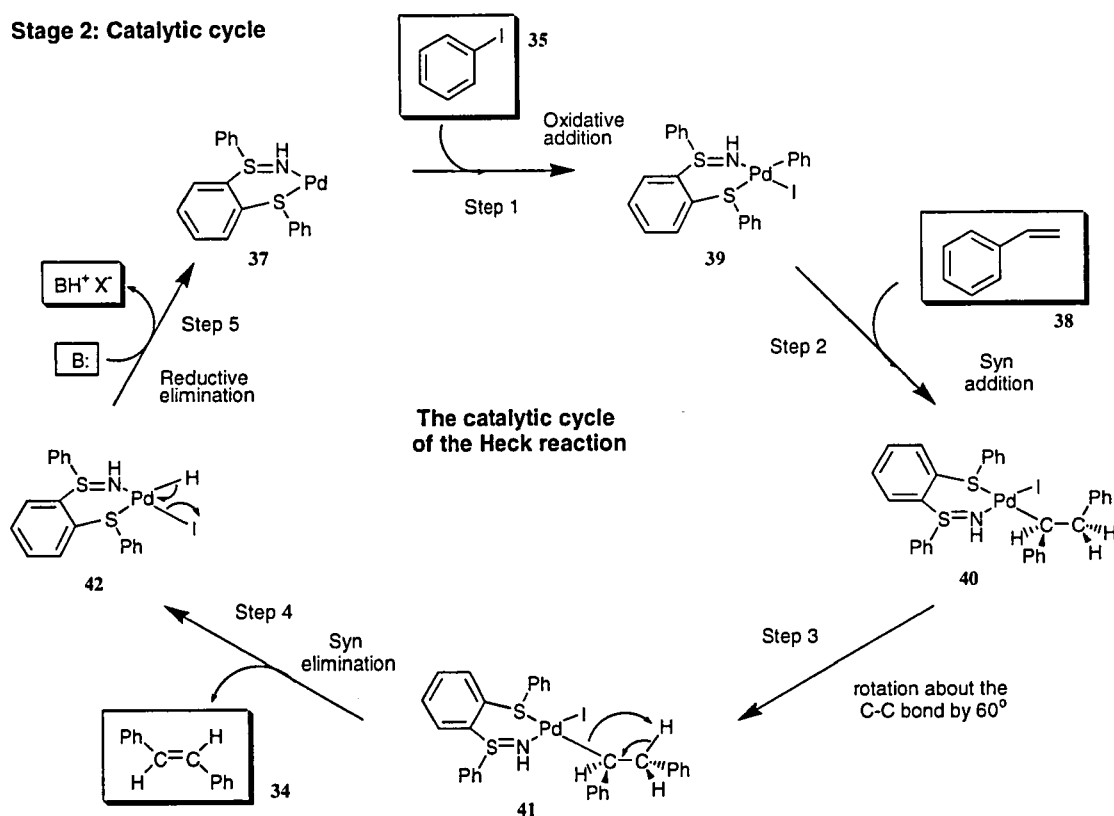
Scheme 16: The catalytic cycle of the Heck reaction using 30 as the catalyst.

The reaction gave *trans* stilbene **34** in yields of 46%, these are comparatively average to other catalysts used in this reaction. The reaction was performed under only one set of conditions, which leaves the opportunity of optimising the parameters (temperature, solvent, time and catalytic concentration) in future reactions in order to increase subsequent yields.

3.2.8 Reaction of [1,2-(PhSNH)C₆H₄PhS].H₂O 10b with CuCl₂

The 2:1 reaction of the hydrated ligand **10b** with CuCl₂ produced two types of crystals with the formula [Cu{(S(Ph)C₆H₄S(Ph)NH)₂}Cl₂] **43**, drawing similarities with the previously reported analogous reaction using **2**.[18] The reaction was performed in acetonitrile and then the appropriate recrystallisation technique was employed to

produce two types of material, blue crystals **43a** and a green amorphous solid **43b**. Both **43a** and **43b** yielded from dissolving in dichloromethane, adding a small amount of petroleum ether (60-80°) and subsequently allowing the solvents to evaporate.

The IR data suggests the presence of two allogons (**scheme 17**) as we see two N-H stretches present in the blue crystals (3311,3277cm^{-1}) and only one corresponding stretch in the green material (3314 cm^{-1}). X-ray crystallography of the blue crystals has shown that there are two ligands, nitrogen bound, present around the metal centre in a *trans* arrangement. The disorder in the structure of the blue crystals shows that the S-Ph atoms can have one of two possible spatial arrangements that would affect the packing of the structure.

Square planar
blue crystals

Distorted tetrahedral
green crystals
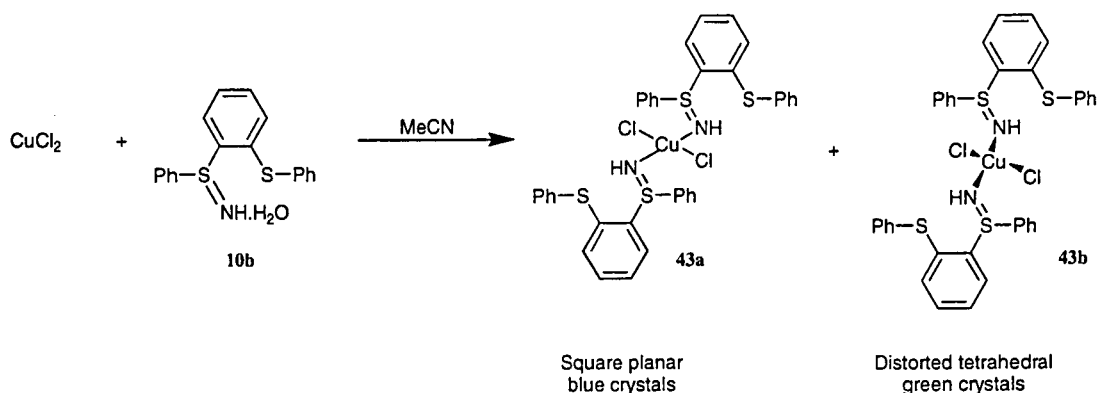
Scheme 17: Proposed isomers of [Cu{(S(Ph)C₆H₄S(Ph)NH)₂}Cl₂] 43

Previous attempts to coordinate four Ph$_2$SNH **2** ligands around a copper centre were successful which led us to undertake the analogous reaction using **10b**. In this instance the 4:1 reaction of **10b** with CuCl$_2$ was unsuccessful, the sulfimide proved to be too large a molecule with the bulky phenyl groups being the cause of steric hinderance. Then it is not surprising that a 6:1 reaction of **10b** with CoCl$_2$ was also

63

unsuccessful using the mixed sulfide/sulfimide ligand also we suspect due to steric hinderance of the phenyl groups.

3.2.9 Reaction of [1,2-(PhSNH)C$_6$H$_4$PhS] 10a with [COD]$_2$Rh$_2$Cl$_2$ 44

The reaction of **44** with **10a** proved to be most interesting. This reaction ran smoothly and quickly, with the addition of AgSbF$_6$ providing a source of counter ion. The recrystallisation by slow diffusion of Et$_2$O vapour into a DCM solution gave golden coloured plate like crystals, with the formula [Rh[COD]{(PhSNH)C$_6$H$_4$PhS}] **45**, which unfortunately proved unsuitable for X-ray crystallography (this is only a predicted product and is based on the reaction of other ligands similar to 10a and the products that they give with this metal complex).

Infrared data exhibited peaks at 3112 and 917 cm^{-1} both due to the N-H and S=N stretches of the sulfimide respectively. The mass spectrometry data proved useful by showing a peak at [520] attributable to the mass ion, followed by a peak at [505] due to the loss of the NH unit of the sulfimide. The ^{1}H NMR data for the structure performed in CDCl$_3$ shows a group of phenyl multiplets at 7.45-7.61 δppm integrating as 10H. Two sets of doublet of doublets are present at 7.98 and 7.03 δppm which integrate 2 x 2H and are attributable to phenyl protons which have shifted due to close interactions with other phenyl protons. At 5.15 and 4.69 δppm we see multiplets which integrate to 2 x 2H and can be assigned to the alkenic protons which are complexed to the rhodium atom. The multiplet peaks observed at 2.98 and 2.12 δppm integrate to 2 x 4H and represent the aliphatic protons that make up the rest of the COD structure.

If we compare the peaks attributable to the aliphatic protons in the COD moiety we see that they have shifted downfield to the analogous peaks seen in the rhodium starting material **44** (2.98 and 2.12 δppm compared with 2.50 and 1.73 δppm respectively). By far the most interesting observation is the way in which the alkenic protons at 5.15 and 4.69 δppm are split into two when the starting material shows just one peak for these protons at 4.21 δppm, it is interesting to note that these protons also exhibit a downfield shift.
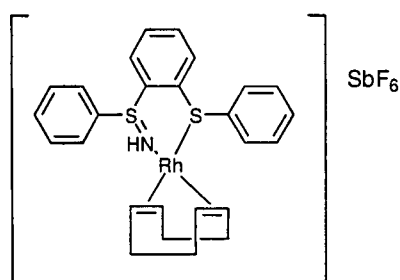
Figure 28: Proposed structure of [Rh[COD]{(PhSNH)C₆H₄PhS}] 45

These anomalies can be explained by the fact that they are no longer in a symmetrical environment in our sulfimide complex as they were in the rhodium starting material **44**. The spectrocopic data gives us the confidence to derive a structure in which we would see the ligand bound to the rhodium atom, by both the sulfur of the sulfide and the nitrogen of the sulfimide, in a bidentate fashion (**figure 28**).

3.2.10 Reaction of [1,2-(PhSNH)C₆H₄PhS] 10a with Ru₂(Cy)₂Cl₄ 46

In a further attempt to prove the ability of **10a** to act in a bidentate fashion, the reaction of the dimer **46** with **10a** was performed. This reaction gave an orange coloured product, predicted to have the formula [RuCy{(PhSNH)C₆H₄PhS}Cl₂] **47** in

a reasonable yield. This was further recrystallised by slow diffusion of Et$_2$O vapour into a DCM solution. Sadly the recrystallised product was not suitable for use in X-ray crystallography, but from the analytical data we can suggest a structure (based on similar reactions) where the ligand is bound to the ruthenium atom by both the nitrogen of the sulfimide and the sulfur atom of the sulfide (**figure 29**).
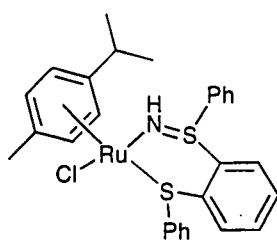
Figure 29: Suggested structure of [RuCy{(PhSNH)C$_6$H$_4$PhS}Cl$_2$] 47

The ^{1}H NMR data for complex **47**, performed in CDCl$_3$, shows a group of phenyl multiplets at 7.12-7.51 δppm integrating as 13H, these peaks have shown a significant shift from those of the uncoordinated ligand (7.53-7.65 δppm). More interesting is that the doublet of doublet peaks are still present but have not shifted significantly, 7.90-7.97 δppm compared with those of the ligand **10a** at 7.93-7.99 δppm. The NMR of the original starting material shows two sets of doublets between 5.31-5.47 δppm which integrate to 4H, on coordination of our ligand we see these are split into four sets of doublets present between 5.02-5.48 δppm, these peaks are attributable to the four aromatic protons present on the cymene moiety. We also observe in the starting material a multiplet peak at 2.82-3.00 δppm, which is seen to split into two multiplets at 3.35-3.52 δppm and 2.85-3.02 δppm integrating to 1H. The latter of the two is similar to that of the starting material, hence we should deduce that there could be

some of it still present in solution, although further duplicated peaks are not observed in any other part of the spectra. A further peak at 2.15 δppm integrating to 3H is due to the methyl protons on the CH_3 functional group of the cymene. The last peak seen on the spectra is a doublet at 1.25-1.28 δppm integrating to 6H and is attributable to protons on the two methyl groups of the propyl moiety.

The mass spectrometry data shows a peak at [580] attributable to the mass ion, further fragmentation results in a peak at [544] mass units due to the loss of a chlorine atom. In the infrared spectra we observe a peak at 3054 cm^{-1}, which is characteristic of the N-H stretch of the sulfimide, and a peak at 926 cm^{-1} showing the S=N bond of the sulfimide. When compared to the spectra of the original ligand a considerable difference in wavenumbers can be seen in the two peaks (*cf.* 3130 and 920 cm^{-1}) both the [N-H] stretch and [S=N] stretch are respectively shifted downfield as a result of their coordination to the ruthenium atom.

Other metal complexes that have been reacted with **10a** are $Mo(pipirazine)_2(CO)_4$ **48**, $ReBr(CO)_5$ **49** and $Fe_3(CO)_{12}$ **50** but spectroscopic results proved inconclusive at determining the nature of the products.

3.3 Reactions of [1,4-(PhSNH)C₆H₄PhS] 12 with various metal complexes

The ligand **12** cannot be used in a bidentate fashion, as the structural conformation (i.e. *para*) does not allow for such reactions. This however does not negate its use as a coordinating ligand as we have readily observed how strongly the nitrogen, of the sulfimide species, coordinates to metal centres.

3.3.1 Reaction of [1,4-(PhSNH)C₆H₄PhS] 12 with Pd(PhCN)₂Cl₂ 29

In the 2:1 reaction of **12** with **29**, performed in THF, results in the formation of, the nitrogen bound sulfimide compound [PdCl₂(1,4-(PhS{NH})(PhS)C₆H₄)₂] **51a** in good yields **(figure 30)**. The resulting pure orange solid was collected by filtration after Et₂O was added to the clear orange solution.
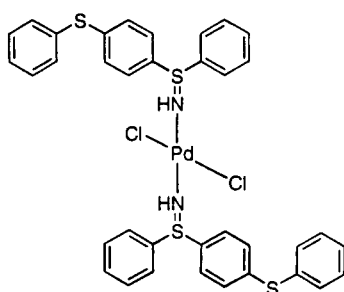
Figure 30: Proposed structure of [PdCl₂(1,4-(PhS{NH})(PhS)C₆H₄)₂] 51a

The ^{1}H NMR data for the structure, performed in CDCl₃, shows a group of phenyl multiplets at 7.17-7.59 δppm integrating as 28H, these peaks have shown a slight shift from those of the ligand **12** (7.14-7.49 δppm). The infrared data shows the presence of the N-H group with a stretch at 3216 cm^{-1} along with the S=N stretch at 906 cm^{-1}. The N-H and S=N stretches differ from that of the original uncoordinated ligand **12** and are seen at 3235 cm^{-1} and 924 cm^{-1} respectively.

The 1:1 reaction was also attempted and performed under the same reaction conditions. Spectroscopic data gave us the ability to suggest a structure where we have a nitrogen bound ligand, a benzonitrile ligand and two chlorine ligands around the palladium centre **(figure 31)**.
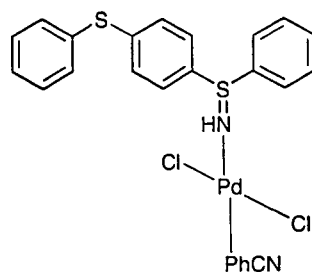
Figure 31: Proposed structure of [Pd (PhCN){(1,4-(PhS{NH})(PhS)C$_6$H$_4$)$_2$}Cl$_2$]

51b

3.3.2 Reaction of [1,4-(PhSNH)C$_6$H$_4$PhS] 12 with CuCl$_2$

The 2:1 reaction of **12** with CuCl$_2$ produced two types of crystals of the formula [Cu{(1,4-(PhS{NH})(PhS)C$_6$H$_4$)$_2$}Cl$_2$] **52** drawing similarities with the previously reported analogous reactions using the ligands **10b** and **2**. The corresponding recrystallisation techniques were employed to produce two forms of material, dark green crystals **52a** and pale green crystals **52b**. The dark green crystals yielded from dissolving in dichloromethane, adding a small amount of petroleum ether (60-80°) and subsequently allowing the solvents to evaporate. However, dark and pale green crystals were obtained by recrystallising from hot MeCN. Both types of crystal proved inadequate to gain a structure using X-ray crystallography (**scheme 18**).
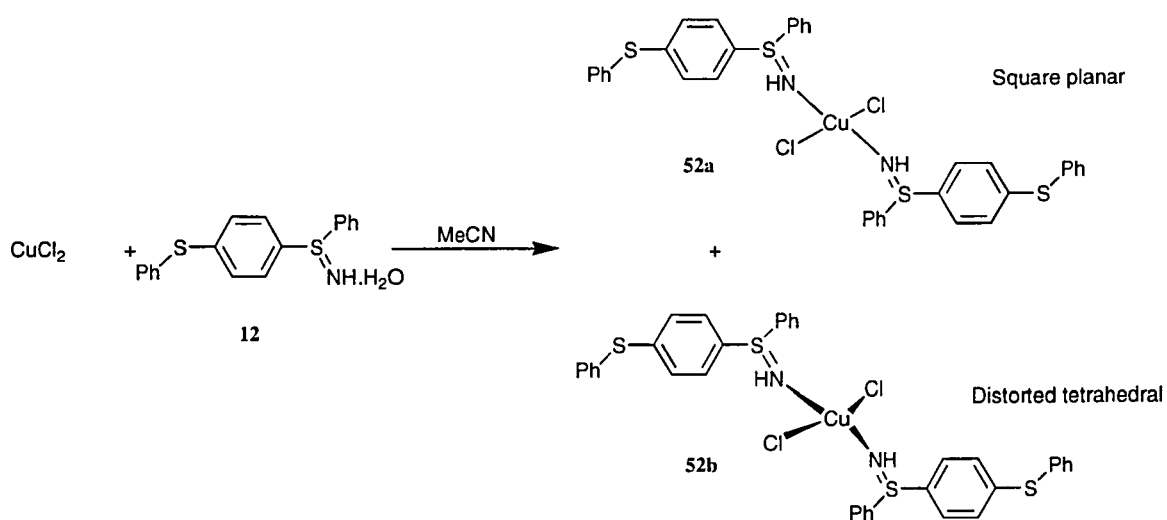
Scheme 18: Two possible isomers of [Cu{(1,4-(PhS{NH})(PhS)C₆H₄)₂}Cl₂] 52

Infrared data shows stretches at 3241 and 922 cm^{-1} which correspond to N-H and S=N bonds respectively. Microanalysis data proved useful in determining the nature of the structure, which we suggest is two ligands nitrogen bound to the copper metal. However we cannot determine whether these two types of crystal are of different configurations (i.e. *trans* or *distorted tetrahedral*) as in the previously reported reaction with **2**, without the use of X-ray crystallography.

3.4 Conclusion

Sulfimide ligands have proved to be most versatile at participating in coordination chemistry. Of all the ligands, the one that proved to be most problematic was compound **7**; this was due to its insolubility in any solvent but methanol. Despite this, a slow reaction in DCM gave us a most interesting dimerised product, the like of which has not been previously observed with any other sulfimide species to date.

Further to this we see the mixed sulfide/sulfimide compound **12** participating in bonding through the nitrogen atom with palladium and copper species. The true potential of this ligand will be in its further use as a bridging ligand, where thiophillic metal atoms can be adjoined to metal complexes, which can only participate in bonding through the nitrogen atom.

When discussing the successes of this research, one has to mention the truly versatile ligand **10**. Here we have both the sulfur and nitrogen atoms in perfect positions to able to create a bidentate complex with a palladium metal species. The palladium(II) metal sulfimide complex shows great potential to compete with other catalysts in reactions, for example the Heck,[17] Suzuki,[19] and Stille.[20] The rhodium and ruthenium reactions using **10** also look promising, all structural data points to the formation of two other bidentate complexes with the two metal centres. The success of the ligand does not stop at its ability to create bidentate metal species; it also possesses the capacity to react with platinum metal nitrile complexes to give the corresponding nitrile–sulfimide addition product. The reaction with $CuCl_2$ was interesting in the fact it was analogous to that of the previously mentioned reaction with **2**. Two types of crystals had formed but there inability to be solved by X-ray crystallography meant that we were unable to confirm whether they were due to two different allogons.

All of the ligands have proved to be most useful within the realms of coordination chemistry. The sulfimides success in this area is of much interest, hence proving they are a viable alternative to nitrogen-phosphorus systems or sulfoxide systems, which have proved their capabilities in previous years. It may take some time to develop these ligand systems in order for them to truly compete but a definite advantage of the

sulfimides is that they are easily synthesised and completely stable in air as the resulting metal complexes.

3.5 References

[1] P.F.Kelly, A.C.Macklin, A.M.Z.Slawin and K.W.Waring, *Polyhedron*, 2000, **19**, 2077-2081

[2] P.F.Kelly, S.-M.Man, A.M.Z.Slawin and K.W.Waring, *Polyhedron*, 1999, 3173

[3] P.F.Kelly, A.M.Z.Slawin and K.W.Waring, *Inorg.Chem.Commun.*, 1998, **1**, 249

[4] P.F.Kelly, A.M.Z.Slawin, K.W.Waring and S. Wilson, *Inorg.Chim.Acta.*, 2001, **312**, 201

[5] P.F.Kelly and A.M.Z.Slawin, *J.Chem.Soc.Chem.Commun.*, 1999, 1081

[6] K.Kitano, R.Tanaka, T.Kimura, T.Tsuda, S.Shimizu, H.Tagaki, T.Nishioka, D.Shiomi, A.Ichimura, I.Kinoshita, K.Isobe and O.Shun'ichiro, *J.Chem.Soc.Dalton Trans.* 2000, 995

[7] F.H.Allen and O.Kennard, Chem.Des.Autom.News., 1993, **8**, 1

[8] F.H.Allen and O.Kennard, Chem.Des.Autom.News., 1993, **8**, 31

[9] M.Nomura, T.Yagisawa, C.Takayama, T.Sugiyama, Y.Yokaguma, K.Shimizu, A.Sugimori and M.Kajitani, *J.Organomet.Chem.*, 2000, **611**, 376

[10] V.A.Starodub, *Zh.Strukt.Khim.*, 1998, **39**, 108

[11] M.R.Bryce, G.R.Davison, A.S.Batsanov and J.A.K.Howard, *J.Chem.Soc.Perkin Trans.1*, 1992, 2295

[12] M.R.Bryce, G.R.Davison, A.S.Batsanov and J.A.K.Howard, *J.Chem.Soc.Perkin Trans.1*, 1997, 1157

[13] M.R.Bryce, S.Yoshida, A.S.Batsanov and J.A.K.Howard, *J.Chem.Soc.Chem.Commun.*, 1992, 478

[14] K.T.Potts and J.S.Baum, *J.Heterocycl.Chem.*, 1991 **28**, 1637

[15] K.-H.Linke and H.G.Kalker, *Z.Anorg.Allg.Chem.*, 1977, **434**, 157

[16] R.Jones, P.F.Kelly, D.J.Williams and J.D.Woollins, *J.Chem.Soc.Dalton Trans.*, 1988, 803

[17] R.F.Heck, *J. Am. Chem. Soc.*, 1969, **91**, 6707

[18] P.F.Kelly, A.M.Z.Slawin and K.W.Waring, *J.Chem.Soc.Dalton Trans.*, 1997, 2853

[19] N.Miyaura and A.Suzuki, *Chem.Rev.* 1985, **95**, 2457

[20] W.J.Scott, G.T.Crisp and J.K.Stille, *J. Am. Chem. Soc.*, 1984, **106**, 4630

Chapter four
Synthesis and coordination chemistry of other
sulfimides
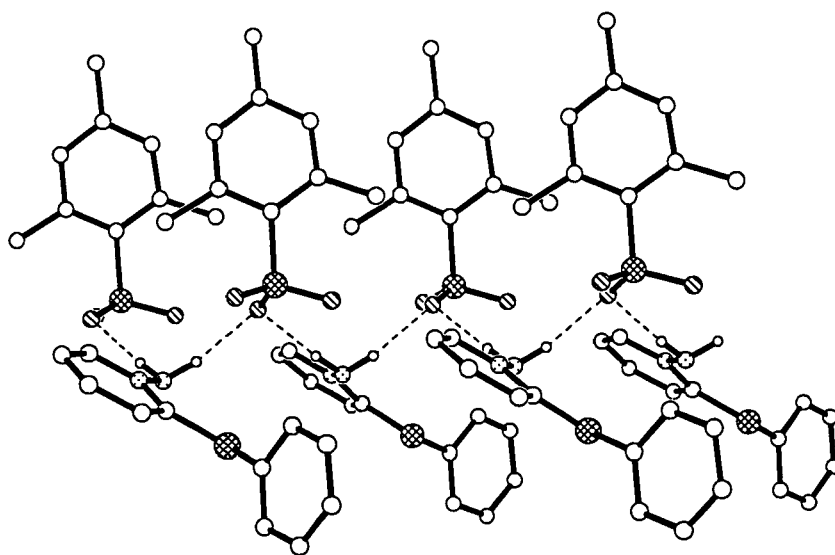
4.0 Synthesis and coordination chemistry of other sulfimides

Following the successes of the *ortho* and *para bis* and mixed sulfides/sulfimides **7, 10** and **12**, the synthesis of another novel ligand was attempted. Recent studies have focussed on so called 'pincer ligands' where tridentate attachment to the metal centre is observed.[1] It was thought that our research interest would fit into this category, knowing of the strong coordinating ability of the nitrogen atom to various metal centres. The other advantage our ligands have is their stability in air, unlike their carbon-phosphorus or nitrogen-phosphorus counterparts. The following are attempts to make such ligands by utilising the *meta* substituents in order to form the tridentate pincer ligands of the type seen in **figure 32**.

R = C, N or P
R' = Alkyl or aromatic
R''= N or P
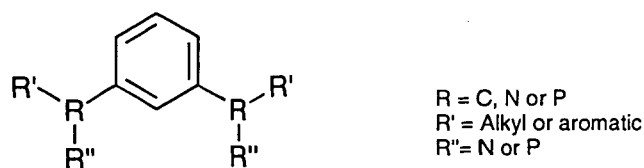
Figure 32: Example of a general pincer ligand

Research has focussed on these ligands because of their ability to activate the C-H bond (orthometallation) when used with a wide variety of metal complexes. These unique compounds have been utilised to form the basis of some important chemical reactions. These include dehydrogenation,[2] coupling,[3] insertion,[4] hydrogenation,[5] addition,[6] activation of hydrocarbons and asymmetric synthesis.[7, 8]

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4.1 Synthesis of *meta bis*-sulfimide species

The simplest starting point was to produce the *meta* analogue of the *bis*-(phenylthio)benzene starting materials **5** and **9**. The reagents were readily available and the reaction was relatively simple and efficient giving reasonable yields of 71%.

4.1.1 Synthesis of [1,3-(PhS{NH₂})₂C₆H₄][mesSO₃]₂ 53

1,3-*bis*(phenylthio)benzene **54** was reacted with **1** gaining success at aminating both sulfur atoms (**figure 33**). During the initial stage of the reaction a gas was found to evolve and a dark red effervescent solution was observed, which after several hours of stirring turned yellow. The solution was dried *in vacuo* and the resulting sticky white solid was washed with several portions of Et₂O and left to dry under vacuum.
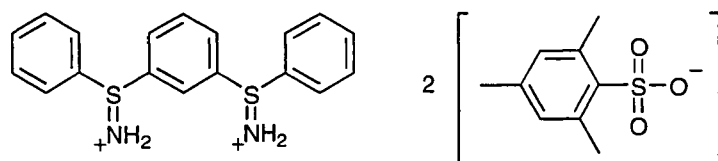
Figure 33: [1,3-(PhS{NH₂})₂C₆H₄][mesSO₃]₂ 53

Infrared results confirm the presence of the mesitylenesulfonate anion at 1185 cm⁻¹ with aromatic stretches at 846, 749 and 682cm⁻¹. From the mass spectrometry data we see the presence of the mass ion plus the mesitylenesulfonate anion with a peak at [526] mass units. The peak of the mass ion at [325] units can be seen next, followed by further loss of 15 mass units at [310] due to loss of NH. The ¹H NMR data reveals a multiplet at 7.19-7.91 δ ppm integrating to 18H and attributable to the aromatic

protons. Singlet peaks at 2.46 and 2.14 δ ppm can be assigned to aliphatic protons of the mesitylenesulfonate anion integrating as 12H and 6H respectively.

Many attempts to recrystallise this product have failed, however the most promising effort was that of replacing the mesitylenesulfonate anion with [BPh$_4$]$^-$ by the addition of Na[BPh$_4$]. Although this appeared to be successful in the formation of the new salt we have been unable to crystallise this material. We eventually gained some success by changing the counter ion to chloride, by the addition of [PPh$_4$]Cl (*via* precipitation of [PPh$_4$][BPh$_4$]); the crystal structure of [1,3-(PhS{NH$_2$})$_2$C$_6$H$_4$][Cl]$_2$ **55** can be seen below (**figure 34**).
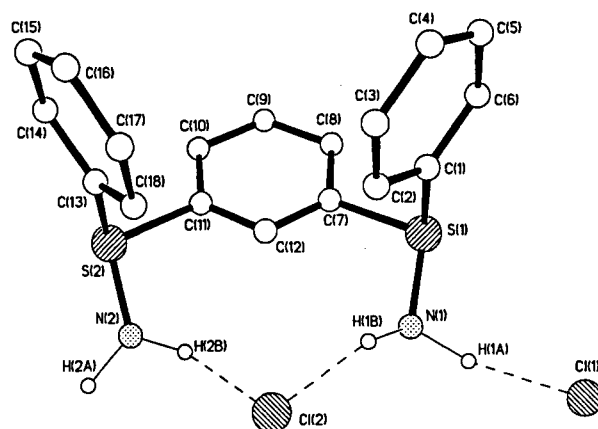
Figure 34: Crystal structure of [1,3-(PhS{NH$_2$})$_2$C$_6$H$_4$][Cl]$_2$ 55

We see that an array formation is produced from hydrogen bonding between the H-Cl atoms (**figure 35**). A *cis* conformation of both phenyl rings can be seen around the two sulfur atoms. The hydrogen bonding between the H-Cl may be causing the molecule to take on this formation in space.
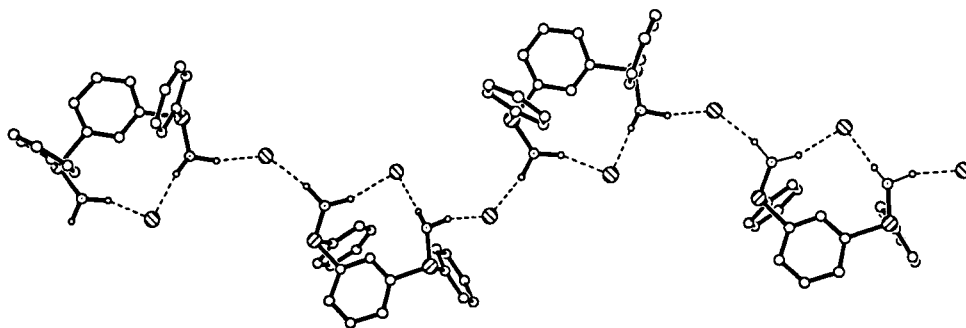
Figure 35: Crystal structure of 55 showing hydrogen bonding array formation

Work within the group is taking place in order to explore these interesting molecular arrays and their applications in the area of hydrogen bonding and supramolecular chemistry.[9]

4.1.2 Synthesis of [1,3-(PhSNH)$_2$C$_6$H$_4$] 56

The thought of deprotonating the above complex seemed relatively straightforward and, as with the other *bis*-sulfimide **7**, we attempted to use DBU. This was much more troublesome than first anticipated. After the DBU had reacted the solution was reduced to dryness and then washed with several portions of distilled water, a technique that had been previously found to be successful at eliminating the DBU salt. Although this seemed to produce a different darker coloured oil, it was found by analysis that this was in fact the starting material **53** (**scheme 19**).

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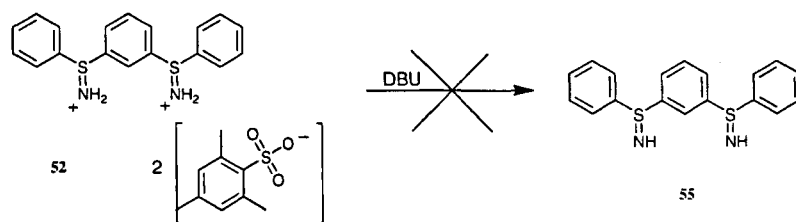
Scheme 19: Unsuccessful deprotonation attempt of 53 using DBU

The conclusion that water was not sufficient at washing away the DBU salt was evident and hence the product was extracted into a less polar solvent, namely toluene. Toluene was chosen because it was unlikely that the DBU salt would dissolve in it due to its polar nature. This was partially successful and appeared to eliminate the DBU salt more efficiently, but not completely, than washing with water.

The oily product was obtained once the toluene portions had been reduced and dried under vacuum. Alas, the ^{1}H NMR data showed the presence of DBU in every case, even after washing with petroleum ether. The purity of this ligand was of some concern as can be seen in the analysis of the following spectroscopic data.

The infrared data shows the presence of a broad stretch at 927 cm^{-1}, attributable to the S=N bond. This indicates that there is some of the desired free sulfimide **56** present in the reaction mixture, as is some of the protonated ligand **53** shown by a broad stretch at 1205cm^{-1} attributable to the mesitylenesulfonate anion. The N-H stretch is observed at 3051cm^{-1} along with aromatic and aliphatic stretches at 2928, 751 and 751cm^{-1} respectively. The ^{1}H NMR data for the product, performed in CDCl$_3$, showed the presence of DBU in all cases despite several extraction procedures using a variety of solvents. The mass spectrometry data using fast atom bombardment (FAB)

contains peaks attributable to the mass ion at [325]. This is followed by the loss of 15

mass units (NH) at [310] due to the S-N bond cleavage.

Other methods of deprotonation were attempted such as using an ion exchange resin,

Amberlite IRA-410; this did not seem to work efficiently, gaining poor yields and

inconclusive results.[10]   Another method used was to try liquid ammonia but this again

proved unsuccessful with no deprotonated product present in the final solution.

4.1.3 Reactions with the ligand [1,3-(PhSNH)$_2$C$_6$H$_4$] 56

Although the purity of the above free *bis*-sulfimide ligand 56 was questionable, it was

thought that the DBU salt, which proved difficult to remove, would not coordinate to

any of the metal centres used, nor prove to be a hinderance to the reactions. The

potential of this ligand to act as a pincer has been preliminarily tested on a variety of

metal complexes. The following table shows these reactions along with infrared data

that suggests the S=N bond stretches are different from that of the uncoordinated

ligand (927cm^{-1}) (table 2).

Table 2: Products formed in reactions of [1,3-(PhSNH)$_2$C$_6$H$_4$] 56 (note that these are suggested formulations though in none of the cases were analytically pure species formed - see text)

Product	Infrared cm^{-1}
[Cu{1,3-(PhSNH)$_2$C$_6$H$_4$}Cl$_2$] 57	3204, 3053, 916
[Pt{1,3-(PhSNH)$_2$C$_6$H$_4$}(PPh$_3$)$_2$] 58	3231, 3045, 934
[Rh(Cl)(H){1,3-(PhSNH)$_2$C$_6$H$_4$}] 59	3231, 3112, 945
[Os{1,3-(PhSNH)$_2$C$_6$H$_4$}Cl$_2$] 60	3028, 951
[Pd{1,3-(PhSNH)$_2$C$_6$H$_4$} (MeCN)$_2$][BF$_4$]$_2$ 61	3051, 923
[RhCl{1,3-(PhSNH)$_2$C$_6$H$_4$}] 62	3230, 3046, 919

In each of these reactions a colour change from that of the original solution was observed. The starting metal complexes were chosen from research literature, in which similar reactions had been performed using a variety of pincer ligands. The proposed structures can be seen in **figure 36**.
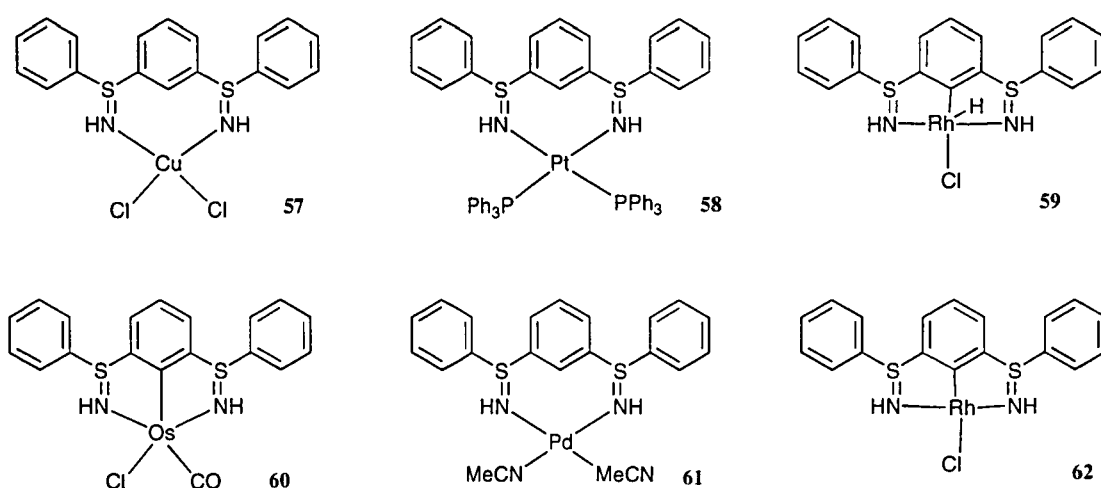

Figure 36: Proposed structures of complexes formed using 56

The reaction of RhCl$_3$ with **56** gave an orange product with a square pyramidal geometry predicted to have the formula [Rh(Cl)(H){1,3-(PhSNH)$_2$C$_6$H$_4$}] **59** (based on similar reactions). This was found to exhibit an S=N stretching frequency, at 945 cm^{-1}, different from that of the original ligand **56** (cf. 927 cm^{-1}) in the infrared region.[11] Similarly the reaction of **56** with the dimer [Rh$_2$(C$_2$H$_2$)$_4$Cl$_2$] gave a yellow product (reported in similar cases to be of square planar geometry) with the suggested formula of [RhCl{1,3-(PhSNH)$_2$C$_6$H$_4$}] **62**.[12] Infrared analysis shows the S=N stretch occurs at 919 cm^{-1} exhibiting less difference in wavenumber from the original ligand (cf. 927 cm^{-1}) than the corresponding rhodium complex **59**. Our interest in developing these complexes derives from the synthesis of similar types of rhodium complexes, which have been utilised as catalysts to assist in various industrial processes, such as the carbonylation of methanol to acetic acid.[13,14]

The reaction of (NEt$_4$)$_2$OsCl$_6$ and **56** was used to give a 16-electron, square pyramidal osmium complex of the formula [Os{1,3-(PhSNH)$_2$C$_6$H$_4$}Cl$_2$] **60**.[15] The crude product was analysed by infrared data which displayed an S=N stretch at 951 cm^{-1}, some 18 cm^{-1} difference from that of **56** (cf. 927 cm^{-1}). The complexes [Cu{1,3-(PhSNH)$_2$C$_6$H$_4$}Cl$_2$] **57**, [Pt{1,3-(PhSNH)$_2$C$_6$H$_4$}(PPh$_3$)$_2$] **58** and [Pd{1,3-(PhSNH)$_2$C$_6$H$_4$} (MeCN)$_2$][BF$_4$]$_2$ **61** exhibited small differences in the infrared region showing S=N stretch wavenumbers at 916, 934 and 923 cm^{-1} respectively, from that of the original ligand **56** (cf. 927 cm^{-1}).

This led us to believe that the reactions were successful at coordinating to the metal centres, but unfortunately every avenue of recrystallisation technique attempted gave unsatisfactory results, leaving us no choice but to abandon further research in this

area, until a satisfactory recrystallisation technique could be developed for the purification of **56**.

4.2 Synthesis of mixed imine/sulfimide [1,3-(PhSNH)C₆H₄(PhCNH)] 63

Recent research has shown the imine moiety to be most successful at creating tridentate bonds with metal centres when present in a pincer ligand.[16] Therefore the synthesis of a mixed imine/sulfimide pincer ligand seemed a logical target. The imine was made by a simple Grignard reaction before the sulfide [1,3-(PhS)C₆H₄Br] **64** was subsequently aminated using **1**. PhMgBr was used as the Grignard reagent which gave the product [1,3-(PhS)C₆H₄(MgBr)] **65**, then benzonitrile was used to attach the suitable imine group giving [1,3-(PhS)C₆H₄(PhCNH] **66** (**scheme 20**). The sulfur was aminated using **1** to theoretically give the product [1,3-(PhSNH₂⁺)C₆H₄(PhCNH][mesSO₃] **67**. Following this a suitable deprotonating reagent was chosen to give the free mixed sulfimide/imine **63**, in this case it was thought that DBU would suffice.
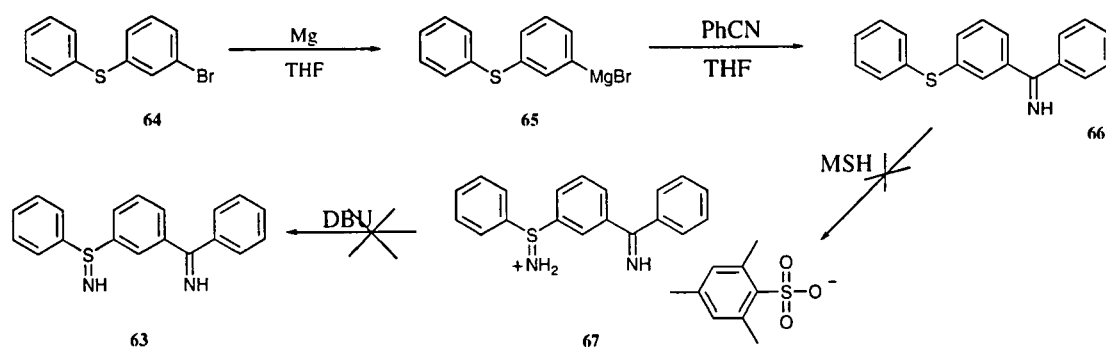
**Scheme 20: Attempt to make [1,3-(PhSNH)C₆H₄(PhCNH)] 63**

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Unfortunately this procedure was not successful, proof that the sulfur had been aminated to give **67** was inconclusive. The resulting red product was analysed using mass spectrometry and was found to contain none of the desired sulfimide/imine product. Another method of producing the imine moiety was the use of butyl lithium instead of the Grignard reagent; this proved to be a failure and was not taken any further.

4.3 Synthesis of pyridine sulfimides

The advantage of producing the pyridine analogue was to obtain an extra nucleophilic, strongly coordinating site within a strategic position in the ligand. The *bis*-pyridine precursor was readily synthesised from the commercially available dibromopyridine compound [$C_5H_3NBr_2$] **68**.

4.3.1 Synthesis of [2,6-(PhS{NH$_2$})$_2$C$_5$H$_3$N][mesSO$_3$]$_2$ 69

2,6-*bis*(phenylthio)pyridine **70** was used in the reaction with two equivalents of **1**. The exothermic reaction proceeded in a vigorous fashion, initially with a gas being evolved. After overnight stirring a golden coloured solution was observed which was then reduced to dryness and washed with several portions of diethyl ether. A cream coloured sticky solid was produced after drying under vacuum (**scheme 21**).
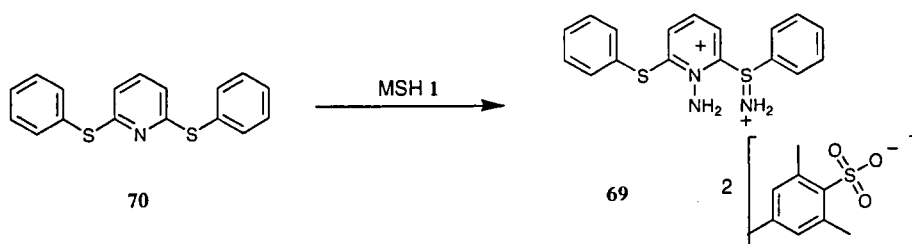

Scheme 21: Reaction of 2,6-bis(phenylthio)pyridine 70 with MSH 1

From the scheme it is observed that the pyridine nitrogen atom has been aminated in preference to the sulfur atom, which was not initially desired. The infrared data shows the presence of the mesitylenesulfonate anion at 1086 cm^{-1} along with the aromatic and aliphatic stretches at 851, 750 and 681 cm^{-1} respectively. The broad nature of the mesitylenesulfonate band prevents the S=N stretch being observed. The ^{1}H NMR data for the product, performed in CDCl$_3$, proved inconclusive at determining the true nature of the product. The mass spectrometry data using fast atom bombardment (FAB) contains peaks attributable to the loss of 201 mass units (mesitylenesulfonate anion) at [326] from the mass ion [527]. This is followed by the loss of 15 mass units (NH) at [311] due to the S=N or N-N bond cleavage.

4.3.2 Synthesis of [2,6-(PhSNH)$_2$C$_5$H$_3$N] 71

This system has also proved to be problematic to deprotonate, just as the 1,3-benzene analogue **53**. Once again a dark coloured solution was observed after the reaction had proceeded and a very dark coloured oil was produced after the work up, in which both previously mentioned water and toluene methods were used. Several different reagents and methods were used, including DBU, but all results from the analysis of the product proved inconclusive in nature (**scheme 22**).
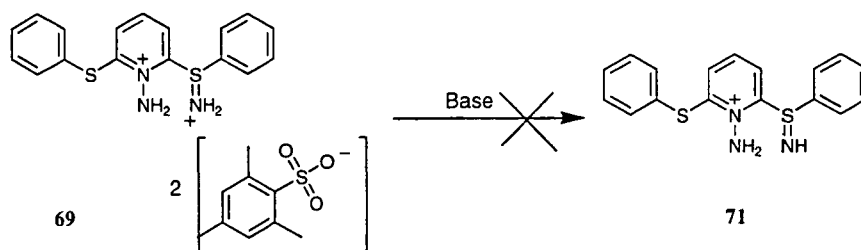
Scheme 22: Unsuccessful attempt at deprotonation of 69 using several different bases

4.3.3 Synthesis of [(PhS)C₅H₃N{NH₂}][mesSO₃] 72

Producing the *mono* SPh analogue [(PhSNH)C₅H₃N] **73** of the *bis*-pyridine ligand **71** seemed an interesting prospect as the absence of the other bulky SPh side group may help to reduce steric hinderance and hence aid in its coordination properties. Unlike the analogous ligand **3**, the advantage of an extra coordination site of the nitrogen of the pyridine made it a potentially feasible ligand to attempt. The reaction of [(PhS)C₅H₃N] **74** with **1** was exothermic and a striking colour change as with the corresponding starting material **70** was observed (**scheme 23**). The crude product was obtained and then recrystallised using MeOH/Et₂O, this gave good quality crystals that were suitable for X-ray crystallography.
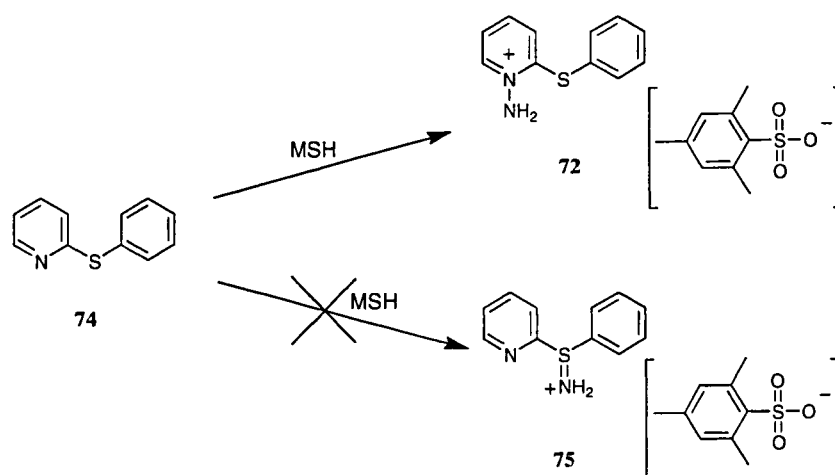
Scheme 23: MSH (1) is successful at aminating the pyridine nitrogen of 74

Interestingly we can see by the crystal structure (**figure 37**) that the pyridine nitrogen is aminated by **1** to give [2-(PhS)C₅H₃N{NH₂}][mesSO₃]₂ **72** in preference to the desired sulfimide product [2-(PhS{NH₂})C₅H₃N][mesSO₃]₂ **75**. This is not unprecedented as research has been performed on these compounds in the past, using **1** as the synthetic reagent of choice.[17,18]
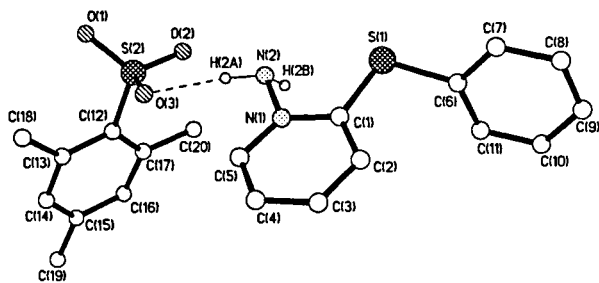
Figure 37: Crystal structure of 72. Selected bond distances (Å) and angles (°):

N(1)–N(2) 1.415(3), C(5)–N(1)–C(1) 122.2(2), C(5)–N(1)–N(2) 120.9(2), C(1)–

N(1)–N(2) 116.8(2), N(1)–C(1)–C(2) 118.4(2).

The N-N bond length is shown to be 1.415 Å, the C(1)–N(1)–N(2) bond angle is

116.8° compared with the larger C(5)–N(1)–N(2) bond angle which measures at

120.9°. This shows that the N=N bond lies 4° closer in space to the carbon atom that

is attached to the sulfur. This may be attributable to the hydrogen bonding that occurs

with the oxygen atom of the mesitylenesulfonate anion thus placing strain on the N-N

bond to conform to this configuration. As a result of this we see the formation of an

extended array system **(figure 38)**.

Figure 38: Crystal structure of 72 showing array formation

The infrared data shows the presence of the mesitylenesulfonate anion at 1185 cm^{-1} along with the aromatic and aliphatic stretches at 3110, 3052, 1185, 845 and 756 cm^{-1} respectively. The ^{1}H NMR data for the product, performed in DMSO–d$_6$, shows several singlet peaks that are due to phenyl protons at 7.70, 7.49, 7.29 and 7.12 δppm all integrating to 1H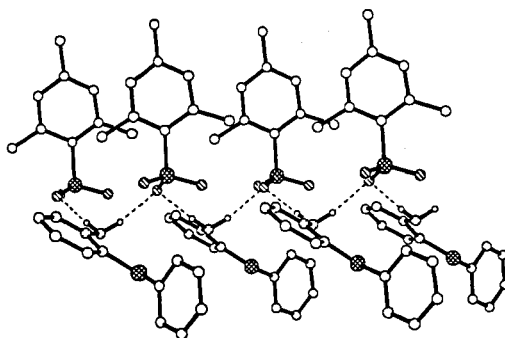 respectively. These do not correspond to the protons in the structure and one can only guess that something is occurring such as the fragmentation and rearrangement of the molecule in solution. The alkyl protons on the mesitylenesulfonate anion can be seen at 2.86 and 2.54 δppm integrating as 6H and 3H respectively. The mass spectrometry using fast atom bombardment (FAB) contains peaks attributable to the mass ion [203]. This is followed by the loss of 15 mass units (NH) at [188] due to the N-N bond cleavage. Microanalysis for this product proved accurate at determining the purity of the crystals.

It was decided that the starting pyridine **74** would be reacted with a 2:1 stoichiometric amount of **1** to see if a mixed sulfimide/N-imine ligand of the formula [2-(PhS{NH$_2$})C$_5$H$_3$N{NH$_2$}][mesSO$_3$]$_2$ **76** could be achieved (**scheme 24**). Mass spectrometry data indicates the mass ion at [203] units, which is attributable to the pyridine nitrogen being aminated with no sign of sulfur amination taking place. Interestingly ^{1}H NMR shows four singlet peaks present at 7.32, 7.12, 6.92, 6.76 δppm integrating once again to 1H each, these are markedly different than before when only the pyridine nitrogen was aminated. We also observe a different splitting pattern of the aliphatic protons of the mesitylenesulfonate anion. Two sets of singlets at 2.57 and 2.50 δppm, and 2.27 and 2.17 δppm, are observed, integrating to 12H and 6H respectively. Due to the unconvincing mass spectrometry results and inability to

grow crystals suitable for X-ray crystallography this avenue of research was abandoned.
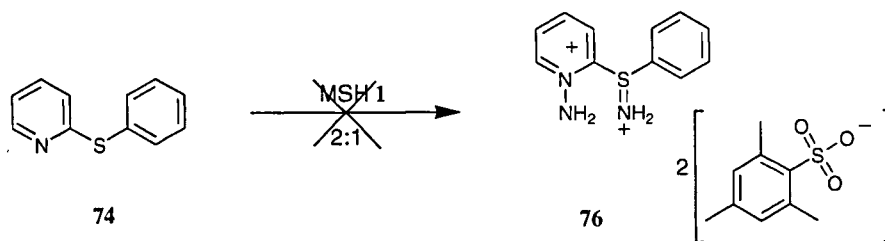
Scheme 24: MSH 1 does not successfully aminate both sites of the starting material 74

It should also be mentioned that some work has been done towards protecting the pyridine nitrogen of **70** by protonating it using HCl, to give $[(PhS)_2C_5H_3N(H)]Cl$ **77**, before reacting with **1** so as to gain a true mixed pyridine/sulfimide ligand **78** (**scheme 25**). Initial results were promising and this is an area that should be allocated some time in future research. The major problem will be to find a suitable way of deprotonating them in order to produce useful pyridine/sulfimide mixed ligands.
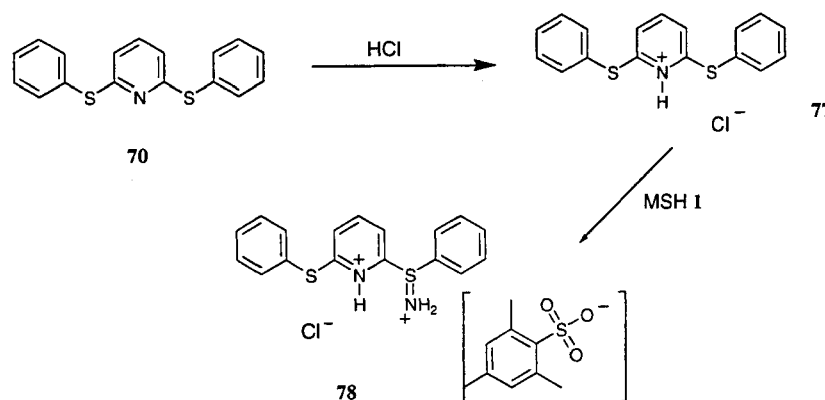
Scheme 25: Proposed reaction scheme for the protection of the pyridine of 70 using HCl and the subsequent reaction with 1

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4.4 Reactions using [2,6-(PhS)₂C₅H₃N] 70

Aromatic heterocyclic ligands such as pyridine readily form complexes with various metal centres including copper, platinum and palladium. These ligands have π-electron system associated with their aromatic rings and therefore in the addition to the σ-component there is the possibility of a π-component in the metal-nitrogen bond. Hence these ligands show some properties that are of a similar nature to that of tertiary phosphine ligands.[19]

It was therefore thought that the readily synthesised precursor **70** would be suitable for use as a ligand in its own right (**figure 39**). Here in the following reactions we see the ease that the pyridine moiety acts as a source of nitrogen for coordination to the metal centre of some common metal complexes.
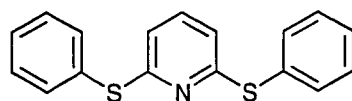
Figure 39: Proposed structure of [2,6-(PhS)₂C₅H₃N] 70

This is slightly off the track of the intended research but it includes some intriguing and unique results from these species of ligands.

4.4.1 Reaction of [2,6-(PhS)₂C₅H₃N] 70 with Pd(PhCN)₂Cl₂ 29

An interesting starting point was thought to be the reaction of the ligand **70** with the palladium complex **29**. This decision was partly due to the success of the ligand **10** and its coordination with **29**. The palladium complex was stirred in a solution of

DCM with a 2:1 stoichiometric amount of **70** added. An initial change of colour was observed after addition of the ligand and an almost immediate precipitate had formed with continuous stirring. The yellow flocculent solid that was produced was microcrystalline in nature.

It was therefore decided to perform the reaction again, but after initial stirring, the reaction was left to stand in order to gain larger crystals. This technique proved to be profitable and orange cubic crystals of the formula $[\{2,6-[(PhS)_2 C_5H_3N]\}_2\}\{(PhS)_2\}Pd_2Cl_2]$ **79** were obtained and the structure solved using X-ray crystallography (**figure 40**).
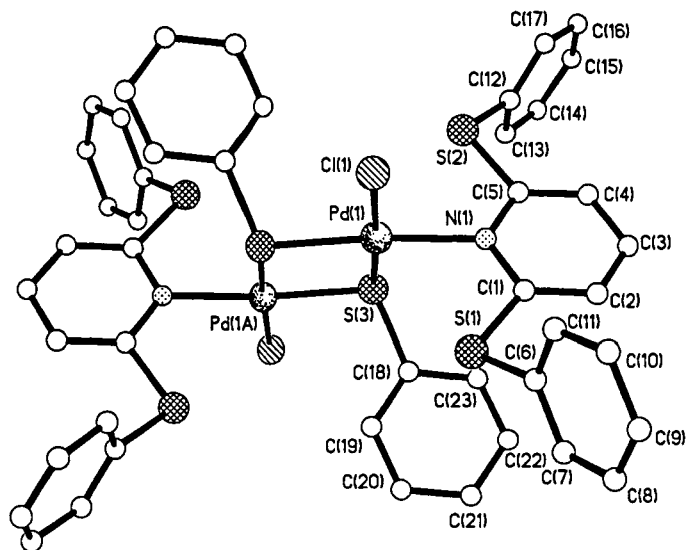
Figure 40: Crystal structure of 79. Selected bond distances (Å) and angles (°):

Pd(1)–N(1) 2.080(7), Pd(1)–S(3') 2.283(2), Pd(1)–S(3) 2.302(2), Pd(1)–Cl(1)

2.317(2), N(1)–Pd(1)–S(3') 174.9(2), N(1)–Pd(1)–S(3) 91.16(19), S(3')–Pd(1)–S(3)

84.84(9), N(1)–Pd(1)–Cl(1) 91.87(19), S(3')–Pd(1)–Cl(1) 92.32(8), S(3)–Pd(1)–

Cl(1) 175.34(8).

Previous examples of this type of SPh bridging with palladium compounds have been observed when using polymeric palladium starting materials and also Pd(MeCN)₂Cl₂.[20] This however is the first reaction where the ligand has fragmented to give the two types of coordinating ligands within the same reaction mixture. These previous reactions can give us some clues as to what is happening to the molecule when the reaction takes place. Mercaptide ions (RS⁻) are highly polarisable and therefore form strong complexes with soft metal ions. As mentioned previously the pyridine ligand also forms strong bonds with metal centres, below we see the suggested mechanism for this reaction (**scheme 26**).
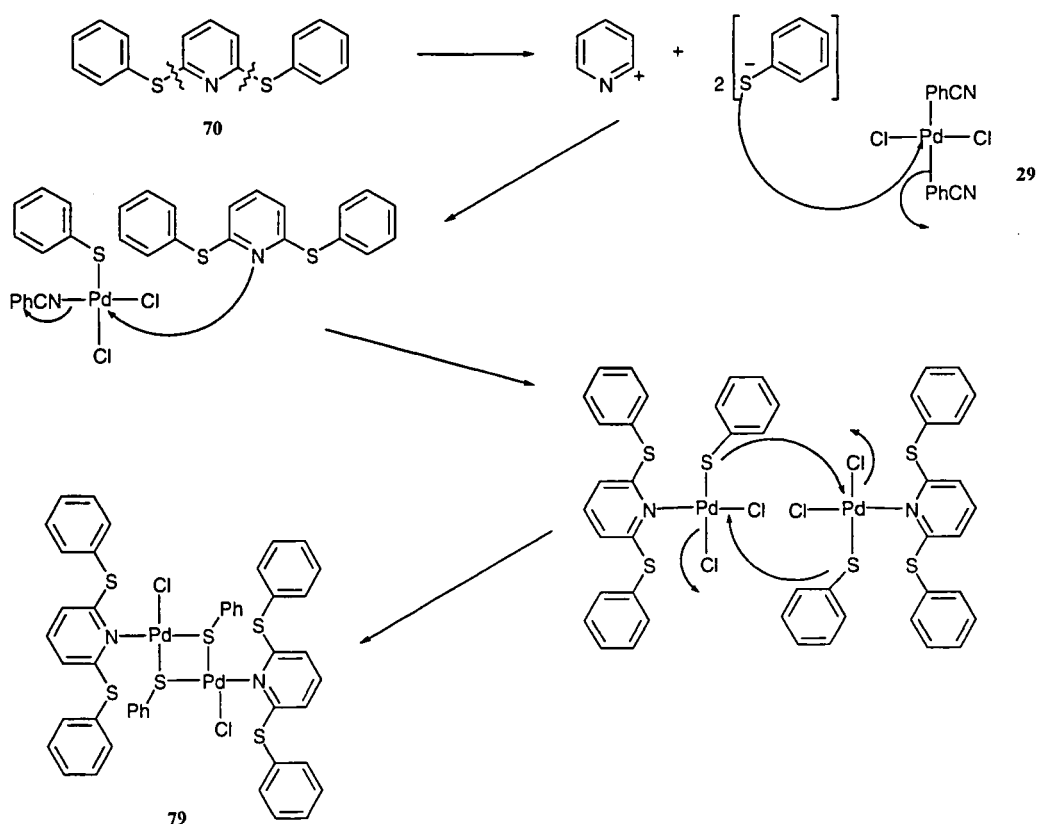
Scheme 26: Proposed mechanism for formation of 79

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To hasten a guess one would say that the mercaptide ion fragments attack first, due to their highly polarisable nature, in turn kicking out one of the more weakly bound PhCN units. The neutral nitrogen on the pyridine then attacks the palladium atom, which in turn ejects the other PhCN ligand. Hence we get the resulting palladium dimer bridged by two mercaptide molecules with two pyridine sulfide ligands and two chloride ligands around each metal centre (**scheme 26**).

In order to ascertain whether the aforementioned product only forms in 2:1 stoichiometric amounts, the reactions were undertaken using varying stoichiometric amounts of the ligand. These reactions were left over a period of weeks and all produced the same results analysed by infrared spectrometry, thus proving that this reaction preferentially fragments, regardless of ligand amounts, with no *bis*-pyridine palladium dichloride product formed.

4.4.2 Reaction of [2,6-(PhS)$_2$C$_5$H$_3$N] 70 with CuCl$_2$

A 2:1 Reaction of the ligand **70** with CuCl$_2$ was performed in acetonitrile with stirring. A slight blue precipitate had formed after five minutes of stirring which was discontinued and left to stand for several weeks in solution. Large blue block type crystals had formed which proved suitable for use in X-ray crystallography. The crystal structure shows a structure with two ligands in a square planar conformation around the central copper atom with the formula [{2,6-(PhS)$_2$C$_5$H$_3$N}$_2$CuCl$_2$] **80** (**figure 41**).
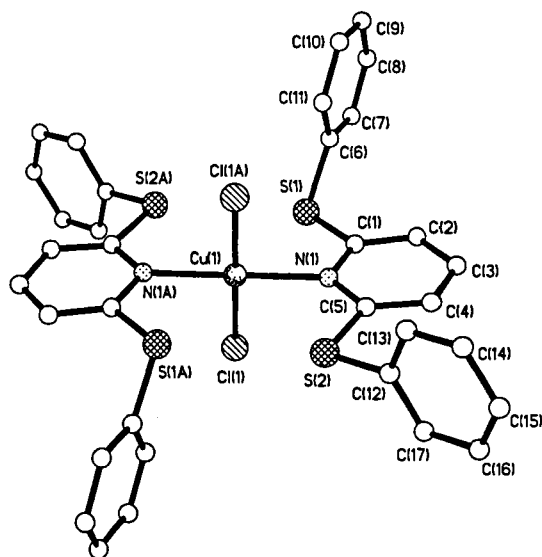
Figure 41: X-ray crystal structure of 80. Selected bond distances (Å) and angles (°): Cu(1)-N(1) 2.071(16), Cu(1)-N(1') 2.071(16), Cu(1)-Cl(1') 2.219(5),Cu(1)-Cl(1) 2.219(5), N(1)-Cu(1)-N(1') 180.0(13), N(1)-Cu(1)-Cl(1') 89.15(5), N(1')-Cu(1)-Cl(1') 90.85(5), N(1)-Cu(1)-Cl(1) 90.85(5), N(1')-Cu(1)-Cl(1) 89.15(5), Cl(1')-Cu(1)-Cl(1) 180.0(2).

This is a symmetrical structure in a *trans* conformation, the Cu-N bond lengths are equidistant at 2.071Å and the N-Cu-Cl bond angles are also equidistant at 90°. The phenyl rings attached to both sulfur atoms arrange themselves in space in order to be as far away from each other as possible. The infrared data shows the presence of the aromatic and aliphatic stretches at 3052, 1417, 1174, 758 and 692 cm^{-1} respectively. Mass spectrometry data does not show the mass ion but a peak is seen at [653] units, which is attributable to the loss of a chlorine atom. Microanalysis data proved effective in determining the purity of the molecule by being within satisfactory parameters of the required values.

92

4.5 Synthesis of thio-crown sulfimide

Here we see the groundwork to some interesting chemistry, which is currently being developed by other members of the Kelly group. The sulfur atoms in crown thio-ethers can be used to form many different compounds, with this in mind we attempted to synthesise a new class of thio-crown sulfimide ligands.

4.5.1 Synthesis of [14-aneS$_4$NH$_2$$^+$($^-OSO_2C_6H_2$(CH$_3$)$_3$)] 81

The reaction of **1** with a thio-crown ether of the formula [C$_{10}$H$_{20}$S$_4$] **82** gave the product [14-aneS$_4$NH$_2$$^+$($^-OSO_2C_6H_2$(CH$_3$)$_3$)] **81**, where only one of the four sulfur atoms was aminated (**figure 42**). After stirring for a few hours a precipitate had formed this was then filtered and washed with CH$_2$Cl$_2$ before being dried *in vacuo*. The solid was completely insoluble in all common solvents, this made it difficult to gain full characterisation of the product but mass spectrometry and microanalysis results were obtained.
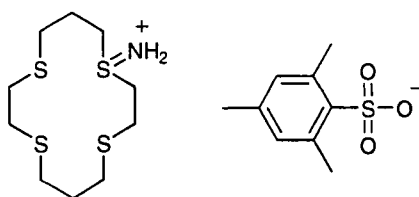

Figure 42: Proposed structure of 81

Some attempts were also made to synthesise other products where all four sulfur sites were aminated by **1** but the major product seen was that where only one site was

aminated, although traces of two sulfimide sites were observed using mass spectrometry. Colleagues are exploring further work in this area.

4.6 Attempted synthesis of aliphatic bridged sulfimides

The positive advantages of making sulfimides with aliphatic bridging chains are to produce less sterically hindered ligands than that of the aromatic sulfimides **5** and **9**. The aliphatic-chained species also have the ability to rotate around the carbon atoms, which can increase their chances of forming bidentate bonds with metal centres. The disulfides that were reacted with **1** included [(PhS)$_2$CH$_2$] **83** and [1,3-(PhS)$_2$C$_3$H$_6$] **84** both of which proved complicated to characterise (**figure 43**).

83   **84**
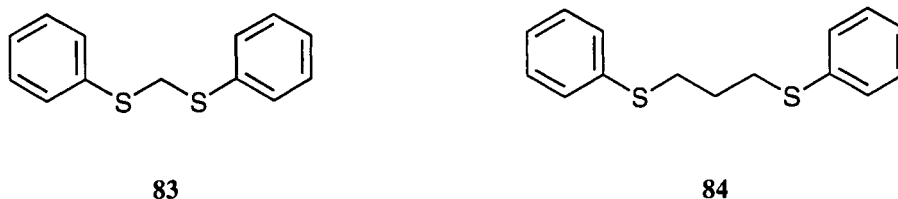
Figure 43: Structures of aliphatic *bis*-sulfide starting materials 83 and 84

We are unsure what **1** does to the molecule in the reaction, particularly with the methyl chained species **83**; a red solution and solid was produced but we were unable to determine the structure by means of spectroscopic analysis. **1** does however seem to have been successful in aminating both sulfur atoms in the reaction with the propyl chained species **84**, microanalysis and other data suggests that this is the case but unfortunately attempts to recrystallise this product have failed.

4.7 Attempted synthesis of *ortho* and *meta* bromo-phenyl sulfimide ligands

Two ligand syntheses were attempted where *ortho* and *meta* analogues of the ligands **10** and **60** were produced with a bromine group present in the relevant position around the ring. These were performed in the hope that new groups could be attached (as in the case of the imine moiety **63**) or that the complexes could be bridged by the bromine to metal centres. The synthesis of the starting sulfide products proved straightforward and gave good yields after distillation. They were then reacted with a 1:1 stoichiometric amount of **1** in order to aminate the sulfur atom (**85** and **86** respectively). Results from analysis proved to be quite promising revealing that the sulfur atom had been successfully aminated without interference of the bromine atom (**figure 44**).

85   86
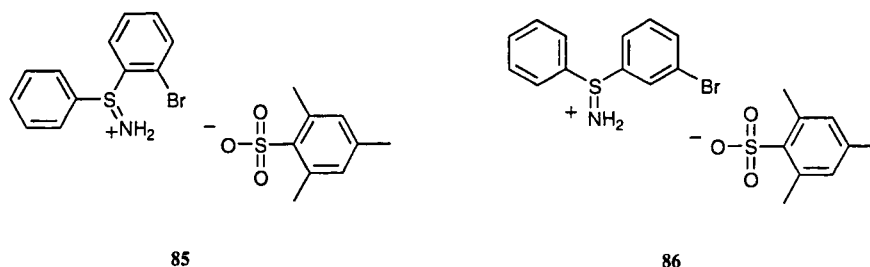
Figure 44: Successful amination of the sulfur atoms using MSH 1

Mass spectrometry data for the *ortho* ligand **85** showed the presence of the mass ion at [282] units. ^{1}H NMR, performed in CDCl$_3$ produced a doublet of doublet peak at 8.36-8.39 δppm which integrated to 1H attributable to the aromatic proton next to the S=NH$_2$$^+$ group. The other aromatic protons are observed as a multiplet at 7.25-7.65 δppm and integrate to 8H. The peaks attributable to the aliphatic protons of the mesitylenesulfonate anion are observed as singlets at 2.45 and 2.12 δppm, which

integrate to 6H and 3H respectively. The presence of the mesitylenesulfonate anion is seen in the infrared data at 1186 cm^{-1} along with reasonable microanalysis results.

Similarly the *meta* analogue **86** showed the same fragmentation pattern using fast atom bombardment mass spectrometry, with the mass ion present at [282] units. ^{1}H NMR, also performed in CDCl$_3$, produced two multiplets at 7.67-7.73 and 7.18-7.50 δppm integrating as 9H and attributable to aromatic protons. We observed two singlets at 2.44 and 2.14 δppm integrating as 6H and 3H respectively and attributable to the aliphatic protons of the mesitylenesulfonate anion. The presence of the mesitylenesulfonate anion can also be seen in the infrared data at 1182 cm^{-1}.

4.8 Conclusion

Problems concerning the deprotonation of the entire novel sulfimides attempted in this chapter are of great concern. Many methods were tried but alas all proved unsuccessful in our hands, if further research is continued in this area solving this problem will be of the utmost importance in producing viable mixed ligands. The success of coordination chemistry of the *bis*-pyridine ligand **70** did however prove to be a profitable undertaking; the fragmentation of the ligand with palladium species is definitely something that deserves further research.
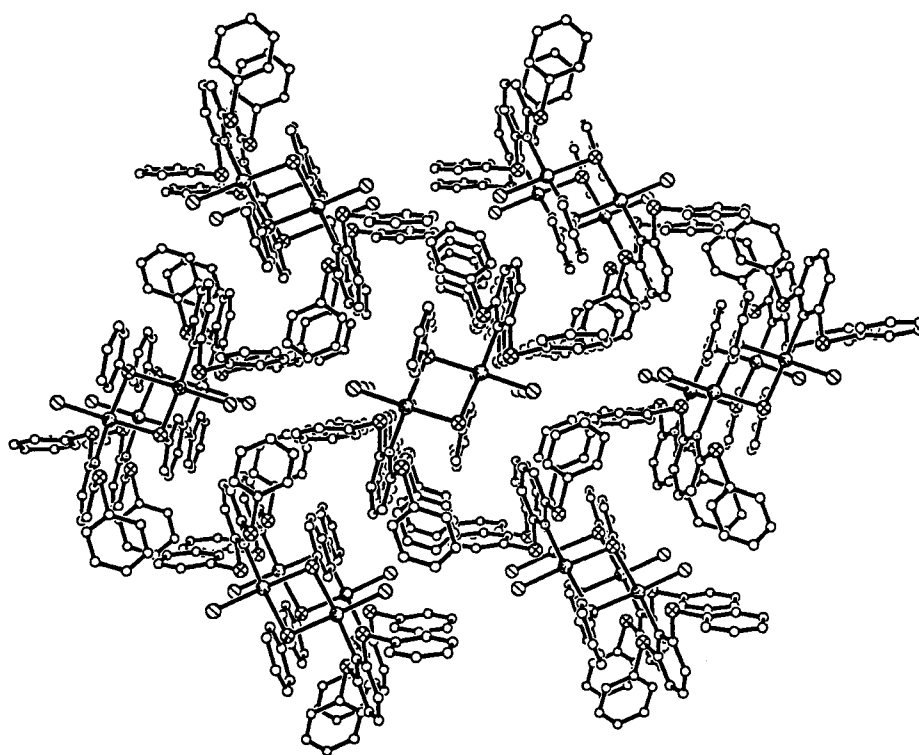
4.9 References

[1] D.M.Grove, G.van Koten, J.N.Louwen, J.G.Noltes, A.L.Spek and H.J.C.Ubbels, *J. Am. Chem. Soc.*, 1982, **104**, 6609 (and references therein)

[2] M.Gupta, W.C.Kaska and C.M.Jensen, *Chem. Commun.*, 1997, 461 (and references therein)

[3] M.Ohff, A.Ohff, M.E.van der Boom and D.Milstein, *J. Am. Chem. Soc.* 1997, **119**, 11687 (and references therein)

[4] J.G.Donkervoort, G.L.Vicaro, J.T.B.H.Jastrzebski, R.A.Gossage, G.Cahiez and G.van Koten, *J. Organomet. Chem.*, 1998, **61**,558 (and references therein)

[5] C.Bianchini, P.Barbaro, G.Scapacci, E.Farnetti and M.Grazrani, *Organometallics*, 1998, **17**, 3308 (and references therein)

[6] D.M.Grove, G.van Koten and J.A.M.van Beek, *J. Organomet. Chem.*, 1989, 372, C1 (and references therein)

[7] B.Rybtchinski, A.Vigalok, Y.Ben-David and D.J.Milstein, *J. Am. Chem. Soc.*, 1996, **118**, 12406 (and references therein)

[8] Longmire, J. Xumu, Z., *Organometallics*, 1998, **17**, 4374 (and references therein)

[9] M.R.J.Elsegood, K.E.Holmes and P.F.Kelly, *Crys.Eng.Commun.*, 2002, **4**, 172

[10] S.Furukawa and S.Oae. Sulfilimines and related derivatives, ACS. Washington DC. 1983

[11] S.Nemeh, C.Jensen, E.Binamira-Soriaga and W.C.Kaska, *Organometallics*, 1983, **2**, 1442

[12] H.F.Haarman, J.M.Ernsting, M.Kranenburg, H.Kooijman, N.Veldman, A.L.Spek, P.W.N.M.van Leeuwen and K.Vrieze, *Organometallics*, 1997, **16**, 887

[13] D.Forster and T.C.Singleton, *J.Mol.Catal.*, 1982, **17**, 299

[14] D.Forster, *Adv.Organomet.Chem.*, 1979, **17**, 255

[15] D.G.Gusev, F.M.Dolgushin and M.Y.Antipin, *Organometallics*, 2001, **20**, 1001

[16] G.J.P.Britovsek, V.C.Gibson, S.Mastroianni, D.C.H.Oakes, C.Redshaw, G.A.Solan, A.J.P.White and D.J.Williams, *Eur. J. Inorg. Chem.*, 2001, 431-437

[17] Y.Tamura and M.Ikeda, *Adv.in Heterocycl.Chem.*, **29**, 71

[18] D.Edmont, Y.Buisson, P.Treillard, C.Plisson and J.Chenault, *Synth.Commun.*, 2000, **30**, 217

[19] F.R. Hartley, The chemistry of platinum and palladium, ASP Ltd, London. 1973

[20] T.Boschi, B.Crociani, L.Toniolo and U.Belluco, *Inorg.Chem.*, 1970, **9**, 532

Chapter five

Conclusion

5.0 Conclusion and further work

The synthesis of the novel sulfimide compounds and their subsequent coordination chemistry has provided mixed results. For instance we have the success of the ortho mixed sulfide/sulfimide compound **10** that has provided us with a wide array of coordination reactions with various metal complexes. All of these reactions provided stable complexes and in the case of the platinum reaction have shown the ability to undergo nucleophilic addition with the nitrile group to form a metallocycle **21**. The preparation of sulfimides of the general type [HN=S(C$_6$H$_4$X)Ph], where X is a coordinating group, will give the ability to liberate novel tridentate ligands. The formation of metal-activated organonitriles products is going to be an ongoing quest for many research groups in the future.

Surely the most promising of the reactions with the ortho mixed sulfide/sulfimide ligand **10** is that with (PhCN)$_2$PdCl$_2$ **28** which shows the true potential of the ligand to act in a bidentate fashion. The resulting complex **29** was preliminarily tested as a catalyst in the Heck reaction and initial results proved quite interesting and definitely warrant further testing, including replication and differentiation of conditions in the reaction. Potential research in this area should focus on testing the palladium complex to see if it is useful in many different catalytic reactions, including the Stille and Suzuki coupling.

One should also note the significance of the complex [Rh[COD]{(PhSNH)C$_6$H$_4$PhS}] **44** in relation to using the sulfimides as catalysts. Further work should focus on full

characterisation in the form of producing an X-ray crystal structure and also testing in a variety of catalytic reactions. Further research should also include studies centred on the complex [RuCy{(PhSNH)C$_6$H$_4$PhS}Cl$_2$] **46**, further structural characterisation is needed but the potential is there for its use as a catalyst.

The success of the *bis*-sulfimide species **7** was limited in the coordination chemistry that could be attempted due to its insolubility in most organic solvents. However, despite this we did have success at creating the novel bridged palladium dimerised product. The ability to create novel bridging ligands, similar to **7** and **12**, is an area that shall continue to be of interest, including the possibility of bridging two different metal centres.

The synthesis of a *meta* pincer ligand **55** has had mixed results, so far only the protonated product of **52** has been fully characterised, with many different deprotonation reactions being tried giving no conclusive results. If further research is to be performed in this area this is definitely going to be the test of their success. These ligands have the potential to be extremely useful at coordinating to metal centres and hence as use in catalysis.

Future research will focus on the adaptation of these ligands by the introduction of a variety of coordinating functional groups, creating many analogues of the type seen in this research document. This was attempted with a mixed sulfimide/imine ligand **62** but many groups, such as diphenylphosphine, can replace the sulfimide moiety on one side of the molecule. These will be very interesting ligands as the two different groups should enhance the bonding with a variety of metal complexes.

The pyridine analogues **70** and **72** were the least successful of our attempts as the amination occurred at the nitrogen, one solution to this problem, as preliminarily seen here, is the introduction of a protecting group at the nitrogen, leaving the only place for amination to occur at the sulfur atom as in the case of compound **77**. Once again the most testing aspect of creating these complexes lie in the discovery of a successful deprotonation technique. However if this can be achieved the ligands possess great potential for use in a variety of coordination reactions.

One other option that is being considered is that of transforming the N-H bonds of the sulfimides into N-Br bonds. This will enable the sulfimide to form different groups that might make bonding to metal species more attractive. An attempt has initially been made to join two of the sulfimide units together using this method but further studies are needed on a larger scale to be conclusive.

A matter of much interest is the sulfimides ability to hydrogen bond and form interstitial sites in which counterions could be placed. An emphasis can also be placed on the formation of chiral sulfimides with the tricoordinate sulfur atom being surrounded by different groups. This is a most important area of current research within the field of asymmetric synthesis. The synthesis and subsequent coordination chemistry of novel sulfimide species has proved to give many interesting results. Their continuing success in the future will depend on the adaptation of mixed systems in order to create viable and competitive complexes that will be useful to industry.

Chapter six

Experimental

6.0 Experimental

All infrared spectra were obtained using a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer, thin film spectra were acquired using potassium bromide plates and solid samples were obtained using potassium bromide discs under pressure.

All ^{1}H and ^{13}C spectra were measured at 250.13 and 62.86 MHz respectively, using a Bruker AC 250 MHz spectrometer or at 400.13 and 100.62 MHz using a Bruker DPX 400 MHz spectrometer. ^{195}Pt NMR spectra were measured at 53.77 MHz using a Bruker AC 250 MHz spectrometer. ^{31}P NMR spectra were recorded on a Jeol FX90Q spectrometer operating at 36.21 MHz. The solvent used for NMR spectroscopy was $CDCl_3$ (unless stated otherwise) using TMS (tetramethylsilane) as the internal reference. Chemical shifts are given in parts per million (ppm).

The mass spectra were recorded using a Jeol-SX102 instrument utilising fast atom bombardment (F.A.B.) and by the EPSRC national mass spectrometry service at the University of Wales, Swansea.

Powder diffraction was carried out using a Bruker D8 powder diffractometer with Anton Parr HTK 1200 furnace attachment.
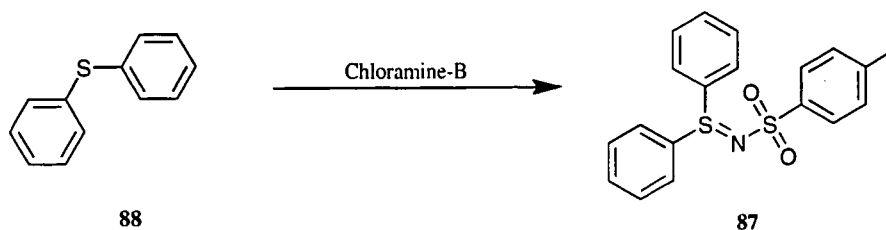
Melting points were recorded using an Electrothermal-IA 9100 melting point instrument and are uncorrected.

Microanalyses were performed on a Perkin Elmer Elemental Analyser 2400 CHN.
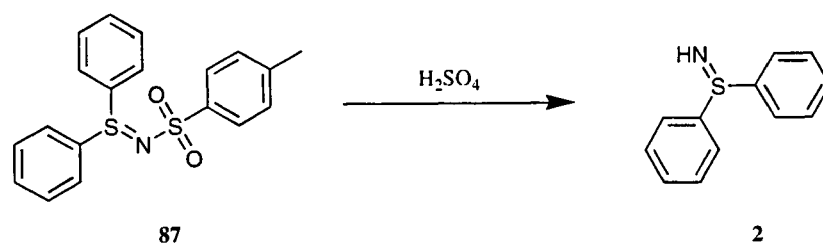
Reactions monitored using thin layer chromatography (TLC) on aluminium backed plates with Merck Kiesel 60 F254 silica gel. TLC visualised by UV radiation at a wavelength of 254 nm.

The reactions requiring anhydrous conditions were carried out using glassware dried overnight at 150 °C, under a nitrogen atmosphere unless otherwise stated. Light petroleum ether (bp 40-60 °C) was distilled from calcium chloride prior to use. Dichloromethane and acetonitrile were distilled under a nitrogen atmosphere over calcium hydride. Tetrahydrofuran (THF) and diethyl ether (Et$_2$O) were distilled under a nitrogen atmosphere from the sodium/benzophenone ketyl radical.

[Ph$_2$SNSO$_2$Ph] 87

Ph$_2$S **88** (21ml, 0.12mol) and chloramine-B (41g, 0.12mol) in methanol (230ml) were treated dropwise with acetic acid (6ml) in methanol (30ml) at 20-30°C. The mixture was left to stir at room temperature for one hour, afterwhich it was then poured into a cold solution of NaOH (6g) in H$_2$O (530ml). The resulting precipitate was collected, washed with distilled water and left to dry. Typical Yield: 29.7g, (76%); mp 124-126°C.
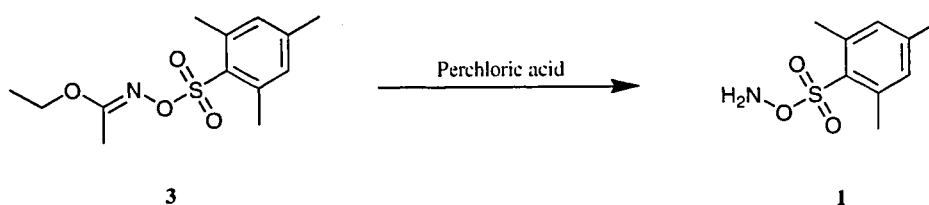
[Ph₂SNH] 2

87 → 2

H₂SO₄

A modification of the route of Vlasova *et al* was used; thus [Ph₂SNSO₂Ph] **87** (7g, 0.02mol) was added in a number of portions to well stirred, degassed 95% H_2SO_4 (25ml) under a blanket of N_2. The resulting mixture was then heated at 80°C for 15 minutes before being cooled and then cautiously poured onto ice (200ml). The mixture was then taken to pH 11 by slow addition of 5M NaOH solution; the response appeared to be variable at this point – on some occasions solid had precipitated, which was filtered and recrystallised from Et_2O, on other occasions only a pale orange oil was apparent. In the latter case, the entire mixture was extracted into warm Et_2O (typically 2 × 50ml), the solvent reduced in volume and the resulting colourless crystalline mass filtered. Yield 1.8 g (45%). IR 3110cm⁻¹ [ν N-H], 935cm⁻¹ [ν N-S]. Mpt: 69-70°C (lit. 69°C).

[(CH₃)₃C₆H₂SO₃NC(CH₃)OC₂H₅)] 3

89 → 3

Ethylacetohydroxamate

Ethylacetohydroxamate (25g, 0.243mol) and triethylamine (34ml) in dimethylformamide (70ml) was treated with small portions of mesitylenesulfonyl chloride **89** (53g, 0.243mol) with stirring, in an ice bath. After addition was complete, the mixture was stirred for 20 minutes at 0°C and then poured into ice water. The
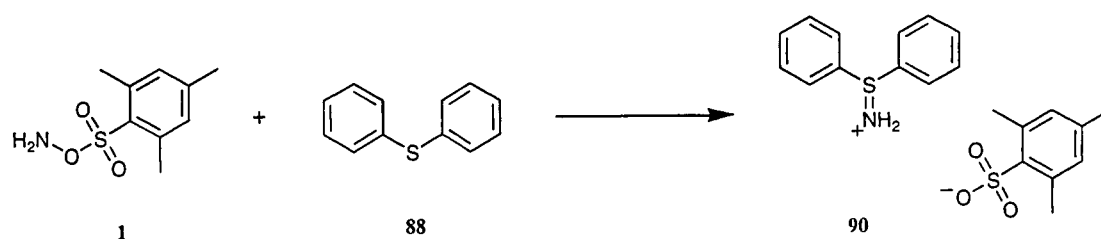
103

white precipitate was filtered, washed with more distilled water and then dissolved in Et$_2$O and dried over Na$_2$SO$_4$. The solution was reduced *in vacuo* after which the resulting yellow oil was recrystallised from Et$_2$O/petroleum ether (bp 60-80°C). Typical yield: 52.8g, (76%); Mpt: 54-56°C (lit. 54-56°C).

[(CH$_3$)$_3$C$_6$H$_2$SO$_3$NH$_2$] 1

A solution of ethyl-O-mesitylenesulfonylacetohydroxamate **3** (14g, 0.05mol) in 1,4-dioxane (7ml), was treated with 70% perchloric acid (4ml) at 0°C in small portions with stirring over a period of 10 minutes. The reaction mixture was poured into ice water to give a white solid that was filtered and washed with water. The solid was then dissolved in Et$_2$O and the water extracted from the solution. Petroleum ether (bp 60-80°C) was then added to the ethereal solution until the white solid of the product **1** was observed. Typical yield: 5.5g, (49%); IR: 3035 [v N-H], 1180 cm^{-1} [v mes]; Mpt: 92-93°C (lit. 93-94°C).
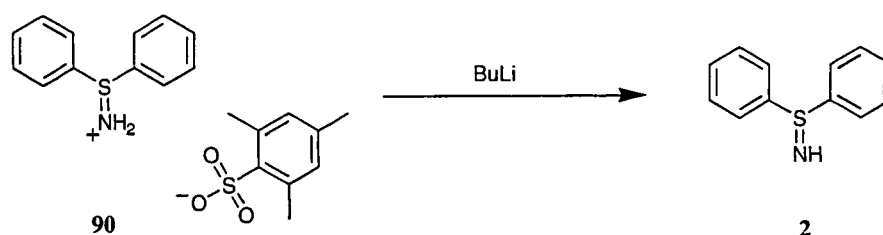
[Ph$_2$SNH$_2^+$] 90

MSH **1** (7.8g, 0.036mol), dissolved in CH$_2$Cl$_2$ (20ml) under a blanket of N$_2$, was treated dropwise with diphenyl sulfide **88** (5ml, 0.036mol), with stirring, and left to

react for 24 hours. The mixture was then reduced in volume and Et$_2$O added, the resulting solid was filtered and washed with more Et$_2$O, which was subsequently recrystallised from CH$_2$Cl$_2$/Et$_2$O. Typical yield: 3.5g, (24%); IR: 2970 [ν N-H], 963cm^{-1} [ν N-S]. ^{m}/$_e$ (M = [(PhS{NH$_2$)$^+$($^-$OSO$_2$C$_6$H$_2$(CH$_3$)$_3$)]): 202 [M-H]$^+$, 186 [M-NH$_2$]$^+$; Mpt: 117-119°C (lit. 119-120°C).

[Ph$_2$SNH] 2

Ph$_2$SNH$_2$$^+$ **90** (0.75g, 1.87mmol) was suspended in dry, degassed toluene (20ml) under a blanket of N$_2$ and treated dropwise with butyl lithium 2.5M (0.748ml) and subsequently left to stir for 3 hours. A yellow coloured solution was noted on addition of the butyl lithium but this then turned clear with further stirring. The solution was then dried *in vacuo* and the solid recrystallised from warm Et$_2$O to yield white needles of **2**. Yield: 0.14g, (37.2%); IR 3110cm^{-1} [ν N-H], 935cm^{-1} [ν N-S]. Mpt: 69-70°C (lit. 69°C).

[1,2-(PhS)$_2$C$_6$H$_5$] 9
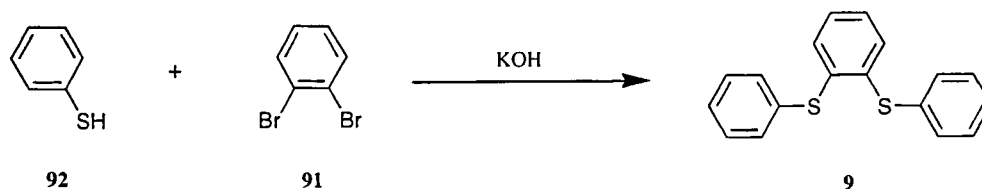
1,2-dibromobenzene **91** (25g, 0.106mol), potassium hydroxide pellets (12g, 0.215mol) in dimethylacetimide (100ml) were treated with benzenethiol **92** (22ml, 0.212mol) and

placed under reflux at 160°C for 7 days. The solution was cooled and washed with water (3 × 200ml), the resulting oil was then recrystallised by dissolving in Et$_2$O and adding methanol to yield a white crystalline solid **9**. Typical yield: 14.4g, (46%); IR: 3050, 743, 706, 687 cm^{-1}. $^m/_e$ (M = [(PhS)$_2$C$_6$H$_4$]): 294 [M-H]$^+$. ^{1}H NMR (CDCl$_3$): δ 7.26-7.40 (10H, m, Ph), 7.13-7.15 (4H, m, Ph). Found C 72.7, H 4.8; Calc for C$_{18}$H$_{14}$S$_2$ C 73.5, H 4.8.
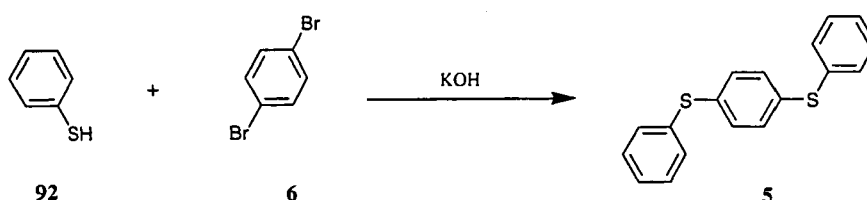
[1,4-(PhS)$_2$C$_6$H$_5$] 5

1,4-dibromobenzene **6** (25g, 0.106mol), potassium hydroxide pellets (12g, 0.215mol) in dimethylacetimide (100ml) were treated wi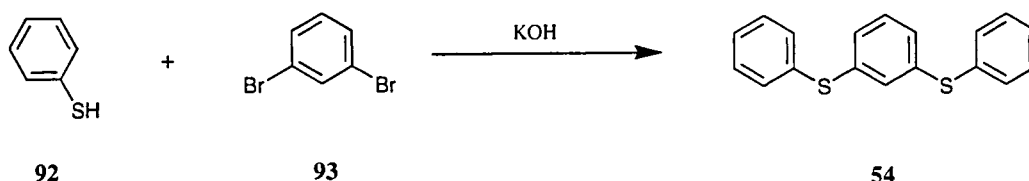th benzenethiol **92** (22ml, 0.212mol) and placed under reflux at 160°C for 7 days. The solution was cooled and washed with water (3 × 200ml), the resulting oil was then recrystallised by dissolving in Et$_2$O and adding methanol to yield a white crystalline solid. Typical yield: 20.3g, (80%). IR: 828, 739, 687 cm^{-1}. $^m/_e$ (M = [(PhS)$_2$C$_6$H$_4$]): 294 [M-H]$^+$. Found C 72.8, H 4.7; Calc for C$_{18}$H$_{14}$S$_2$ C 73.5, H 4.8. Mpt: 67-70°C.

[1,3-(PhS)$_2$C$_6$H$_5$] 54

1,3-dibromobenzene **93** (20.0g, 0.085mol), potassium hydroxide pellets (11.0g, 0.190mol in dimethylacetimide (100ml) were treated with benzenethiol **92** (19.0g,

0.173mol) and placed under reflux at 160°C for 7 days. The solution was cooled and washed with water (3 × 200ml), the resulting oil was then washed with water and subsequently separated using CH_2Cl_2, these portions were then reduced to yield a dark oil. Typical yield: 17.8g, (71.2%). IR: 3057, 777, 740, 688 cm^{-1}. $^m/_e$ (M = [(PhS)$_2$C$_6$H$_4$]): 294 [M-H]$^+$. ^{1}H NMR (CDCl$_3$): δ 7.18-7.53 (14H, m, Ph). Found C 71.5, H 4.7; Calc for $C_{18}H_{14}S_2$ C 73.5, H 4.8.
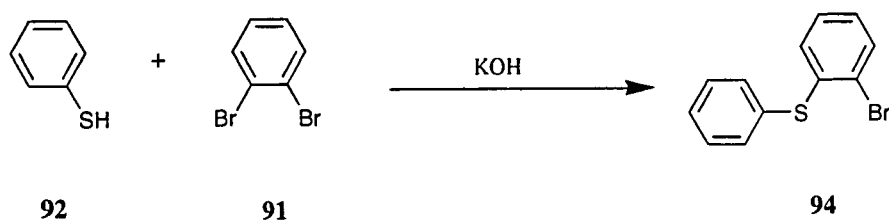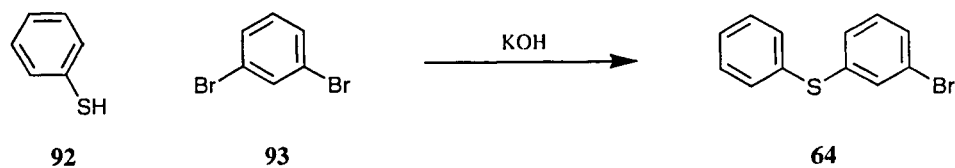

[1,2-(PhS)C₆H₅Br] 94

1,2-dibromobenzene **91** (15.0g, 0.064mol), potassium hydroxide pellets (3.58g, 0.064mol) in dimethylacetimide (100ml) were treated with benzenethiol **92** (7.05g, 0.064mol) and placed under reflux at 160°C for 24 hours. The solution was cooled and washed with water (3 × 200ml), the resulting oil was separated using CH_2Cl_2 and then vacuum distillation was performed using the vacuum line with the product **94** distilling at 160°C. Typical yield: 7.85g (47%). IR: 3058, 743, 689 cm^{-1}. $^m/_e$ (M = [(PhS)C₆H₄Br]): 266 [M$^+$], 294. ^{1}H NMR (CDCl$_3$): δ 6.99-7.61 (14H, m, Ph). Found C 53.7, H 3.5; Calc for $C_{12}H_9SBr$ C 54.3, H 3.4.

[1,3-(PhS)C$_6$H$_5$Br] 64

1,3-dibromobenzene **93** (15.0g, 0.064mol), potassium hydroxide pellets (3.58g, 0.064mol) in dimethylacetimide (100ml) were treated with benzenethiol **92** (7.05g, 0.064mol and placed under reflux at 160°C for 24 hours. The solution was cooled and washed with water (3 × 200ml), the resulting oil was separated using CH$_2$Cl$_2$ and then reduced *in vacuo*. Typical Yield: 12.8g (76%). IR: 3057, 1649, 868, 773, 754, 690 cm^{-1}. $^m/_e$ (M = [(PhS)C$_6$H$_4$Br]): 266 [M$^+$]. ^{1}H NMR (CDCl$_3$): δ 7.03-7.58 (9H, m, Ph). Found C 50.5, H 3.4; Calc for C$_{12}$H$_9$SBr C 54.3, H 3.4.

[2,6-(PhSNH$_2^+$)$_2$C$_5$H$_2$N($^-$OSO$_2$C$_6$H$_2$(CH$_3$)$_3$)$_2$] 70
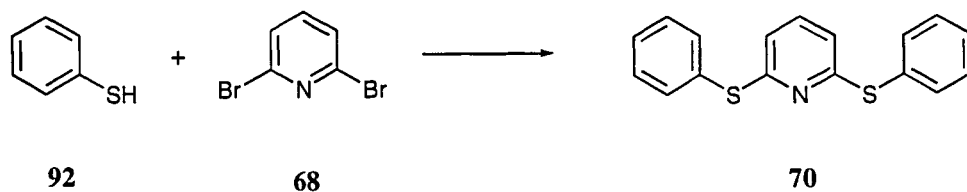
2,6-dibromopyridine **68** (21.4g, 0.091mol), potassium hydroxide pellets (10.1g, 0.181mol) in dimethylacetimide (100ml) were treated with benzenethiol **92** (20.0g, 0.181mol) and placed under reflux at 160°C for 7 days. The solution was cooled and washed with water (3 × 200ml), the white solid was then subsequently filtered and washed with more water. Typical yield: 19.4g (72.5%). IR: 790, 779, 757, 757, 691 cm^{-1}. $^m/_e$ (M = [(PhS)$_2$C$_5$H$_4$N]): 296 [M$^+$]. ^{1}H NMR (CDCl$_3$): δ 7.09-7.52 (10H, m, Ph), 6.45-6.47 (3H,(d,d), Ph). Found C 68.6, H 4.6, N 4.7; Calc for C$_{17}$H$_{13}$NS$_2$ C 69.1, H 4.4, N 4.8.

**[2-(PhSNH$_2^+$)C$_5$H$_4$N($^-$OSO$_2$C$_6$H$_2$(CH$_3$)$_3$)] 74**
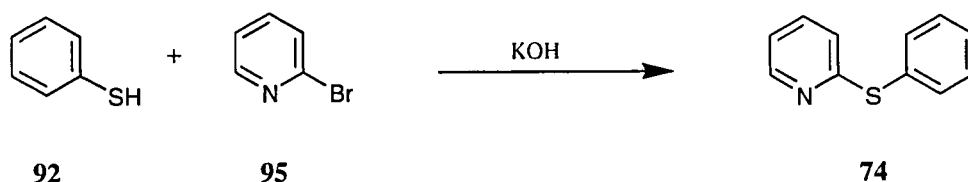
2-bromopyridine **95** (25.0g, 0.160mol) and potassium hydroxide pellets (8.96g, 0.160mol) in dimethylacetimide (100ml) were treated with benzenethiol **92** (20.0g, 0.181mol) and placed under reflux at 160°C for 7 days. The solution was cooled and washed with water (3 × 200ml), the resulting oil was then separated using DCM, these portions were then reduced to yield a dark oil. Typical yield: 11.8g, (39%). IR: 3049, 750, 690 cm^{-1}. $^m/_e$ (M = [(PhS)C$_5$H$_4$N]): 186 [M$^+$]. ^{1}H NMR (CDCl$_3$): δ 8.31-8.33 (1H, (m), Ph), 7.30-7.51 (6H, m, Ph), 6.78-6.80 (2H, (d,d), Ph). Found C 67.0, H 4.2, N 7.1; Calc for C$_{11}$H$_9$NS C 70.6, H 4.8, N 7.5.

[1,4-(PhSNH$_2^+$)$_2$C$_6$H$_4$($^-$OSO$_2$C$_6$H$_2$(CH$_3$)$_3$)$_2$] 4
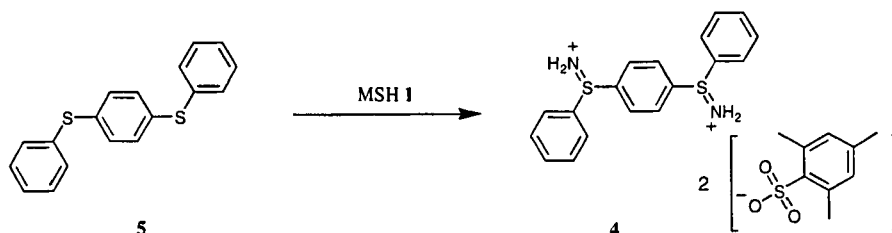
MSH **1** (2.89g, 4.14 mmol) in CH$_2$Cl$_2$ (10 ml) was treated with 1,4-(PhS)$_2$C$_6$H$_4$ **5** (0.61g, 2.07 mmol) in an equal volume of the same solvent with stirring. After 24 hours the solution was filtered and the resulting solid washed with CH$_2$Cl$_2$ (3 x 20 ml) then dried *in vacuo* to give a white solid **4** which was then recrystallised from MeOH/Et$_2$O. Yield 1.296 g (86%). IR: 1209, 1190, 846, 749, 685 cm^{-1}. $^m/_e$ (M = [(PhS{NH$_2$})$_2$C$_6$H$_4$]): 525[M+mesSO$_3$)$^+$, 325 [M-H]$^+$, 310 [M-NH$_2$]$^+$. ^{1}H NMR (DMSO – d$_6$): δ 7.25-7.65 (14H, m, Ph), 6.28 (4H, s(br), mes CH), 2.03 (12H, s, Me),

1.71 (6H,s, Me). Found C 59.3, H 5.2, N 3.8; Calc for $C_{36}H_{40}N_2S_4O_6 \cdot H_2O$ C 59.6, H 5.6, N 3.9. Mpt: 212-214 °C

[1,4-(PhSNH)$_2$C$_6$H$_4$] 7
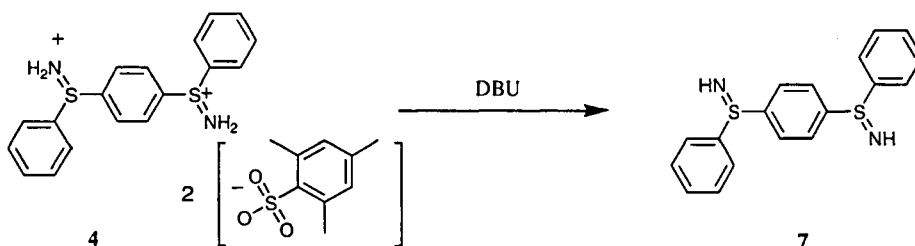
A suspension of [1,4-(PhSNH$_2^+$)$_2$C$_6$H$_4$(¯OSO$_2$C$_6$H$_2$(CH$_3$)$_3$)$_2$] 4 (0.524g, 0.67mmol) in CH$_2$Cl$_2$ (10 ml) was treated with a solution of DBU (1.471g, 9.66mmol) in an equal volume of the same solvent with vigorous stirring. During addition the solid at first dissolved and then by the time addition was complete a precipitate had appeared. After stirring for a few hours the solvent was removed *in vacuo* and the product triturated with water to give a white solid 7. Microanalysis indicated the presence of two waters of hydration. Yield 0.1 g (40%). IR 3111 [v N-H], 928cm^{-1} [v N-S]. $^m/_e$ (M = [(PhS{NH})$_2$C$_6$H$_4$]): 325 [MH]$^+$, 310 [M-N]$^+$, 200 [M-PhSNH]$^+$. ^{1}H NMR (DMSO–d$_6$): δ 7.00-7.32 (14H, m, Ph). Found C 66.4, H 4.9, N 8.5; Calc for $C_{18}H_{16}N_2S_2 \cdot 2H_2O$ C 66.6, H 5.0, N 8.6. Mpt: 194°C (dec)

[1,2-(PhSNH$_2^+$)C$_6$H$_4$(PhS)(¯OSO$_2$C$_6$H$_2$(CH$_3$)$_3$)] 8
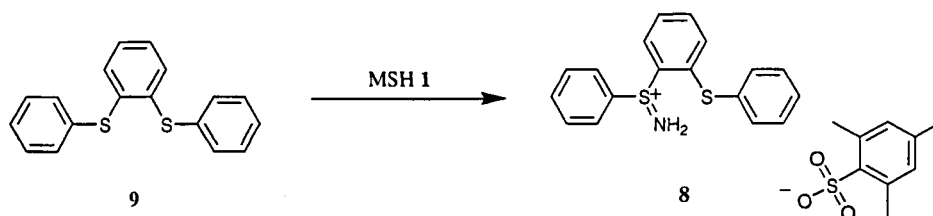
A solution of 1,2-(PhS)$_2$C$_6$H$_4$ 9 (3.56g, 0.012 mol) in CH$_2$Cl$_2$ (10 ml) was treated with a solution of MSH 1 (2.6g, 0.012 mol) in an equal volume of the same solvent, added

slowly with stirring. After stirring for a further 24 hours the solution was filtered through celite, the filtrate reduced to 5 ml *in vacuo* and the crude product precipitated by addition of excess Et$_2$O. Recrystallisation by addition of Et$_2$O to a methanol solution resulted in pure white solid **8**. Yield 3.23g (87%); IR 3084 [v N-H], 847 cm^{-1} [v N-S]. $^m/_e$ (M = [(PhS{NH$_2$$^+$})(PhS)C$_6H_4$]): 310 [M]$^+$, 294 [M-NH$_2$]$^+$. ^{1}H NMR (CDCl$_3$): δ 8.50-8.53 (1H, m, Ph), 6.94-7.70 (13H, m, Ph), 6.75 (2H, s(br), mes CH) ,3.1 (1H, broad, NH), 2.55 (6H, s, Me), 2.20 (3H,s, Me). Found C 62.9, H 5.2, N 2.5; Calc for C$_{27}$H$_{27}$NS$_3$O$_3$ C 63.6, H 5.3, N 2.8. Mpt: 132-134°C.

[1,2-(PhSNH)C$_6$H$_4$(PhS)] 10

A solution of [1,2-(PhSNH$_2$$^+$)C$_6H_4$(PhS)($^-OSO_2C_6H_2$(CH$_3$)$_3$)] **8** (3.43g, 6.74 mmol) in CH$_2$Cl$_2$ (10 ml) was treated with a solution of DBU (3.59g, 23.59 mmol) in an equal volume of the same solvent. After stirring for a few hours the solvent was removed *in vacuo* and the product triturated with water to give a white solid, the microanalysis results indicate one water of hydration **10b** which could then be removed *in vacuo* to give an oil **10a**. Yield 1.4g (67%). IR 3130 [v N-H], 920 cm^{-1} [v N-S]. $^m/_e$ (M = [(PhS{NH})(PhS)C$_6$H$_4$]): 310 [MH]$^+$, 294 [M-NH]$^+$. ^{1}H NMR (CDCl$_3$): δ 7.94-7.97 (1H, m, Ph), 7.17-7.53 (13H, m, Ph), 1.61 (s, water). Found C 66.2, H 5.0, N 3.9; Calc for C$_{18}$H$_{15}$NS$_2$.H$_2$O C 66.0, H 5.2, N 4.3. Mpt: 48-50°C.
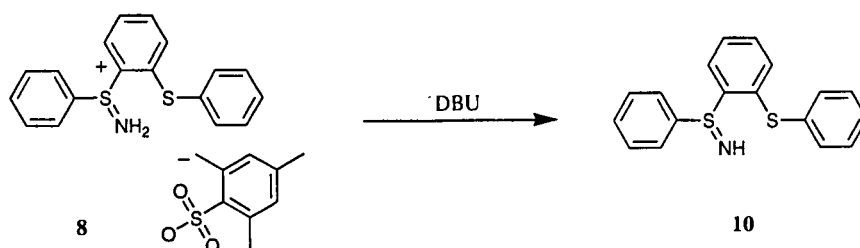
[1,4-(PhSNH₂⁺)C₆H₄ PhS(⁻OSO₂C₆H₂(CH₃)₃)] 11

$[1,4\text{-}(PhSNH_2{}^+)C_6H_4\,PhS({}^-OSO_2C_6H_2(CH_3)_3)]$ **11**

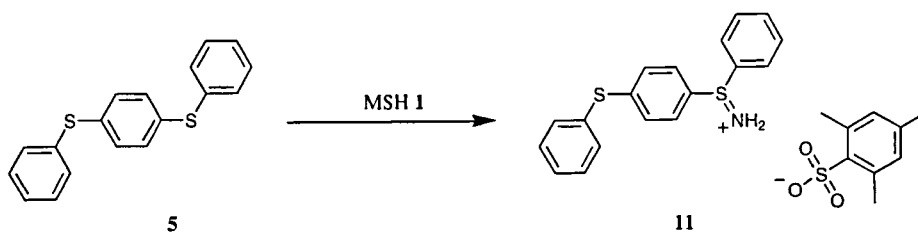A solution of MSH **1** (2.89g, 4.14 mmol) in CH_2Cl_2 (10 ml) was treated with a solution of 1,4-(PhS)₂C₆H₄ **5** (0.61g, 2.07 mmol) in an equal volume of the same solvent, with stirring. After stirring for a further 24 hours the solution was filtered through celite, the filtrate reduced to 5 ml *in vacuo* and the crude product precipitated by addition of excess Et_2O to give a white solid **11** which was then recrystallised from MeOH/Et₂O. Yield 1.62 g (86%). IR 1192, 1086, 851, 816, 750, 679 cm⁻¹. $^m/_e$ (M = [(PhS{NH₂})C₆H₄PhS]): 510[M+mesSO₃]⁺, 310 [M-NH₂]⁺. ¹H NMR (CDCl₃): δ 7.98-8.02 (1H, d, Ph), 7.00-7.67 (15H, m, Ph), 2.43 (6H, s, Me), 2.14 (3H,s, Me).

[1,4-(PhSNH)C₆H₄(PhS)] 12

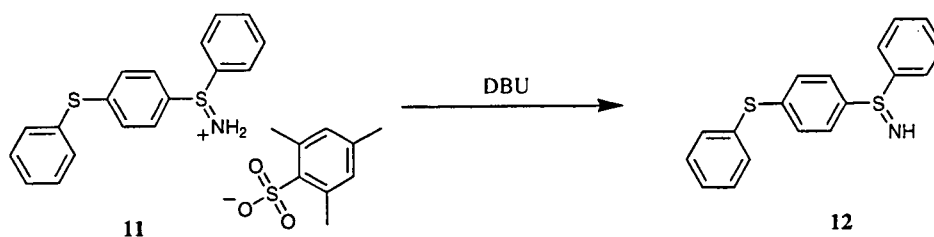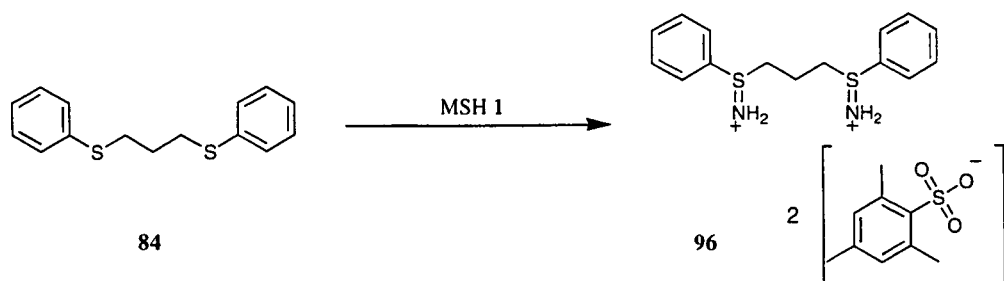$[1,4\text{-}(PhSNH)C_6H_4(PhS)]$ **12**

A solution of [1,4-(PhSNH₂⁺)C₆H₄ PhS(⁻OSO₂C₆H₂(CH₃)₃)] **11** (3.43g, 6.74 mmol) in CH_2Cl_2 (10 ml) was treated with a solution of DBU (3.59g, 23.59 mmol) in an equal volume of the same solvent. After stirring for a few hours the solvent was removed *in vacuo* and the product triturated with water to give a white solid **12**. Yield 0.117g (56%). IR 3235 [v N-H], 924 cm⁻¹ [v N-S]. $^m/_e$ (M = [(PhS{NH})(PhS)C₆H₄]): 310 [MH]⁺, 294 [M-NH]⁺. ¹H NMR (CDCl₃): δ 7.14-7.49 (15H, m, Ph). Mpt: 104-106°C.

[1,3-(PhSNH$_2$$^+$)$_2C_3H_6$ PhS($^-$OSO$_2$C$_6$H$_2$(CH$_3$)$_3$)$_2$] 96

A solution of 1,3-(PhS)$_2$(CH$_2$)$_3$ **84** (1.54ml, 7.68mmol) in CH$_2$Cl$_2$ (10 ml) was treated

with a solution of MSH **1** (2.87g, 0.013 mol) in an equal volume of the same solvent,

added slowly with stirring. After stirring for a further 48 hours the solution was

reduced to 5 ml *in vacuo* and the crude product precipitated by addition of excess

Et$_2$O. Recrystallisation by addition of Et$_2$O to a methanol solution resulted in pure

white solid **96**. Yield 2.734g (51%). IR: 2972, 1185, 846, 749, 682 cm^{-1}. $^m/_e$ (M =

[(PhS{NH$_2$})$_2$C$_3$H$_6$]): 526 [M-O$_3$SC$_6$H$_2$(CH$_3$)$_3$], 325 [M]$^+$, 310 [M-NH]$^+$. ^{1}H NMR

(CDCl$_3$) δ 7.18-7.91 (18H, m, Ph), 2.46 (12H, s, Me), 2.14 (6H, s, Me). Found C 58.4,

H 5.8, N 3.5; Calc for C$_{33}$H$_{42}$N$_2$S$_4$O$_6$ C 59.6, H 5.6, N 3.9.

[1,3-(PhSNH$_2$$^+$)$_2CH_2$PhS($^-OSO_2C_6H_2$(CH$_3$)$_3$)$_2$] 97
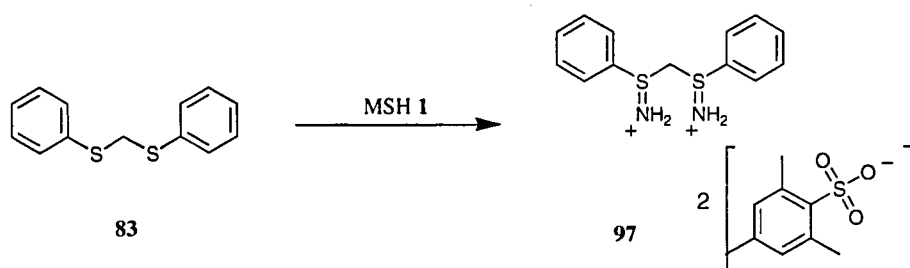
A solution of 1,3-(PhS)$_2$(CH$_2$) **83** (1.54ml, 7.68mmol) in CH$_2$Cl$_2$ (10 ml) was treated

with a solution of MSH **1** (2.87g, 0.013 mol) in an equal volume of the same solvent,

added slowly with stirring. After stirring for a further 48 hours it was noted that the

solution had a red colouration and a white solid was present. The solid was filtered

and the solution was dried *in vacuo*. Yield (solid): 0.59g (11%).
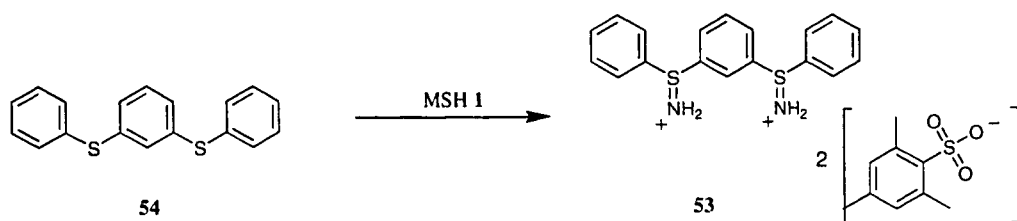
[1,3-(PhSNH₂⁺)₂C₆H₄(⁻OSO₂C₆H₂(CH₃)₃)₂] 53
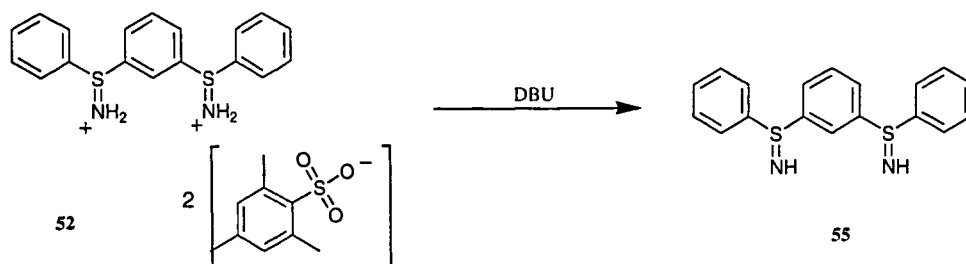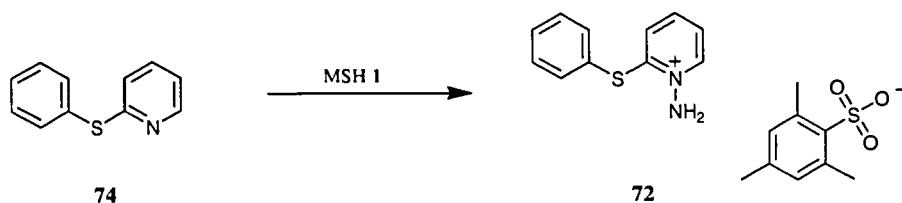

A solution of 1,3-(PhS)₂C₆H₄ **54** (1.169g, 3.98mmol) in CH₂Cl₂ (10 ml) was treated with a solution of MSH **1** (2.0g, 9.3mmol) in an equal volume of the same solvent, added slowly with stirring. After stirring for a further 24 hours the yellow solution was reduced to 5 ml *in vacuo* and the crude product precipitated by addition of excess Et₂O. Yield 2.13g (74%); IR 1185, 1086, 1014, 846, 749, 682 cm⁻¹. $^m/_e$ (M = [(PhS{NH₂⁺})₂C₆H₄]): 526[M+mesSO₃]⁺, 325 [M]⁺, 310 [M-NH₂]⁺. ¹H NMR (CDCl₃): δ 7.19-7.91 (18H, m, Ph), 2.46 (12H, s, Me), 2.14 (6H, s, Me). Found C 58.4, H 5.8, N 3.5; Calc for C₃₆H₃₆N₂S₄O₆ C 59.6, H 5.6, N 3.8.

[1,3-(PhSNH)₂C₆H₄] 55

A solution of [1,3-(PhSNH₂⁺)₂C₆H₄(⁻OSO₂C₆H₂(CH₃)₃)₂] **52** (0.922g, 1.27 mmol) in CH₂Cl₂ (10 ml) was treated with a solution of DBU (1.36g, 8.91 mmol) in an equal volume of the same solvent with vigorous stirring. After stirring for a few hours the solvent was removed *in vacuo* and the product was then washed with hot toluene and these portions were reduced to yield a dark oil. Yield 0.070 g (17.0%). IR 3226, 3051, 927 cm⁻¹. $^m/_e$ (M = [(PhS{NH₂⁺})₂C₆H₄]): 325 [M]⁺, 310 [M-NH₂]⁺, 294 [M-(NH₂)₂]⁺.

[2-(PhS)C$_5$H$_3$N(NH$_2$$^+$)($^-OSO_2C_6H_2$(CH$_3$)$_3$)] 72

A solution of [2-(PhS)C$_5$H$_3$N] **74** (3.48g, 0.019 mmol) in CH$_2$Cl$_2$ (10 ml) was treated with a solution of MSH **1** (4.00g, 0.019 mmol) in an equal volume of the same solvent, added slowly with stirring. After stirring for a further 24 hours the yellow solution was reduced to 5 ml *in vacuo* and the crude product precipitated by addition of excess Et$_2$O. Yield 3.62g (47.4%); IR 3110, 3052, 1185, 845 and 756 cm^{-1}. $^m/_e$ (M = [(PhS)C$_5$H$_4$N{NH$_2$}]): 203 [M]$^+$, 188 [M-NH$_2$]$^+$. ^{1}H NMR (DMSO-d$_6$): δ 7.70 (1H, s, Ph), 7.49 (1H, s, Ph), 7.29 (1H, s, Ph), 7.12 (1H, d, Ph), 2.86 (6H, s, Me), 2.54 (3H,s, Me). Found C 59.8, H 5.5, N 7.0; Calc for C$_{20}$H$_{22}$N$_2$S$_2$O$_3$ C 59.7, H 5.5, N 7.0.

[2-(PhSNH$_2$$^+$)C$_5H_3$N(NH$_2$$^+$)($^-OSO_2C_6H_2$(CH$_3$)$_3$)] 76

A solution of [2-{(PhS)C$_5$H$_3$N}] **74** (1.49g, 7.9 mmol) in CH$_2$Cl$_2$ (10 ml) was treated with a solution of MSH **1** (3.42g, 0.016 mol) in an equal volume of the same solvent, added slowly with stirring. After stirring for three weeks the yellow solution was reduced to 5 ml *in vacuo* and the crude product precipitated by addition of excess Et$_2$O. The crude product was then dissolved in MeOH and recrystallised from Et$_2$O to yield clear crystals which were cleaned by addition of CH$_2$Cl$_2$. Yield 2.93g (60.1%); IR 3178, 3028, 1174, 849, 781 and 753cm^{-1}. $^m/_e$ (M = [(PhS)C$_5$H$_4$N{NH$_2$}]): 203

[M]$^+$, 188 [M-NH]$^+$. Found C 51.4, H 7.0, N 6.7; Calc for $C_{29}H_{35}N_3S_3O_6$ C 56.4, H 5.7, N 6.8.

[2,6-(PhS)$_2$C$_5$H$_3$NH$^+$)(Cl$^-$)] 77

A suspension of [2,6-(PhS)$_2$C$_5$H$_3$N] **70** (1.0g, 3.5 mmol) in Et$_2$O (10 ml) was treated dropwise with HCl (5ml) whilst stirring. The clear yellow solution was reduced *in vacuo* and then washed with Et$_2$O to yield a white solid. Yield 0.92g (78%);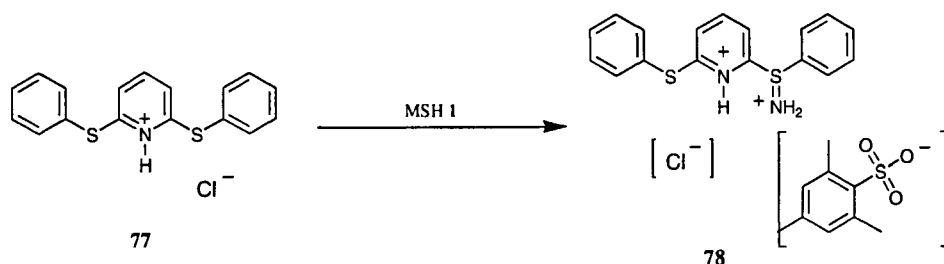 ^{1}H NMR (DMSO-d$_6$): δ 7.45-7.57 (11H, m, Ph), 6.63-6.65 (2H, (d), Ph). IR 3051, 779 and 757 cm^{-1}. Found C 67.5, H 4.7, N 4.8; Calc for C$_{17}$H$_{14}$NS$_2$Cl C 68.9, H 4.7, N 4.7.

[2,6-(PhSNH$_2$$^+$)C$_5H_3$NH(PhS)($^-OSO_2C_6H_2$(CH$_3$)$_3$)] 78
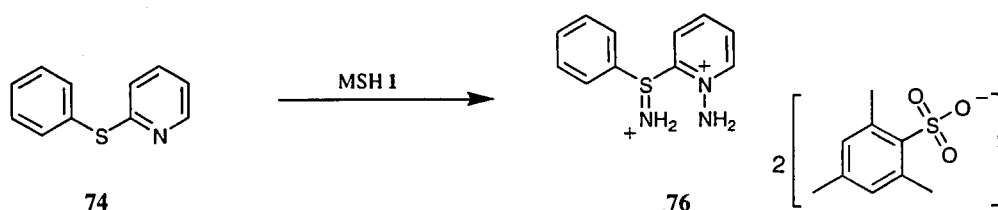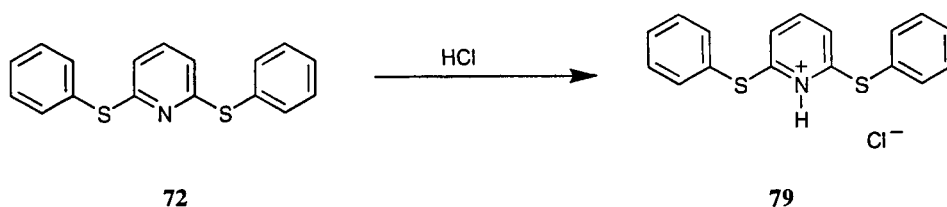
A solution of [2,6-(PhS)$_2$C$_5$H$_3$NH$^+$)(Cl$^-$)] **77** (0.50g, 1.52 mmol) in CH$_2$Cl$_2$ (10 ml) was treated with a solution of MSH **1** (0.327g, 1.52 mmol) in an equal volume of the same solvent, added slowly with stirring. After stirring for a further 24 hours the highly coloured purple solution was reduced *in vacuo* and the crude product precipitated by addition of excess Et$_2$O. The crude product was then dissolved in MeOH and recrystallized from Et$_2$O to yield clear crystals which were cleaned by addition of CH$_2$Cl$_2$. Yield 0.49g (59%); IR 3188, 3068, 1175, 845 and 687 cm^{-1}. $^m/_e$

(M = [(PhS)$_2$C$_5$H$_3$N{NH$_2$}]): 311 [M]$^+$, 296[M-NH]$^+$. ^{1}H NMR (DMSO-d$_6$): δ 7.16

(4H, s, Ph), 6.75 (1H, s, Ph), 3.35 (3H, s), 2.49 (6H, s, Me), 2.17 (3H,s, Me).

[2,6-(PhS)$_2$C$_5$H$_3$N(NH$_2$$^+$)($^-OSO_2C_6H_2$(CH$_3$)$_3$)] 98

70   98

A solution of [2,6-(PhS)$_2$C$_5$H$_3$N] **70** (0.25g, 0.847 mmol) in CH$_2$Cl$_2$ (10 ml) was

treated with a solution of MSH **1** (0.182g, 0.847 mmol) in an equal volume of the
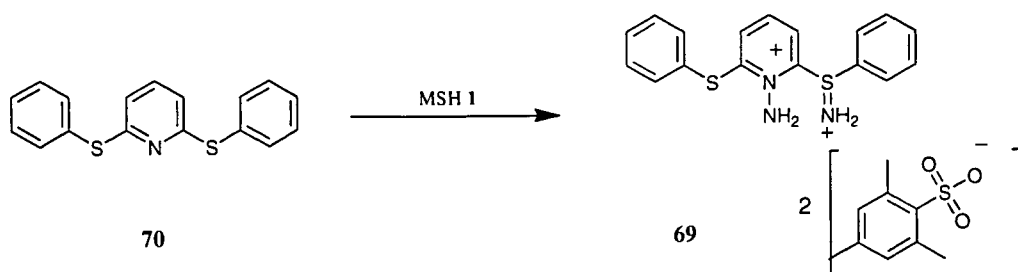
same solvent, added slowly with stirring. After stirring for a further 24 hours the

yellow solution was reduced to 5 ml *in vacuo* and the crude product precipitated by

addition of excess Et$_2$O. Yield 0.26g (60%); IR 3050, 2970, 1171, 850, 787 and 748

cm^{-1}. ^{m}/$_e$ (M = [(PhS)$_2$C$_5$H$_3$N{NH$_2$}]): 311 [M]$^+$, 296 [M-NH]$^+$. ^{1}H NMR (CDCl$_3$): δ

7.27-7.84 (15H, m, Ph), 2.50 (6H, (s), Me), 2.16 (3H, (s), Me).

[2,6-(PhSNH$_2$$^+$)C$_5H_3$N(NH$_2$$^+$)(PhS)($^-OSO_2C_6H_2$(CH$_3$)$_3$)$_2$] 69

70   69

A solution of 2,6-(PhS)$_2$C$_5$H$_3$N **70** (2.1g, 7.0mmol) in CH$_2$Cl$_2$ (10 ml) was treated with a

solution of MSH **1** (3.0g, 14.0 mmol) in an equal volume of the same solvent, added slowly

with stirring. After stirring for a further 24 hours the yellow solution was reduced to 5 ml *in*

vacuo and the crude product precipitated by addition of excess Et$_2$O. Yield 2.9g (57%); IR

1186, 1086, 1013, 851, 750, 681 cm^{-1}. ^{m}/$_e$ (M = [(PhS{NH$_2$})$_2$C$_5$H$_4$N]): 527 [M$^+$+mesSO$_3$)$^+$,

326 [M]$^+$, 311 [M-NH]$^+$. Found C 56.9, H 5.1, N 3.1; Calc for C$_{35}$H$_{39}$N$_3$S$_4$O$_6$ C 57.9, H 5.4, N 5.8.

[2,6-(PhSNH)C$_5$H$_3$N(NH$_2$$^+$)($^-OSO_2C_6H_2$(CH$_3$)$_3$)] 71
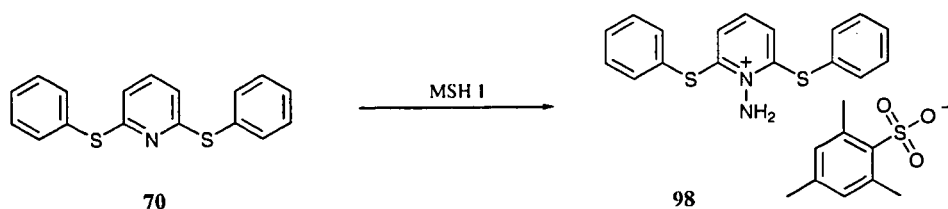
69   DBU   **71**
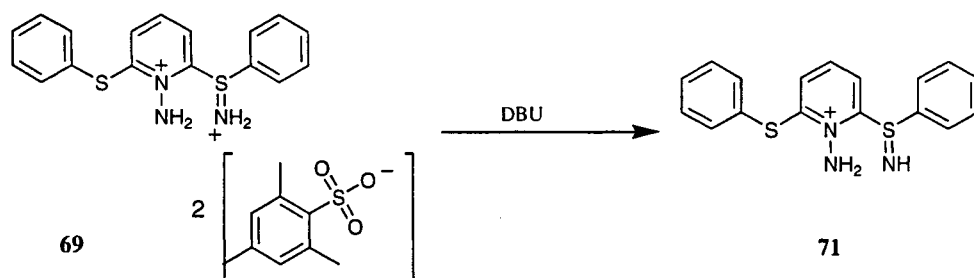
A solution of [2,6-(PhSNH$_2$$^+$)$_2C_5H_3$N($^-OSO_2C_6H_2$(CH$_3$)$_3$)$_2$] **69** (4.915g, 6.80 mmol) in CH$_2$Cl$_2$ (10 ml) was treated with a solution of DBU (7.247g, 0.048 mol) in an equal volume of the same solvent with vigorous stirring. After stirring for a few hours the solvent was removed *in vacuo* and the product was then washed with toluene and these portions were then reduced to give a dark oil. Yield 0.27g (12%). IR 1175, 1086, 1013, 938 [v N-S], 852, 750, 680 cm^{-1}. ^{m}/$_e$ (M = [(PhS{NH})$_2$C$_6$H$_4$]): 327 [MH]$^+$, 311 [M-N]$^+$. Found C 57.1, H 5.0, N 5.6; Calc for C$_{26}$H$_{27}$N$_3$S$_3$O$_3$ C 59.6, H 5.7, N 6.9.

[1,2-(PhSNH$_2$$^+$)C$_6H_4$(Br)($^-OSO_2C_6H_2$(CH$_3$)$_3$)] 85

94   MSH 1   **85**
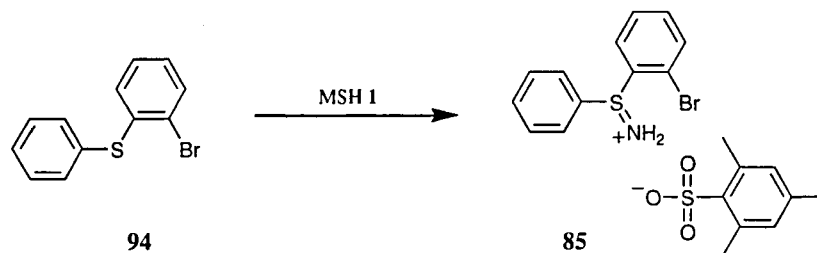
A solution of [1,2-(PhS)C$_6$H$_4$(Br)] **94** (3.7g, 0.014mol) in CH$_2$Cl$_2$ (10 ml) was treated with a solution of MSH **1** (3.0g, 0.014mol) in an equal volume of the same solvent, added slowly with stirring. After stirring for a further 24 hours the yellow solution
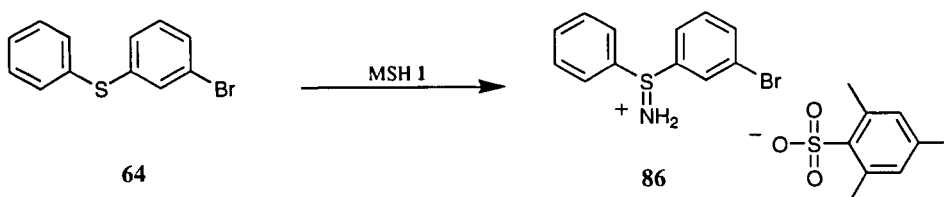
was reduced to 5 ml *in vacuo* and the crude product precipitated by addition of excess

Et$_2$O. Yield 2.57g (38%). IR 1209, 1086, 1014, 846, 753, 682 cm^{-1}. $^m/_e$ (M =

[(PhS{NH$_2$})C$_6$H$_4$Br]): 282 [M]$^+$. ^{1}H NMR (CDCl$_3$): δ 8.36-8.39 (1H, (d,d), Ph),

7.25-7.65 (8H, m, Ph), 2.45 (6H, s, Me), 2.12 (3H, s, Me). Found C 51.6, H 4.8, N

2.6; Calc forC$_{21}$H$_{22}$NBrS$_2$O$_3$ C 52.5, H 4.6, N 2.9.

[1,2-(PhSNH)C$_6$H$_4$(Br)] 99
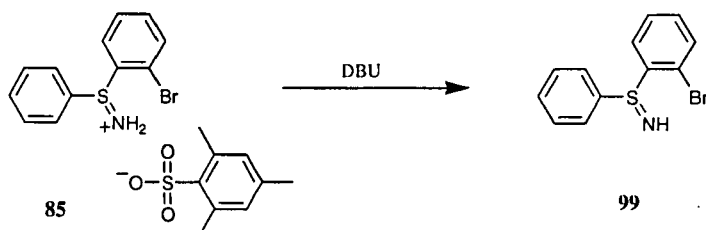
A solution of [1,2-(PhSNH$_2$$^+$)C$_6H_4$Br($^-OSO_2C_6H_2$(CH$_3$)$_3$)] **85** (4.18g, 0.015mol) in

CH$_2$Cl$_2$ (10 ml) was treated with a solution of DBU (7.99g, 0.053mol) in an equal

volume of the same solvent with vigorous stirring. After stirring for a few hours the

solvent was removed *in vacuo* and the product was then washed with toluene and

these portions were then reduced to give a yellow oil. Yield 0.36g (9%). IR 3222,

3046, 1614, 1200, 1113, 1086, 933 cm^{-1}. $^m/_e$ (M = [(PhS{NH})C$_6$H$_4$Br]): 280 [M]$^+$.

]$^+$. ^{1}H NMR (CDCl$_3$): δ 7.79 (1H, d, Ph), 7.20-7.45 (8H, m, Ph), 3.21-3.61 (m, CH-

DBU), 2.39-2.58 (m, CH-DBU), 1.49-1.62 (m, CH-DBU).

[1,3-(PhSNH$_2$$^+$)C$_6H_4$(Br)($^-OSO_2C_6H_2$(CH$_3$)$_3$)] 86

64   MSH 1 →   **86**

A solution of 1,3-(PhS)C$_6$H$_4$(Br) **64** (3.98g, 0.015mol) in CH$_2$Cl$_2$ (10 ml) was treated with a solution of MSH **1** (3.29g, 0.015mol) in an equal volume of the same solvent, added slowly with stirring. After stirring for a further 24 hours the yellow solution was reduced to 5 ml *in vacuo* and the crude product precipitated by addition of excess Et$_2$O. Yield 3.69g (51%). IR 1182, 843, 750, 678 cm^{-1}. $^m/_e$ (M = [(PhS{NH$_2$})C$_6$H$_4$Br]): 527[M+mesSO$_3$)$^+$, 282 [M]$^+$. ^{1}H NMR (CDCl$_3$): δ 7.50-7.73 (11H, m, Ph), 2.44 (6H, s, Me), 2.14 (3H, s, Me). Found C 51.8, H 4.9, N 2.8; Calc for C$_{21}$H$_{22}$NBrS$_2$O$_3$ C 52.5, H 4.6, N 2.9.
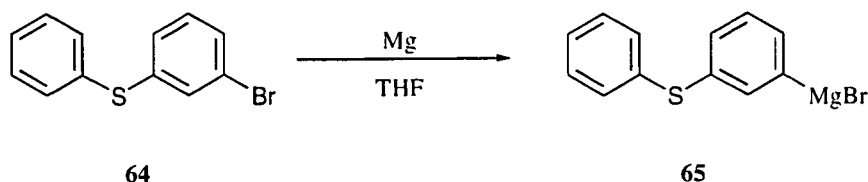
[1,3-(PhSNH)C$_6$H$_4$(Br)] 100

86   DBU →   **100**
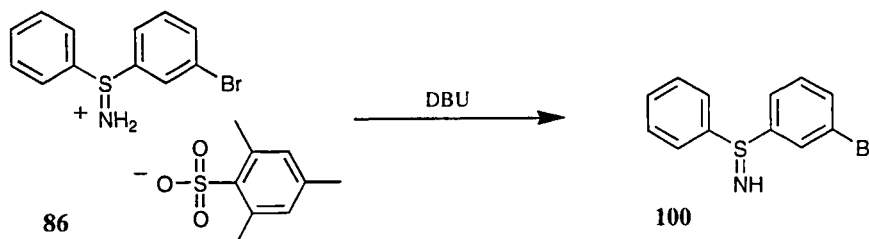
A solution of [1,3-(PhSNH$_2$$^+$)C$_6H_4$Br($^-OSO_2C_6H_2$(CH$_3$)$_3$)] **86** (1.39g, 2.89mmol) in CH$_2$Cl$_2$ (10 ml) was treated with a solution of DBU (1.54g, 0.010mol) in an equal volume of the same solvent with vigorous stirring. After stirring for five minutes the solvent was removed *in vacuo* and the product was then washed with toluene, these portions were then reduced to give a yellow oil. Yield 0.81g (10%). $^m/_e$ (M = [(PhS{NH})C$_6$H$_4$Br]): 280 [M]$^+$, 266[M-NH]$^+$.

[1,3-(PhS)C₆H₄(MgBr)] 65

64   65

A slurry, prepared using dry magnesium turnings (0.374g, 0.015mol) in dry degassed

THF (10ml) was treated with [1,3-(PhS)C₆H₄Br] **64** (3.84g, 0.014mol), dissolved in

dry, degassed THF (100ml) with continuous stirring. The solution was heated at 60 °C

for 30 minutes and then left to cool to room temperature. Yield 1.214g (100%)

[1,3-(PhS)C₆H₄(PhCNH)] 66

65   66

Benzonitrile (1.442g, 0.014mol) dissolved in dry, degassed THF (20ml) was treated

with [1,3-(PhS)C₆H₄(MgBr)] **65** (4.214g, 0.014mol) and left to stir overnight. The

solution was quenched using dry MeOH (30ml) and then the unwanted by-product

filtered after the addition of Et₂O (50ml) leaving a yellow oil.   Yield = 3.49g (77%);

IR 3059, 2228, 924, 739, 688 cm⁻¹. ᵐ/ₑ (M = [(PhS)C₆H₄(PhCNH)]): 294

[M⁺[(PhS)₂C₆H₄]], 290 [M⁺]. ¹H NMR (CDCl₃): δ 7.05-7.58 (14H, m, Ph).

[1,3-(PhS)C₆H₄(LiBr)] 101

64   **101**

[1,3-(PhS)C₆H₄Br] **64** (2.0g, 7.5mmol) dissolved in dry, degassed THF (20ml) was treated dropwise with butyl lithium 1.6M (4.7ml, 7.5mmol) and left to stir for 30 minutes. Benzonitrile (0.773g, 7.5mmol) was added dropwise and stirred overnight. The solution was quenched using dry MeOH (30ml) and then reduced *in vacuo*.

[1,3-(PhSNH2)C₆H₄(PhCNH)][(⁻OSO₂C₆H₂(CH₃)₃)] 67

66   **67**

A solution of [1,3-(PhS)C₆H₄(PhCNH)] **66** (0.774g, 2.7mmol) in CH₂Cl₂ (10 ml) was treated with a solution of MSH **1** (0.639g, 2.97mmol) in an equal volume of the same solvent, added slowly with stirring. After stirring for a further 24 hours the yellow solution was reduced to 5 ml *in vacuo* and the crude product precipitated by addition of excess Et₂O. Yield 0.37g (27%). IR 3167, 3026, 1188, 1086, 1014, 748, 682 cm⁻¹.

$^m/_e$ (M=[(PhS)C₆H₄(PhCNH)]): 325 [[(PhS)₂C₆H₄]], 310 [M⁺-NH₂⁺], 306 [M⁺[(PhS)C₆H₄(PhCNH)]], 294 [M⁺[(PhS)₂C₆H₄]], 290 [M⁺-NH₂⁺].

[1,3-(PhSNH)C₆H₄(PhCNH)] 63

A solution of [1,3-(PhSNH₂)C₆H₄(PhCNH)][(⁻OSO₂C₆H₂(CH₃)₃)] **67** (0.480g, 0.95mmol) in CH₂Cl₂ (10 ml) was treated with a solution of DBU (0.507g, 3.33mmol) in an equal volume of the same solvent with vigorous stirring. After stirring for a few hours the solvent was removed *in vacuo* and the product was then washed with toluene and these portions were then reduced to give a yellow oil. Yield 0.067g (23%). IR 3053, 2927, 1613, 917, 748, 693 cm⁻¹. ᵐ/ₑ (M = [(PhS)C₆H₄(PhCNH)]): 294 [M⁺[(PhS)₂C₆H₄]].

[14-aneS₄NH₂⁺(⁻OSO₂C₆H₂(CH₃)₃)] 81

A solution of [14-aneS₄] **82** (0.1g, 0.37 mmol) was treated dropwise with a solution of MSH **1** (0.08g, 0.37 mmol) in CH₂Cl₂ (10ml). A precipitate appeared within a short time of the start of the addition; after stirring overnight the resulting precipitate was filtered, washed with CH₂Cl₂, and dried *in vacuo* yielding a white solid of very low solubility. Yield 0.092g (51%). IR 3230, 3064 [ν N-H], 851 cm⁻¹ [ν N-S]. ᵐ/ₑ (M = [(C₁₉H₃₃NS₅O₃)]): 284 [M]⁺. Found C 46.9, H 7.1, N 3.1; Calc for C₁₉H₃₃NS₅O₃ C 47.2, H 6.9, N 2.9. Insoluble. Mpt 150°C (dec).

[14-aneS₄NH₂⁺(⁻OSO₂C₆H₂(CH₃)₃)Pd] 102

[(CH₃CN)₄Pd][BF₄]₂ (0.052g, 0.117mmol) was dissolved in degassed, dried MeCN (10ml) and treated with [14-aneS₄NH₂⁺(⁻OSO₂C₆H₂(CH₃)₃)] **81** (0.057g,0.117mmol) which was then left to stir for 1 hour. A change of colour was noted (intense yellow) after the addition of the ligand, which had dissolved in solution after approximately 10 minutes. The solvent was reduced and Et₂O was added to produce a yellow solid that was filtered and dried. Yield: 0.025g (42%)

[Br₂PdN(H)S(Ph)C₆H₄S(Ph)N(H)]₂ 16

A solution of [PPh₄]₂[Pd₂Br₆] **13** (0.102g, 0.074mmol) in CH₂Cl₂ (20ml) was treated with [1,4-(PhSNH)₂C₆H₄].2H₂O **7b** (0.050g, 0.15mmol) and the mixture stirred for several days during which time a red-brown microcrystalline product was generated. This was filtered from the solution and washed with CH₂Cl₂ and then Et₂O before being dried *in vacuo*. Yield 0.044g (50%). IR 3260 [v N-H], 880 cm⁻¹ [v N-S]. Found: C 36.3, H 2.6, N 4.4; Calc for Br₂PdC₁₈H₁₆S₂N₂ C 36.8, H 2.7, N 4.8%.

[Cl₂PdN(H)S(Ph)C₆H₄S(Ph)N(H)]₂ 18

[PPh₄]₂[Pd₂Cl₆] **14** (0.102g, 0.074mmol) in CH₂Cl₂ (20ml) was treated with [1,4-(PhSNH)₂C₆H₄].2H₂O **7b** (0.050g, 0.15mmol) and the mixture stirred for several days during which time a reddish-brown product was generated. This was filtered from the solution and washed with CH₂Cl₂ and then Et₂O before being dried *in vacuo*. Yield 0.045g (61%). IR 3260 [ν N-H], 898 cm⁻¹ [ν N-S]. Found: C 39.9,H 3.2, N 4.64%; Calc for Cl₂PdC₁₈H₁₆S₂N₂ C 43.2, H 3.2, N 5.6%.

[I₂PdN(H)S(Ph)C₆H₄S(Ph)N(H)]₂ 17
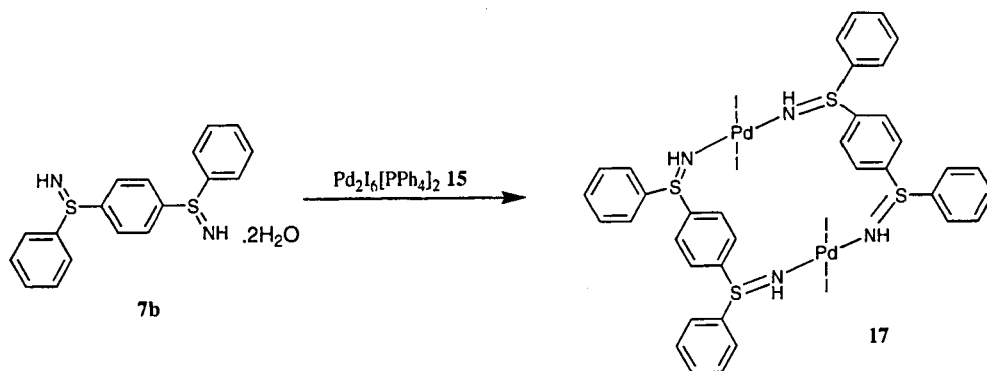

[PPh₄]₂[Pd₂I₆] **15** (0.202g, 0.122mmol) in CH₂Cl₂ (20ml) was treated with [1,4-(PhSNH)₂C₆H₄].2H₂O **7b** (0.079g, 0.244mmol) and the mixture stirred for several days during which time a reddish brown product was generated. This was filtered from the solution and washed with CH₂Cl₂ and then Et₂O before being dried *in vacuo*.

125

Yield: 0.105g (63%). IR 3260 [ν N-H], 880 cm^{-1} [ν N-S]. Found: C 31.9, H 2.4, N 4.1; Calc for I$_2$PdC$_{18}$H$_{16}$S$_2$N$_2$ C 31.6, H 2.4, N 4.1%.

[1,4-(PhSNBr)$_2$C$_6$H$_4$] 103

A solution of N-bromosuccinimide (0.024g, 0.136mmol) in acetone (10ml) was treated with 1,4-bis sulfimide **7b** (0.022g, 0.068mmol) with stirring. The yellow solid precipitate was then filtered and washed with acetone. Yield: 0.027g (82%); IR 3052 [ν N-H], 926 cm^{-1} [ν N-S]

[Pt(PhSC$_6$H$_4$S(Ph)NC(Me)NH)Cl$_2$] 21

A solution of [PtCl$_2$(MeCN)$_2$] **20** (0.109g, 0.314 mmol) in MeCN (10 ml) was treated with a solution of [1,2-(PhSNH)C$_6$H$_4$(PhS)] **10a** (0.097g, 0.314 mmol) in an equal volume of the same solvent added dropwise with stirring. After stirring at 50°C for four hours the mixture was cooled and the resulting precipitate filtered off and then recrystallised from CH$_2$Cl$_2$/Et$_2$O. Yield: 0.094g (49%). IR 3342, 3062, 800 cm^{-1}. $^m/_e$ (M = [(Cl$_2$PtC$_{20}$H$_{18}$S$_2$N$_2$)]): 616[M$^+$], 581[M$^+$- Cl$^-$]. ^{1}H NMR (CDCl$_3$): δppm 8.23-8.26 (2H, (d,d) CH-Ph), 7.26-7.75 (13H, m, CH-Ph), 2.37 (3H, s, Me): ^{13}C NMR (CDCl$_3$): δppm 18.12 (CH$_3$), 125.7 (C-H), 126.9 (C-H), 127.5 (C-H), 127.7 (C-H),

126

128.1 (C-H), 128.6 (C-H), 128.8 (C-H), 128.9 (C-H), 129.7 (C-H), 131.2 (C-H), 131.4 (C-H), 131.8 (C-H), 132.0 (C-H), 132.7 (C-H), 133.0 (C-H), 133.2 (C-H), 133.4 (C-H), 182.3 (C=N): ^{195}Pt NMR (CDCl$_3$): δppm –3087 (s): Found: C 38.7, H 2.8, N 4.3; Calc for PtC$_{20}$H$_{18}$S$_2$N$_2$Cl$_2$ C 38.9, H 2.9, N 4.5%. Mpt: 215°C (dec)

[Pt{(PhSC$_6$H$_4$S(Ph)NC(Me)NH)}(PPh$_3$)Cl$_2$] 104

A solution of [Pt(PhSC$_6$H$_4$S(Ph)NC(Me)NH)Cl$_2$] 21 (0.040g, 0.065mmol) in CH$_2$Cl$_2$ (10 ml) was treated with PPh$_3$ (0.017g, 0.065mmol) added dropwise with stirring. After 20 minutes the solution was reduced to dryness *in vacuo*. Yield: 0.033g (58%).

[Pt{(PhSNH)C$_6$H$_4$(SPh)}(DMSO)Cl$_2$] 24

(DMSO)$_2$PtCl$_2$ 22 (0.139g, 0.445mmol) was dissolved in degassed, dried DCM (10ml) under N$_2$. The anhydrous oil [1,2-(PhSNH)C$_6$H$_4$(PhS)] 10a (0.039g, 0.118mmol) was dissolved in CH$_2$Cl$_2$ (5ml) and added dropwise, the pale yellow solution was then left to stir overnight. The solvent was reduced and Et$_2$O was added where a pale yellow precipitate was observed. Yield: 0.052g (67%), IR 3255, 1126, 896 cm^{-1}. (M = [(DMSO)Pt{(PhS{NH$_2$})(PhS)C$_6$H$_4$}(Cl$_2$)]): 652[M]$^+$, 617[M- Cl]$^+$.

[Pt{(PhSNH)C₆H₄(SPh)}(dppe)] 25

$$\text{10a} \xrightarrow{\text{dppePtCl}_2\ \textbf{24}} \text{25}$$
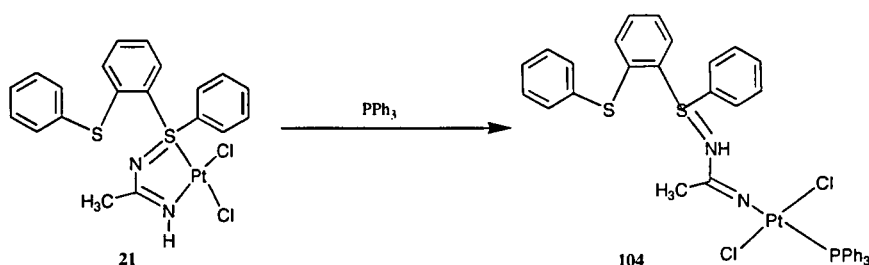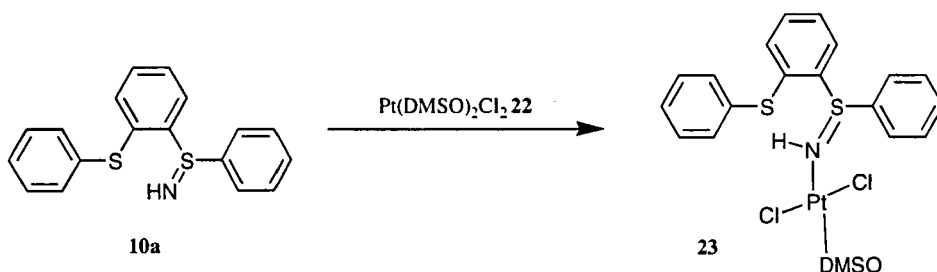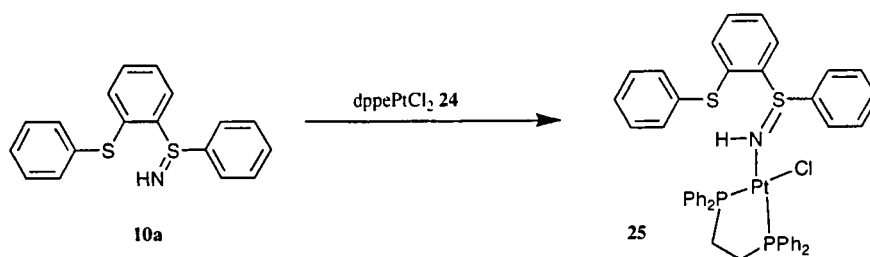
[Pt(dppe)Cl₂] **24** (0.070g, 0.106mmol) was dissolved in degassed, dried CH₂Cl₂ (10ml) under N₂. The anhydrous oil [1,2-(PhSNH)C₆H₄(PhS)] **10a** (0.033g, 0.106mmol) was dissolved in DCM (5ml) and added dropwise, the solution was then left to stir for 1 hour. The solution was filtered through celite and then reduced in vacuo to give an oil which was then recrystallised using CH₂Cl₂/Et₂O. Yield: 0.052g (67%), IR 3057[ν N-H], 930 cm⁻¹ [ν N-S]; $^m/_e$ (M = [dppePt(PhS{NH₂})(PhS)C₆H₄][SbF₆]): 1137[M]⁺, 901[M- SbF₆]⁺. ³¹P NMR (CDCl₃): δ [-1.606 (s,Pt sat), 40.112 (s), 82.073 (s,Pt sat)], [3.608(s,Pt sat), 50.178 (s), 96.990 (s,Pt sat)].

[Cu{(PhSNH)C₆H₄(SPh)}₂Cl₂] 43
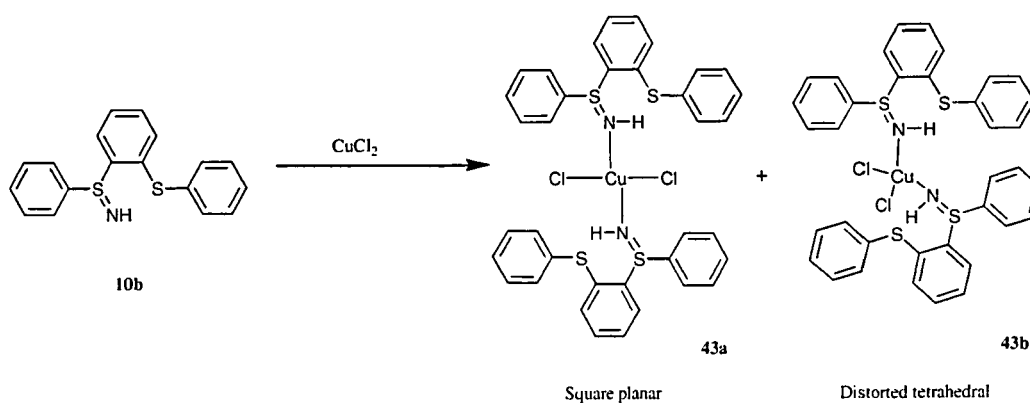
Anhydrous CuCl₂ (0.058g, 0.44mmol) was dissolved in degassed, dried acetonitrile (20ml). The solution was then treated with the hydrated solid [1,2-(PhSNH)C₆H₄(PhS)].H₂O **10b** (0.27g, 0.88mmol) which was left to stir for 24 hours.

The solution was then dried *in vacuo* and then subsequently dissolved in dichloromethane, petroleum ether 60/80° added and then was placed in the freezer until green and blue solid had formed. Yield: 0.145g (44%); IR 3311, 3275, 3053, 918 cm^{-1}; Found: C 56.6, H 4.0, N 3.4; Calc for $Cl_2CuC_{18}H_{15}NS_2$ C 57.4, H 4.0, N 3.7%.

[Pd{1,2-(PhSNH)C$_6$H$_4$(SPh)}Cl$_2$] 30
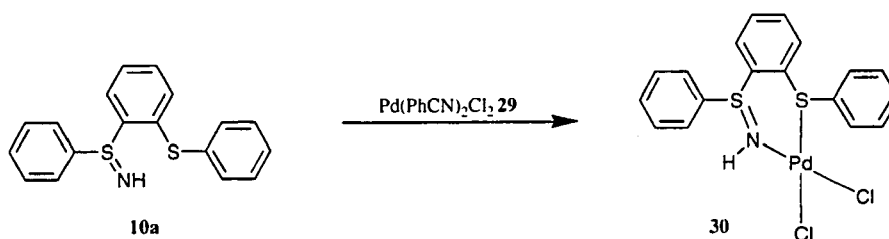
A solution of [PdCl$_2$(PhCN)$_2$] **29** (0.176g, 0.460mmol) in CH$_2$Cl$_2$ (10 ml) was treated with a anhydrous solution of [1,2-(PhSNH)C$_6$H$_4$(PhS)] **10a** (0.142g, 0.460mmol) in an equal volume of the same solvent added dropwise with stirring. After addition of the ligand a precipitate was present which after a minute of stirring had redissolved. The solution was then left to stand for 48 hours and the resulting orange/red or brown crystals were collected. Yield: 0.165g (86.5%). IR 3215, 3053, 944 cm^{-1}. ^{1}H NMR (CDCl$_3$): 7.17-7.85 (14H, m, Ph). Found: C 44.1, H 3.2, N 2.9; Calc for Cl$_2$PdC$_{18}$H$_{15}$S$_2$N C 44.4, H 3.1, N 2.9%.

[Pd{1,2-(PhSNH)C₆H₄(SPh)}(PPh₃)Cl₂] 31

[Pd{1,2-(PhSNH)C₆H₄(SPh)}(PPh₃)Cl₂] 31
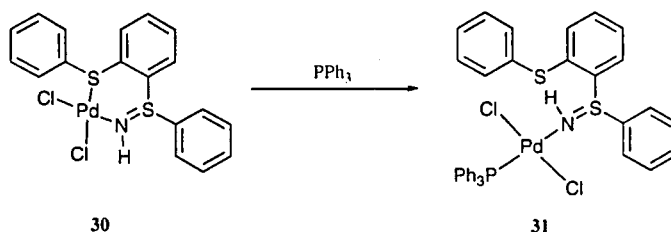
A solution of [Pd{1,2-(PhSNH)C₆H₄(SPh)}Cl₂] **30** (0.039g, 0.08mmol) in CH_2Cl_2 (10 ml) was treated with PPh_3 (0.021g, 0.08mmol) very slowly with stirring. After addition of the PPh_3 the clear solution was reduced in volume and petroleum ether (bp 40/60) was added. The resulting solid was then recrystallised from CH_2Cl_2/Et_2O to yield orange crystals. Yield: 0.036g (61%), IR 3294, 3048, 1096, 911cm⁻¹. ³¹P NMR: ($CDCl_3$) δ 27.742. Found: C 57.7, H 4.0, N 1.9; Calc for $Cl_2PdC_{36}H_{30}S_2NP$ C 57.2, H 3.9, N 1.7 %.

[Pd{1,2-(PPh₃)₂Cl₂] 32

[Pd{1,2-(PPh₃)₂Cl₂] 32
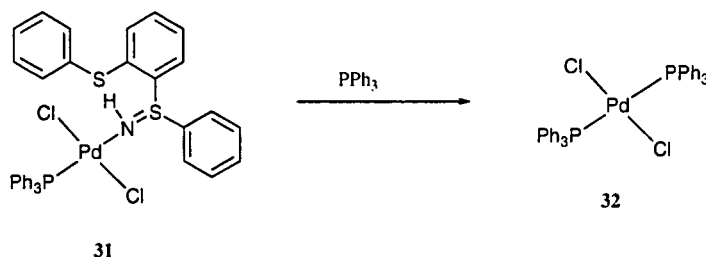
A solution of [Pd{1,2-(PhSNH)C₆H₄(SPh)}(PPh₃)Cl₂] **31** (0.023g, 0.03mmol) in CH_2Cl_2 (10 ml) was treated with PPh_3 (0.008g, 0.03mmol) with stirring. After addition of the PPh_3 a precipitate was present. The resulting solid was then filtered and washed with CH_2Cl_2. Yield: 0.018g (94%). IR 1261 cm⁻¹. ³¹P NMR: ($CDCl_3$) δ 23.376 (s). Found: C 58.7, H 4.5, N 0.2; Calc for $Cl_2PdC_{36}H_{30}P_2$ C 61.6, H 4.3, N 0.0 %.

Heck reaction using [Pd{1,2-(PhSNH)C₆H₄(SPh)}Cl₂] 30 as the catalyst
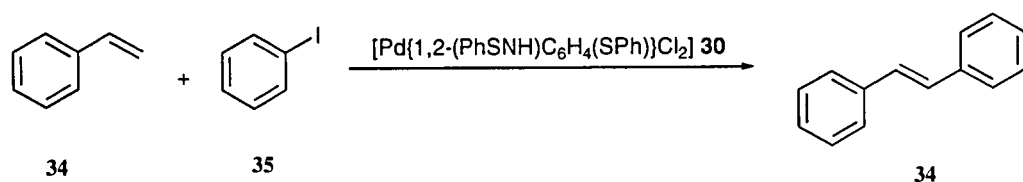
Iodobenzene **35** (1.027g, 4.9mmol), styrene **34** (0.787g, 7.5mmol), tributylamine (1.109g 5.9mmol), dimethylformamide (2ml) and [Pd{1,2-(PhSNH)C₆H₄(SPh)}Cl₂] **30** (0.017g, 3.5×10^{-5} mmol) were heated to 125°C under N_2 for 72 hours. DCM (10ml) was added to the cool solution and then separated using H_2O (10ml). The organic layer was extracted and washed with KCN (2 x 5ml), then H_2O (10ml) and then dried over MgSO₄. The filtered solid was then recrystallised by washing with a methanol solution. Yield: 0.413g (45.9%). ^1H NMR (CDCl₃): δ 7.216-7.376 (10H, m, Ph).

[PdCl₂(1,2-(PhS{NH})(PhS)C₆H₄)₂] 33
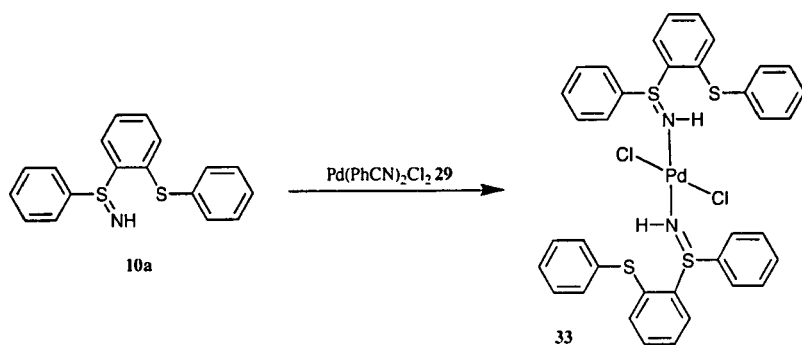
A solution of [PdCl₂(PhCN)₂] **29** (0.035g, 0.092 mmol) in THF (10 ml) was treated with a anhydrous solution of [1,2-(PhSNH)C₆H₄(PhS)] **10a** (0.057g, 0.185 mmol) in an equal volume of the same solvent added dropwise and left to stir for 2 hours. The clear orange solution was then reduced to a small volume, Et₂O added and the resulting orange solid was collected by filtration. Yield: 0.042g (57%). IR 3052, 898 cm⁻¹. Found: C 54.3, H 3.6, N 3.5; Calc for Cl₂PdC₃₆H₃₀S₂N₂ C 54.3, H 3.8, N 3.5%.

[Pd{(Ph₂SNH){1,2-(PhSNH)C₆H₄(SPh)}}Cl₂] 105
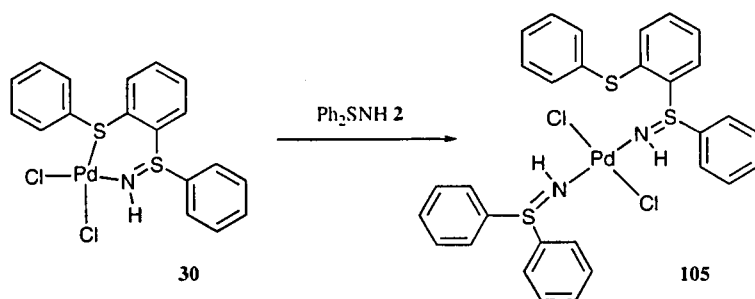
A solution of [Pd{1,2-(PhSNH)C₆H₄(SPh)}Cl₂] **30** (0.044g, 0.09mmol) in CH₂Cl₂ (10 ml) was treated with a solution of Ph₂SNH **2** (0.020g, 0.09mmol) in an equal volume of the same solvent added dropwise with stirring. After addition of the ligand the solution was reduced in volume and recrystallised from CH₂Cl₂/Et₂O to give orange crystals. Yield: 0.015g (24%). IR 3273, 3050, 896 cm⁻¹. Found: C 51.2, H 4.1, N4.0; Calc for Cl₂PdC₃₀H₂₆S₃N₂ C 52.4, H 3.8, N 4.1%.

[Rh(COD){(PhSNH)C₆H₄(SPh)}][SbF₆]₂ 45
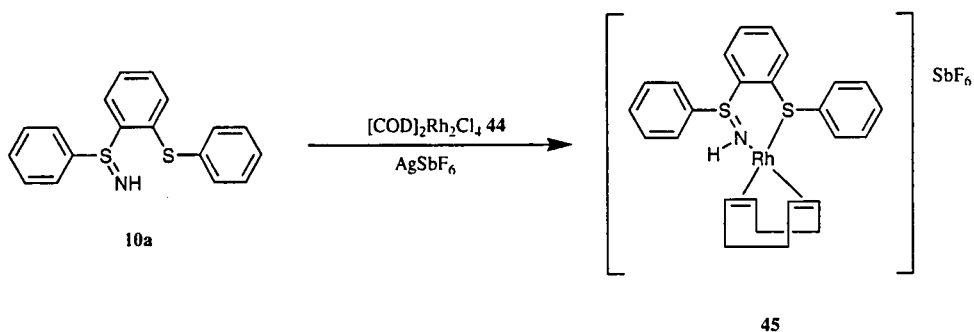
[COD]₂Rh₂Cl₄ **44** (0.516g, 1.05mmol) was dissolved in degassed, dried THF (10ml). The solution was treated with AgSbF₆ (0.720g, 2.09mmol) and left to stir for 2 minutes under a blanket of N₂. The anhydrous oil [1,2-(PhSNH)C₆H₄(PhS)] **10a** (0.685g, 2.09mmol) was added and left to stir for an hour. This solution was dried *in vacuo* to give a brown/gold solid, some crystals were obtained by slow diffusion using CHCl₂/Et₂O. Yield: 0.051g (6%); IR: 2942 [ν N-H], 917 cm⁻¹ [ν N-S]. ᵐ/ₑ (M = [(PhS{NH})(PhS)C₆H₄]): 520 [MH]⁺, 505 [M-NH]⁺. ¹H NMR (CDCl₃): δ 7.97 (1H,

d, Ph), 7.45-7.61 (13H, m, Ph), 2.12 (4H, d, COD), 1.85 (4H, m, COD). Found C

40.5, H 3.6, N 1.2; Calc for $RhC_{26}H_{27}NS_2SbF_6$. C 41.3, H 3.6, N 1.9.

[RuCy{(PhSNH)C₆H₄(SPh)}Cl₂] 47

10a → Cy₂Ru₂Cl₄ **46** → **47**
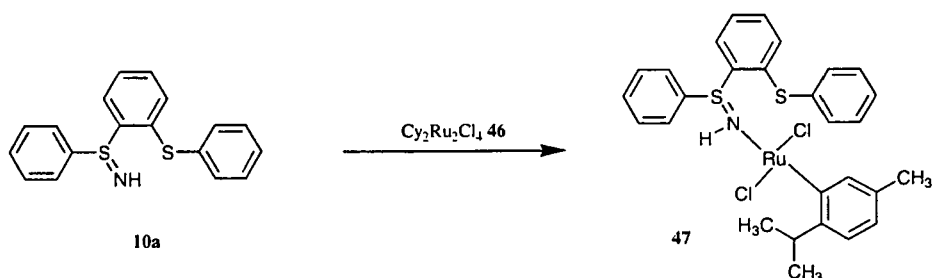
[Ru₂(Cy)₂Cl₄] **46** (0.094g, 0.306mmol) was dissolved in degassed, dried CH_2Cl_2

(10ml) then treated with the anhydrous oil [1,2-(PhSNH)C₆H₄(PhS)] **10a** (0.1g,

0.306mmol) and left to stir for 24 hours. The solution was dried *in vacuo* to give a

red/brown solid, this was subsequently recrystallised by slow diffusion using

MeOH/Et₂O which yielded small red crystals (two types: Clear and amorphous).

Yield: 0.082g (44%). IR 3054 [ν N-H], 925 cm⁻¹ [ν N-S]. ¹H NMR (CDCl₃): δ 7.92

(1H, d, Ph), 7.12-7.51 (13H, m, Ph), 5.48 (1H, d, Ph), 5.32 (1H, d, Ph), 5.15 (1H, d,

Ph), 5.02 (1H, d, Ph), 2.9 (1H, m, CH branched), 2.15 (3H, s, Me), 1.26 (6H, d, Me).

[Mo{(PhSNH)C₆H₄(SPh)}(CO)₄] 106

10a → Mo(pipirazine)₂(CO)₄ **48** → **106**
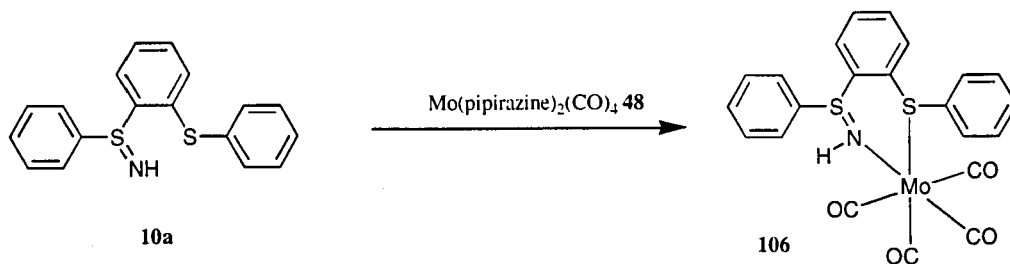
Mo(pipirazine)₂(CO)₄ **48** (0.515g, 1.62mmol) was dissolved in degassed, dried

CH₂Cl₂ (10ml) and treated with the anhydrous oil [1,2-(PhSNH)C₆H₄(PhS)] **10a**

(0.530g, 1.62mmol) which was left to stir for 24 hours under a blanket of N₂. This

133

solution was dried *in vacuo* to give a brown solid. IR 3129 [v N-H], 919 cm^{-1} [v N-S].

[Mo{(PhSNH)C₆H₄(SPh)}(CO)₂(Br)C₃H₆] 107

Allyl bromide

106   107
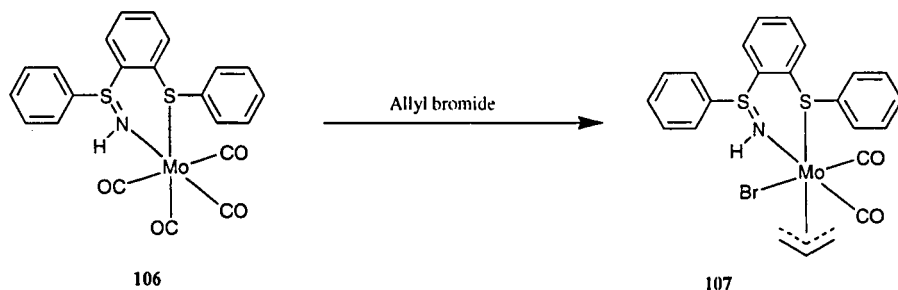
[Mo(1,2-bis(phenylthio)benzene sulfimide)(CO)₄] **106** (0.508g, 0.925mmol) was dissolved in degassed, dried acetonitrile (10ml). Allyl bromide (0.08ml, 0.925mmol) was added and left to stir for 30 minutes under a blanket of N₂. This solution was dried *in vacuo* to give a brown oily residue. IR 3046 [v N-H], 950 cm^{-1} [v S-N].

[Fe(CO)₃{(PhSNH)C₆H₄(SPh)}] 108

Fe₃(CO)₁₂ 50

10a   108
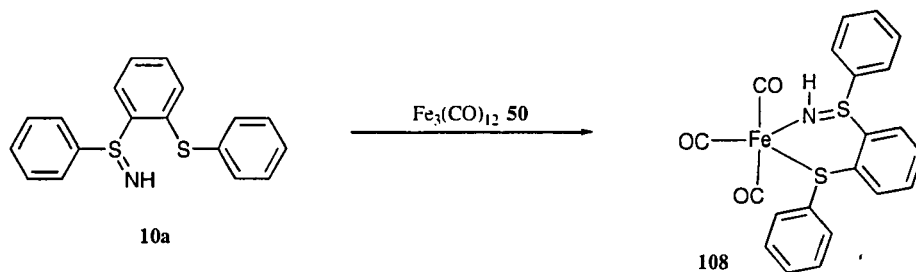
Fe₃CO₁₂ **50** (0.10g, 0.199mmol) was dissolved in degassed, dried CH₂Cl₂ (10ml) and treated with the anhydrous oil [1,2-(PhSNH)C₆H₄(PhS)] **10a** (0.195g, 0.596mmol) and left to stir for 2 hours under a blanket of N₂. This solution was dried *in vacuo* and recrystallised from CH₂Cl₂/hexane to give a brown solid. IR 3048 [v N-H], 1986,1637,919 cm^{-1} [v N-S]. ¹H NMR (CDCl₃): δ 8.15(1H, d, Ph), 7.13-7.36 (13H, m, Ph).

[Re(Br)(CO)₃{(PhSNH)C₆H₄(SPh)}] 109
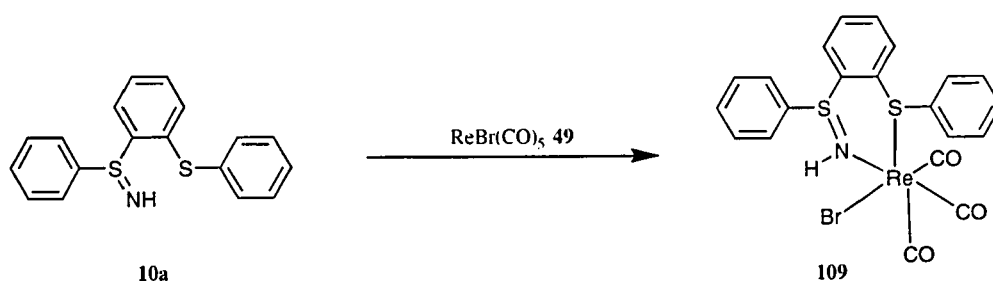
Re(Br)(CO)₅ **49** (0.155g, 0.382mmol) was dissolved in degassed, dried THF (20ml) then treated with the anhydrous oil [1,2-(PhSNH)C₆H₄(PhS)] **10a** (0.125g, 0.382mmol) and left to stir for 1 hour at 70°C under a blanket of N₂. This solution was cooled and dried *in vacuo* to give a dark brown solid. IR: 2035,1917, 917 cm⁻¹; ¹H NMR (CDCl₃): δ 7.78 (1H, m, Ph), 7.31-7.37 (9H, m, Ph), 7.13-7.14 (4H, m, Ph).

[Re(CO)(KTp){(PhSNH)C₆H₄(SPh)}] 110
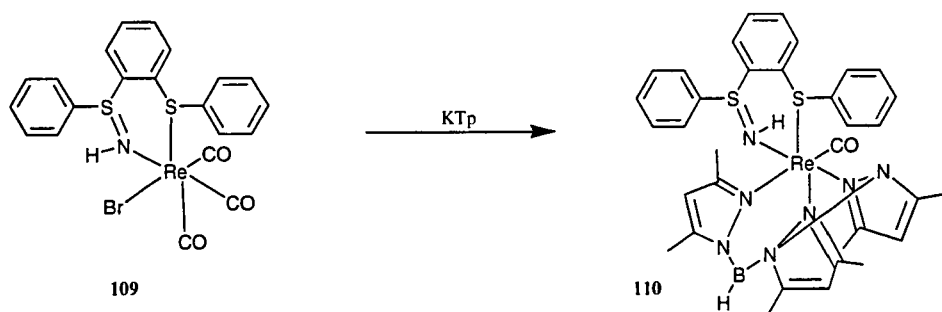
Re(Br)(CO)₃(1,2-bis(phenylthio)benzenesulfimide) **109** (0.197g, 0.299mmol) dissolved in degassed, dried THF (50ml). The solution was treated with KTp (0.101g, 0.299mmol) and then refluxed for 2 hours at 80°C under a blanket of N₂. This solution was cooled and dried *in vacuo* to give a dark brown residue. IR 2022, 1922, 1878,1650 [ν C-O], 902 cm⁻¹ [ν N-S].

[PdCl₂(PhCN(1,4-(PhS{NH})(PhS)C₆H₄))] 51a
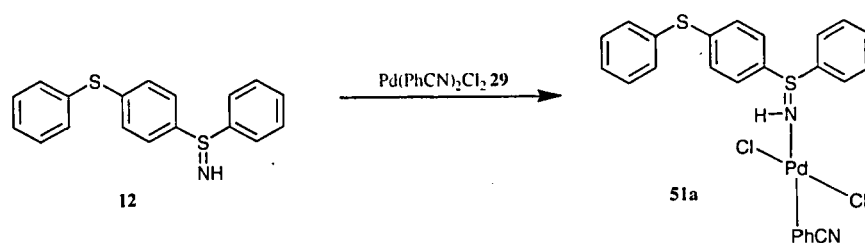
A solution of [PdCl₂(PhCN)₂] **29** (0.063g, 0.165 mmol) in CH₂Cl₂ (10 ml) was treated

with a anhydrous solution of [1,4-(PhS{NH})(PhS)C₆H₄)] **12** (0.051g, 0.165 mmol) in

an equal volume of the same solvent added dropwise with stirring. After addition of

the ligand a precipitate was present and the yellow solid was collected by filtration.

Yield: 0.030g (39%). IR 3200, 3055, 924 cm⁻¹.

[PdCl₂(1,4-(PhS{NH})(PhS)C₆H₄)₂] 51b
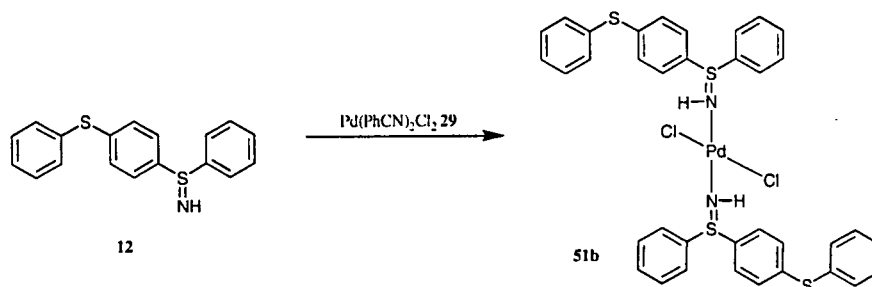
A solution of [PdCl₂(PhCN)₂] **29** (0.032g, 0.084 mmol) in THF (10 ml) was treated

with a anhydrous solution of [1,4-(PhS{NH})(PhS)C₆H₄)] **12** (0.052g, 0.165 mmol) in

an equal volume of the same solvent added dropwise and left to stir for 2 hours. The

clear orange solution was then reduced to a small volume, Et₂O added and the

resulting orange solid was collected by filtration. Yield: 0.032g (47%). ¹H NMR

(CDCl₃) δ 7.17-7.59 (28H, m, Ph). Found: C 52.5, H 4.1, N 3.8; Calc for

Cl₂PdC₃₆H₃₀S₂N₂ C 54.3, H 3.8, N 3.5%.

[Cu(1,4-(PhS{NH})(PhS)C₆H₄)Cl₂] 52
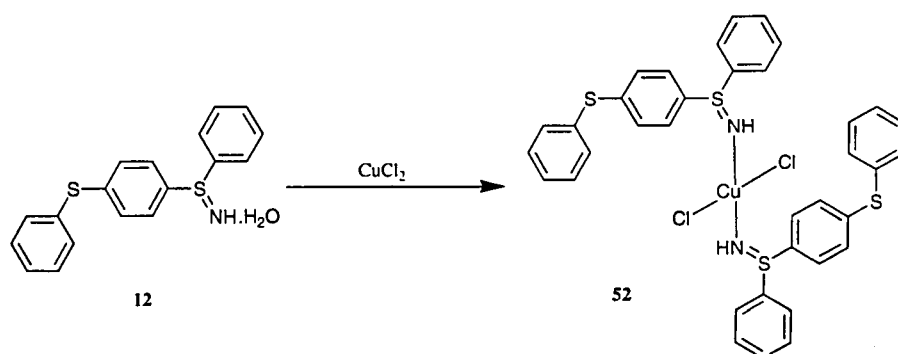
Anhydrous $CuCl_2$ (0.014g, 0.103mmol) was dissolved in degassed, dried acetonitrile (20ml). Then treated with the hydrated solid [1,4-(PhS{NH})(PhS)C₆H₄)Cl₂] **12** (0.075g, 0.206mmol) and left to stir for 24 hours. The solution was then dried *in vacuo* and then subsequently either dissolved in CH_2Cl_2 with petroleum ether (bp 60/80°) added and left to evaporate (dark green crystals), or recrystallised from hot acetonitrile (mixture of dark and pale green crystals). Yield: 0.041g (58%); IR 3241, 3066, 922 cm⁻¹; Found: C 57.2, H 3.8, N 3.6; Calc for $Cl_2CuC_{18}H_{15}NS_2$ C 57.4, H 4.0, N 3.7%.

[1,3-(PhSNH₂⁺)₂C₆H₄][BPh₄]₂ 111
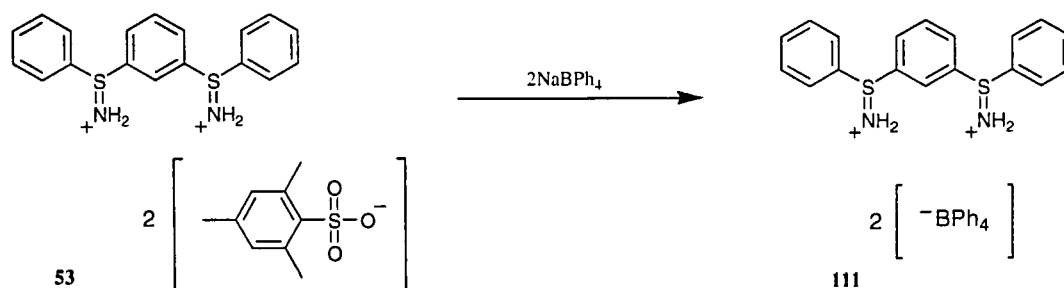
A solution of [1,3-(PhSNH₂⁺)₂C₆H₄(⁻OSO₂C₆H₂(CH₃)₃)₂] **53** (0.832g, 1.14mmol) in MeOH (20ml) was treated with solid NaBPh₄ (.778g, 2.27mmol) with stirring. The precipitate was then filtered, left to dry in air for 20 minutes and recrystallised from MeCN/Et₂O to give colourless crystals. Yield: 0.586g (53.3%). IR 3204, 3053, 916 cm⁻¹.

[Cu{1,3-(PhSNH)₂C₆H₄}Cl₂] 57
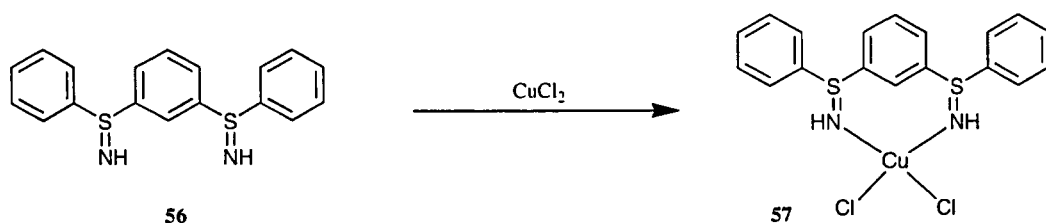
A solution of CuCl₂ (0.029g, 0.216mmol) in MeCN (10ml) was treated with a solution of [1,3-(PhSNH)₂C₆H₄] **56** (0.070g, 0.216mmol) in MeCN (10ml) dropwise with stirring. IR 3204, 3053, 916 cm

[Pt{1,3-(PhSNH)₂C₆H₄}(PPh₃)₂] 58
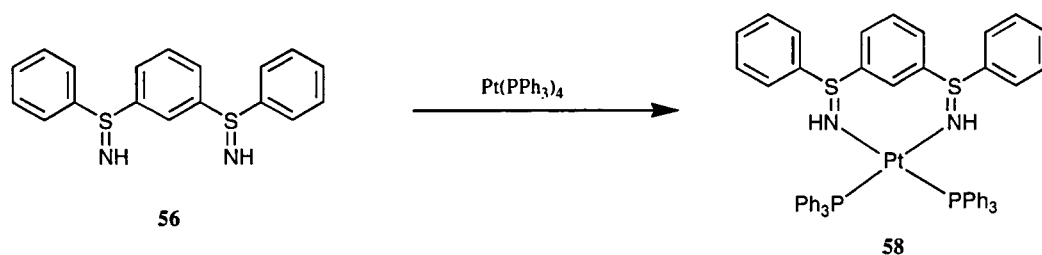
A solution of Pt(PPh₃)₄ (0.052g, 0.040mmol) in CH₂Cl₂ (10ml) was treated with a solution of [1,3-(PhSNH)₂C₆H₄] **56** (0.013g, 0.040mmol) in CH₂Cl₂ (10ml) dropwise with stirring, the solution was then heated to 50°C. The clear yellow solution was reduced in volume and hexane was added, further trituration using hexane gave a solid product. IR 3231, 3108, 3045, 934 cm⁻¹.

[RhCl{1,3-(PhSNH)₂C₆H₄}] 62
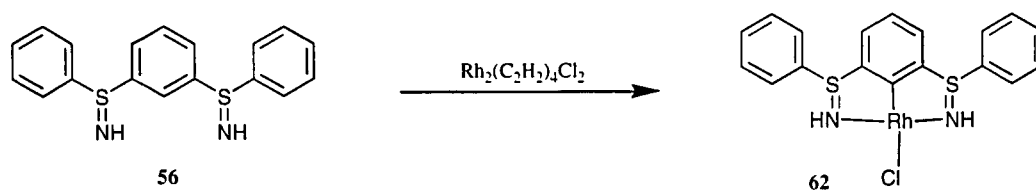
A solution of Cl₂Rh₂(C₂H₂)₄ (0.030g, 0.077mmol) in CH₂Cl₂ (10ml) was treated with a solution of [1,3-(PhSNH)₂C₆H₄] **56** (0.011g, 0.039mmol) in CH₂Cl₂ (10ml)

dropwise and then left to stir for 4 hours. The solution was reduced in volume and then hexane was added to yield a yellow/brown solid. IR 3231, 3112, 945 cm^{-1}.

[Os{1,3-(PhSNH)$_2$C$_6$H$_4$}(CO)Cl] 60
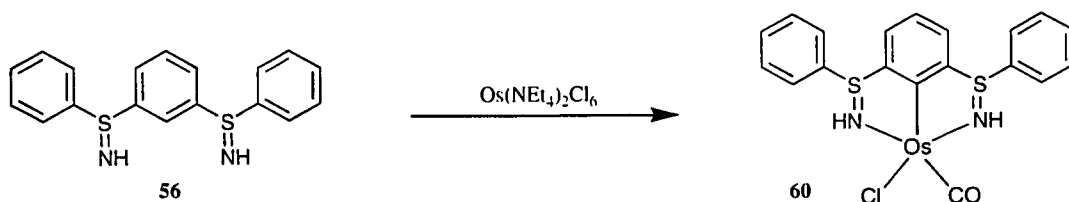
A mixture of (NEt$_4$)$_2$OsCl$_6$ (0.102g, 0.154mmol) and [1,3-(PhSNH)$_2$C$_6$H$_4$] **56** (0.050g, 0.154mmol) in isoamyl alcohol (30ml) along with MeOH (10ml) and Et$_3$N (1ml) was stirred at 130°C for 72 hours. The dark mixture was cooled and the green solid was filtered. IR 3028, 951 cm^{-1}.

[Pd{1,3-(PhSNH)$_2$C$_6$H$_4$} (MeCN)$_2$][BF$_4$]$_2$ 61
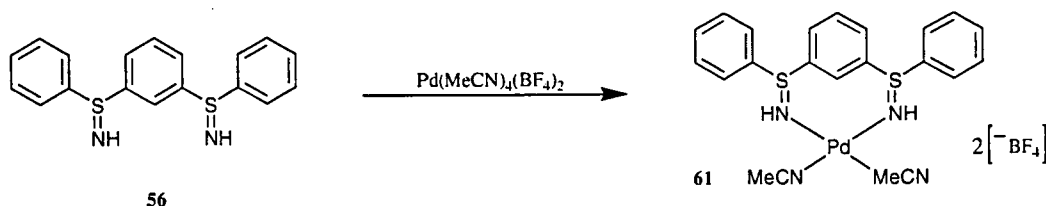
A solution of (MeCN)$_4$Pd(BF$_4$)$_2$ (0.048g, 0.111mmol) in CH$_2$Cl$_2$ (10 ml) was treated with a solution of [1,3-(PhSNH)$_2$C$_6$H$_4$] **56** (0.036g, 0.111mmol) in an equal volume of the same solvent added dropwise with stirring and left for 2 hours. The solution was then reduced and layered with Et$_2$O. Yield: 0.034g; IR 3051, 923 cm^{-1}.

[Rh(Cl)(H){1,3-(PhSNH)₂C₆H₄}] 59

56 → RhCl₃ → **59**
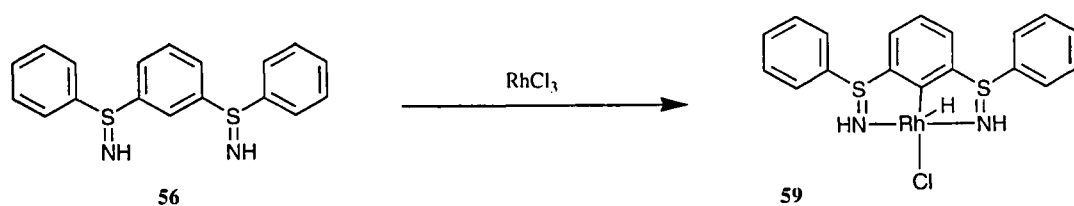
A solution of RhCl₃ (0.082g, 0.391mmol) in propan-2-ol (10ml) was treated with a solution of [1,3-(PhSNH)₂C₆H₄] **56** (0.190g, 0.586mmol) in propan-2-ol (10ml) along with water (0.5ml). The pink mixture was then heated for 12 hours at 70°C after which it was cooled and the orange solid was filtered. IR 3230, 3046, 919 cm⁻¹.

[{2,6-[(PhS)₂ C₅H₃N}]₂}{(PhS)₂}Pd₂Cl₂] 79

70 → Pd(PhCN)₂Cl₂ **29** → **79**
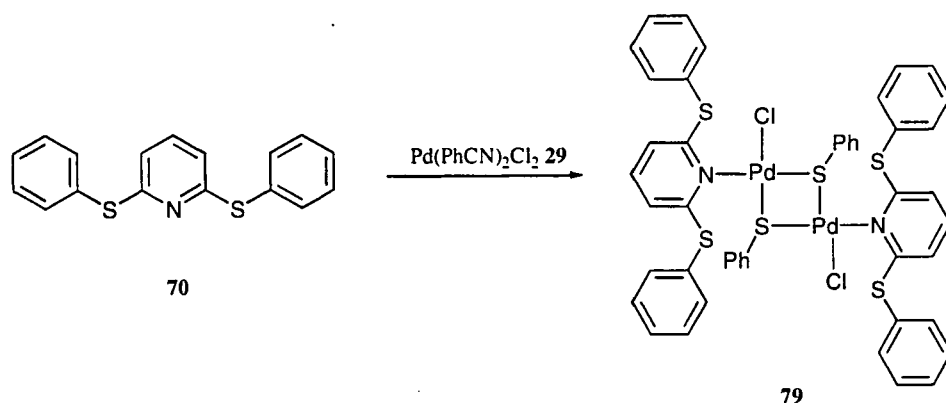
(PhCN)₂PdCl₂ **29** (0.155g, 0.382mmol) was dissolved in THF (10ml) then treated with [2,6-{(PhS)C₅H₃N}] **70** (0.125g, 0.382mmol) and left to stir for 30 seconds where the resulting yellow solid and solution was stoppered, sealed and left to stand overnight. The yellow solution was decanted from the solid and was left to stand for several weeks yielding orange cubic crystals. Yield 0.036g (9%). IR: 3037, 1549, 1422, 798, 751 cm⁻¹; Found C 51.4, H 3.3, N 3.5; Calc for Pd₂C₄₆H₃₆N₂S₆Cl₂. C 50.6, H 3.3, N 2.6.

[{2,6-(PhS)₂C₅H₃N}₂CuCl₂] 80

[{2,6-$(PhS)_2C_5H_3N$}$_2CuCl_2$] 80
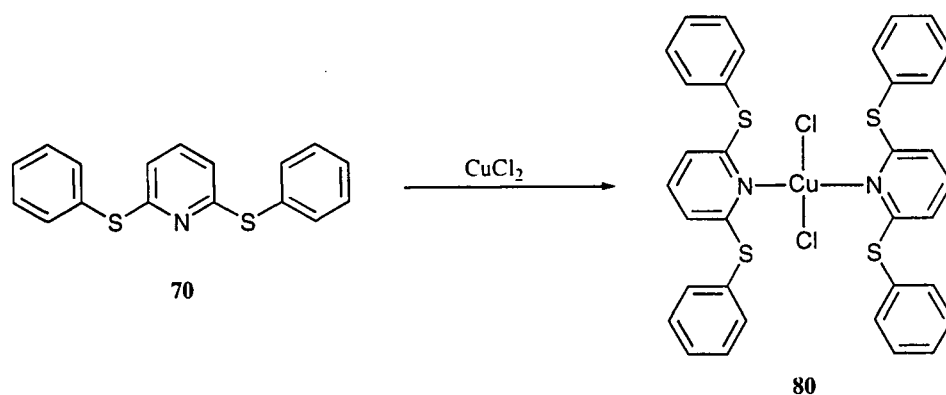
CuCl₂ (0.030g, 0.223mmol) was dissolved in MeCN (10ml) then treated with [2,6-{(PhS)C₅H₃N}] **70** (0.132g, 0.446mmol) and left to stir for 30 seconds where the resulting blue solid and solution was stoppered, sealed and left to stand for several weeks after which a small quantity of blue cubic crystals were observed. Yield 0.032g (19%). IR: 3052, 1417, 1174, 758 and 692 cm⁻¹. ᵐ/ₑ (M = [Cu{(PhS)₂C₆H₄N}Cl₂]): 653 [M-Cl]⁺.Found C 55.6, H 3.5, N 3.8; Calc for CuC₃₄H₂₆N₂S₄Cl₂. C 56.3, H 3.6, N 3.8.

Appendix A
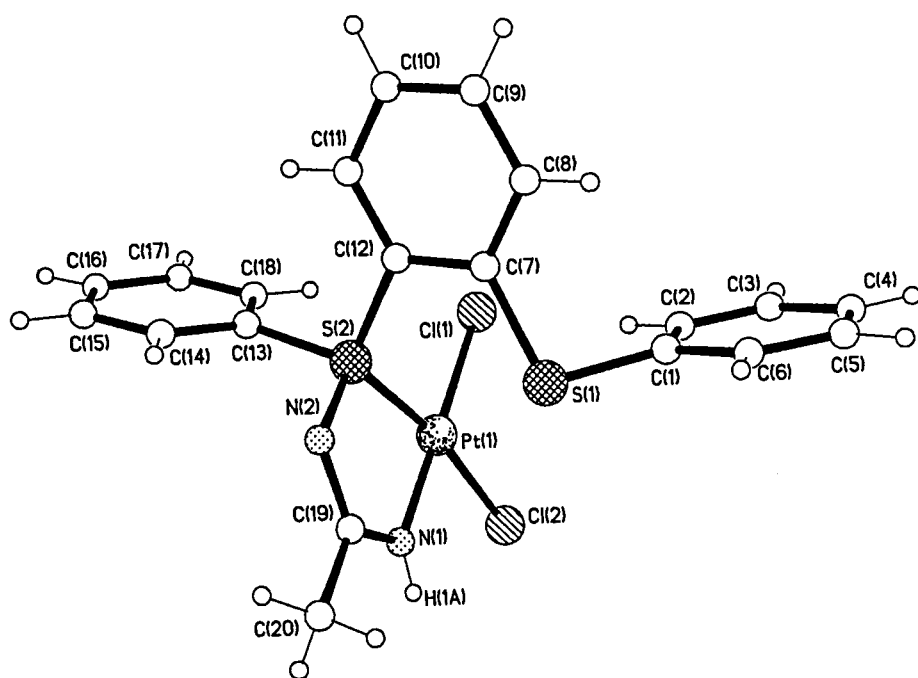
Appendix A: X-ray crystal data

Data was collected at 150 K with a Bruker AXS SMART 1000 CCD diffractometer using Mo-K$_\alpha$ radiation (λ = 0.71073 Å). All structures were solved by direct methods and refined by full-matrix least-squares methods on F^2. NH hydrogens were located from the difference map and their coordinates were freely refined. All other hydrogens were placed in geometrical positions using a riding model as described above. Programs used were Bruker SMART, SAINT, SHELXTL and local programs.

Data was also collected for complex **16** at 150 K on a Bruker AXS SMART 1K CCD area-detector diffractometer using synchrotron radiation (λ = 0.6879 Å) at Daresbury SRS Station 9.8. Absorption correction was applied semi-empirically from equivalent and repeated data. The structure was solved by direct methods and refined by full matrix least squares on F^2. Hydrogen atoms were placed in geometrical positions and allowed to ride on their attached atom with U_{iso}(H) set to be 1.2 times U_{eq} of the carrier atom.

Table 3: Crystal data and structure refinement for compound 7a.

Identification code	pk4
Chemical formula	$C_{18}H_{16}N_2S_2$
Formula weight	324.45
Temperature	150(2) K
Radiation, wavelength	$MoK\alpha$, 0.71073 Å
Crystal system, space group	monoclinic, $P2_1/n$
Unit cell parameters	a = 5.5099(2) Å $\alpha = 90°$
	b = 8.5604(4) Å $\beta = 92.699(2)°$
	c = 16.5197(7) Å $\gamma = 90°$
Cell volume	778.32(6) Å^3
Z	2
Calculated density	1.384 g/cm^3
Absorption coefficient μ	0.339 mm^{-1}
F(000)	340
Crystal colour and size	colourless, $0.37 \times 0.26 \times 0.21$ mm^3
Reflections for cell refinement	5354 (θ range 2.38 to 28.74°)
Data collection method	Bruker SMART 1000 CCD diffractometer
	ω rotation with narrow frames
θ range for data collection	2.47 to 28.76°
Index ranges	h -7 to 7, k -11 to 11, l -22 to 21
Completeness to $\theta = 26.00°$	99.6 %
Intensity decay	0%
Reflections collected	6503
Independent reflections	1844 ($R_{int} = 0.0112$)
Reflections with $F^2 > 2\sigma$	1790
Absorption correction	semi-empirical from equivalents
Min. and max. transmission	0.885 and 0.932
Structure solution	direct methods
Refinement method	Full-matrix least-squares on F^2
Weighting parameters a, b	0.0295, 0.7340
Data / restraints / parameters	1844 / 14 / 109
Final R indices [$F^2 > 2\sigma$]	R1 = 0.0399, wR2 = 0.0979
R indices (all data)	R1 = 0.0407, wR2 = 0.0982
Goodness-of-fit on F^2	1.230
Largest and mean shift/su	0.000 and 0.000
Largest diff. peak and hole	0.560 and -0.267 e Å^{-3}

Table 4: Crystal data and structure refinement for compound 7b.

Identification code	pk3
Chemical formula	$C_{18}H_{20}N_2O_2S_2$
Formula weight	360.48
Temperature	150(2) K
Radiation, wavelength	MoKα, 0.71073 Å
Crystal system, space group	orthorhombic, Pbca
Unit cell parameters	a = 15.9838(16) Å $\alpha = 90°$
	b = 5.2038(5) Å $\beta = 90°$
	c = 20.426(2) Å $\gamma = 90°$
Cell volume	1698.9(3) Å^3
Z	4
Calculated density	1.409 g/cm^3
Absorption coefficient μ	0.327 mm^{-1}
F(000)	760
Crystal colour and size	colourless, $0.17 \times 0.05 \times 0.01$ mm^3
Reflections for cell refinement	1641 (θ range 2.37 to 25.28°)
Data collection method	Bruker SMART 1000 CCD diffractometer ωrotation with narrow frames
θ range for data collection	1.99 to 27.49°
Index ranges	h −20 to 20, k −6 to 6, l −26 to 26
Completeness to $\theta = 26.00°$	99.9 %
Intensity decay	0%
Reflections collected	13039
Independent reflections	1943 ($R_{int} = 0.1024$)
Reflections with $F^2 > 2\sigma$	1152
Absorption correction	semi-empirical from equivalents
Min. and max. transmission	0.947 and 0.997
Structure solution	direct methods
Refinement method	Full-matrix least-squares on F^2
Weighting parameters a, b	0.0399, 3.0515
Data / restraints / parameters	1943 / 0 / 118
Final R indices [$F^2 > 2\sigma$]	R1 = 0.0527, wR2 = 0.1021
R indices (all data)	R1 = 0.1068, wR2 = 0.1278
Goodness-of-fit on F^2	1.021
Largest and mean shift/su	0.001 and 0.000
Largest diff. peak and hole	0.718 and −0.472 e Å^{-3}

Table 5: Crystal data and structure refinement for compound 10b.

Identification code	pk1
Chemical formula	$C_{18}H_{17}NOS_2$
Formula weight	327.45
Temperature	150(2) K
Radiation, wavelength	MoKα, 0.71073 Å
Crystal system, space group	monoclinic, P2$_1$/c
Unit cell parameters	a = 20.698(6) Å α = 90°
	b = 28.122(8) Å β = 94.837(5)°
	c = 5.5475(15) Å γ = 90°
Cell volume	3217.5(15) Å^3
Z	8
Calculated density	1.352 g/cm^3
Absorption coefficient μ	0.332 mm^{-1}
F(000)	1376
Crystal colour and size	colourless, 0.85 × 0.05 × 0.02 mm^3
Reflections for cell refinement	1781 (θ range 2.93 to 28.27°)
Data collection method	Bruker SMART 1K CCD diffractometer ω rotation with narrow frames
θ range for data collection	0.99 to 22.50°
Index ranges	h −22 to 22, k −30 to 29, l −5 to 5
Completeness to θ = 22.50°	100.0 %
Intensity decay	0%
Reflections collected	18565
Independent reflections	4187 (R$_{int}$ = 0.2399)
Reflections with F^2>2σ	2259
Absorption correction	semi-empirical from equivalents
Min. and max. transmission	0.766 and 0.993
Structure solution	direct methods
Refinement method	Full-matrix least-squares on F^2
Weighting parameters a, b	0.1294, 0.0000
Data / restraints / parameters	4187 / 341 / 410
Final R indices [F^2>2σ]	R1 = 0.0995, wR2 = 0.2108
R indices (all data)	R1 = 0.1898, wR2 = 0.2570
Goodness-of-fit on F^2	1.078
Extinction coefficient	0.058(4)
Largest and mean shift/su	0.000 and 0.000
Largest diff. peak and hole	0.835 and −0.667 e Å^{-3}

Table 6: Crystal data and structure refinement for complex 16.

Identification code	dart82
Chemical formula	$C_{36}H_{32}Br_4N_4Pd_2S_4$
Formula weight	1181.34
Temperature	150(2) K
Radiation, wavelength	synchrotron, 0.6877 Å
Crystal system, space group	triclinic, P $\bar{1}$
Unit cell parameters	a = 8.4402(15) Å α = 94.962(3)°
	b = 11.044(2) Å β = 98.383(3)°
	c = 22.519(4) Å γ=101.418(2)°
Cell volume	2021.2(6) Å³
Z	2
Calculated density	1.941 g/cm³
Absorption coefficient μ	5.082 mm⁻¹
F(000)	1144
Crystal colour and size	orange, 0.070 × 0.020 × 0.005 mm³
Reflections for cell refinement	5446 (θ range 2.40 to 25.42°)
Data collection method	Bruker SMART 1K CCD diffractometer
	ω rotation with narrow frames
θ range for data collection	1.83 to 25.46°
Index ranges	h −10 to 10, k −13 to 13, l −28 to 27
Completeness to θ = 25.46°	99.1 %
Intensity decay	20%
Reflections collected	16679
Independent reflections	8215 (R_{int} = 0.0430)
Reflections with $F^2 > 2\sigma$	5244
Absorption correction	semi-empirical from equivalents
Min. and max. transmission	0.717 and 0.975
Structure solution	direct methods
Refinement method	Full-matrix least-squares on F^2
Weighting parameters a, b	0.0452, 0.0000
Data / restraints / parameters	8215 / 49 / 471
Final R indices [$F^2 > 2\sigma$]	R1 = 0.0453, wR2 = 0.0905
R indices (all data)	R1 = 0.0849, wR2 = 0.0991
Goodness-of-fit on F^2	0.924
Extinction coefficient	0.00144(17)
Largest and mean shift/su	0.001 and 0.000
Largest diff. peak and hole	0.942 and −1.144 e Å⁻³

Table 7: Crystal data and structure refinement for complex 21.

Identification code	pk21
Chemical formula	$C_{20}H_{18}Cl_2N_2PtS_2$
Formula weight	616.47
Temperature	150(2) K
Radiation, wavelength	MoKα, 0.71073 Å
Crystal system, space group	monoclinic, P2$_1$/n
Unit cell parameters	a = 9.4631(5) Å α = 90°
	b = 17.7135(9) Å β =100.347(2)°
	c = 12.4772(7) Å γ = 90°
Cell volume	2057.47(19) Å^3
Z	4
Calculated density	1.990 g/cm^3
Absorption coefficient μ	7.291 mm^{-1}
F(000)	1184
Crystal colour and size	yellow, 0.13 × 0.12 × 0.06 mm^3
Reflections for cell refinement	6122 (θ range 2.47 to 28.38°)
Data collection method	Bruker SMART 1000 CCD diffractometer ω rotation with narrow frames
θ range for data collection	2.02 to 25.00°
Index ranges	h −11 to 11, k −21 to 21, l −14 to 14
Completeness to θ = 25.00°	100.0 %
Intensity decay	0%
Reflections collected	14800
Independent reflections	3618 (R$_{int}$ = 0.0340)
Reflections with F^2>2σ	2973
Absorption correction	semi-empirical from equivalents
Min. and max. transmission	0.451 and 0.669
Structure solution	direct methods
Refinement method	Full-matrix least-squares on F^2
Weighting parameters a, b	0.0134, 4.1194
Data / restraints / parameters	3618 / 0 / 248
Final R indices [F^2>2σ]	R1 = 0.0242, wR2 = 0.0447
R indices (all data)	R1 = 0.0386, wR2 = 0.0505
Goodness-of-fit on F^2	1.105
Largest and mean shift/su	0.002 and 0.000
Largest diff. peak and hole	1.056 and −0.631 e Å^{-3}

Table 8: Crystal data and structure refinement for complex 30.

Identification code	pk15
Chemical formula	$C_{18}H_{15}Cl_2NPdS_2$
Formula weight	486.73
Temperature	150(2) K
Radiation, wavelength	MoKα, 0.71073 Å
Crystal system, space group	triclinic, P $\overline{1}$

Unit cell parameters
$$a = 9.5236(8)\ \text{Å} \qquad \alpha = 61.497(2)°$$
$$b = 10.7767(9)\ \text{Å} \qquad \beta = 66.767(2)°$$
$$c = 11.1578(9)\ \text{Å} \qquad \gamma = 67.985(2)°$$

Cell volume	899.72(13) Å^3
Z	2
Calculated density	1.797 g/cm^3
Absorption coefficient μ	1.560 mm^{-1}
F(000)	484
Crystal colour and size	orange, $0.19 \times 0.11 \times 0.08$ mm^3
Reflections for cell refinement	5530 (θ range 1.39 to 28.89°)
Data collection method	Bruker SMART 1000 CCD diffractometer
	ω rotation with narrow frames
θ range for data collection	2.15 to 28.89°
Index ranges	h -12 to 12, k -14 to 14, l -14 to 14
Completeness to $\theta = 26.00°$	99.2 %
Intensity decay	0%
Reflections collected	7941
Independent reflections	4144 (R$_{int}$ = 0.0142)
Reflections with F^2>2σ	3678
Absorption correction	semi-empirical from equivalents
Min. and max. transmission	0.756 and 0.885
Structure solution	Patterson synthesis
Refinement method	Full-matrix least-squares on F^2
Weighting parameters a, b	0.0319, 0.5688
Data / restraints / parameters	4144 / 0 / 220
Final R indices [F^2>2σ]	R1 = 0.0236, wR2 = 0.0588
R indices (all data)	R1 = 0.0287, wR2 = 0.0622
Goodness-of-fit on F^2	1.061
Largest and mean shift/su	0.001 and 0.000
Largest diff. peak and hole	0.953 and -0.698 e Å^{-3}

Table 9: Crystal data and structure refinement for complex 31.

Identification code	pk23
Chemical formula	$C_{36}H_{30}Cl_2NPPdS_2$
Formula weight	749.00
Temperature	150(2) K
Radiation, wavelength	MoKα, 0.71073 Å
Crystal system, space group	triclinic, P $\bar{1}$
Unit cell parameters	a = 9.5178(7) Å α = 90.768(2)°
	b = 9.9441(7) Å β = 99.786(2)°
	c = 17.7459(13) Å γ = 96.508(2)°
Cell volume	1643.6(2) Å^3
Z	2
Calculated density	1.513 g/cm^3
Absorption coefficient μ	0.930 mm^{-1}
F(000)	760
Crystal colour and size	orange, 0.33 × 0.15 × 0.05 mm^3
Reflections for cell refinement	4909 (θ range 2.34 to 27.78°)
Data collection method	Bruker SMART 1000 CCD diffractometer ω rotation with narrow frames
θ range for data collection	2.06 to 25.00°
Index ranges	h −11 to 11, k −11 to 11, l −21 to 21
Completeness to θ = 25.00°	99.6 %
Intensity decay	0%
Reflections collected	12081
Independent reflections	5772 (R_{int} = 0.0276)
Reflections with $F^2 > 2\sigma$	4576
Absorption correction	semi-empirical from equivalents
Min. and max. transmission	0.749 and 0.955
Structure solution	Patterson Synthesis
Refinement method	Full-matrix least-squares on F^2
Weighting parameters a, b	0.0341, 9.0308
Data / restraints / parameters	5772 / 38 / 410
Final R indices [$F^2 > 2\sigma$]	R1 = 0.0553, wR2 = 0.1212
R indices (all data)	R1 = 0.0731, wR2 = 0.1313
Goodness-of-fit on F^2	1.083
Largest and mean shift/su	0.001 and 0.000
Largest diff. peak and hole	2.943 and −1.503 e Å^{-3}

Table 10: Crystal data and structure refinement for complex 33.

Identification code	pk29
Chemical formula	$C_{36}H_{30}Cl_2N_2PdS_4$
Formula weight	796.16
Temperature	150(2) K
Radiation, wavelength	MoKα, 0.71073 Å
Crystal system, space group	triclinic, P $\bar{1}$
Unit cell parameters	a = 8.7806(7) Å $\quad$ α = 81.195(2)°
	b = 9.5314(7) Å $\quad$ β = 71.174(2)°
	c = 10.8053(8) Å $\quad$ γ = 83.362(2)°
Cell volume	843.72(11) Å^3
Z	1
Calculated density	1.567 g/cm^3
Absorption coefficient μ	0.986 mm^{-1}
F(000)	404
Crystal colour and size	orange, 0.33 × 0.19 × 0.07 mm^3
Reflections for cell refinement	4959 (θ range 2.46 to 28.60°)
Data collection method	Bruker SMART 1000 CCD diffractometer
	ω rotation with narrow frames
θ range for data collection	2.01 to 22.50°
Index ranges	h −9 to 9, k −10 to 10, l −11 to 11
Completeness to θ = 22.50°	100.0 %
Intensity decay	0%
Reflections collected	4953
Independent reflections	2212 (R$_{int}$ = 0.0112)
Reflections with F^2>2σ	2097
Absorption correction	semi-empirical from equivalents
Min. and max. transmission	0.737 and 0.934
Structure solution	direct methods
Refinement method	Full-matrix least-squares on F^2
Weighting parameters a, b	0.1152, 9.6592
Data / restraints / parameters	2212 / 83 / 206
Final R indices [F^2>2σ]	R1 = 0.0756, wR2 = 0.2079
R indices (all data)	R1 = 0.0785, wR2 = 0.2106
Goodness-of-fit on F^2	1.096
Extinction coefficient	0.006(4)
Largest and mean shift/su	0.003 and 0.000
Largest diff. peak and hole	2.873 and −1.502 e Å^{-3}

Table 11: Crystal data and structure refinement for compound 72.

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Identification code	pk32
Chemical formula	$C_{20}H_{22}N_2O_3S_2$
Formula weight	402.52
Temperature	150(2) K
Radiation, wavelength	MoKα, 0.71073 Å
Crystal system, space group	monoclinic, P2$_1$/c
Unit cell parameters	a = 11.1895(13) Å $\quad$ α = 90°
	b = 21.093(2) Å $\quad$ β=107.574(2)°
	c = 8.7010(10) Å $\quad$ γ = 90°
Cell volume	1957.8(4) Å^3
Z	4
Calculated density	1.366 g/cm^3
Absorption coefficient μ	0.295 mm^{-1}
F(000)	848
Crystal colour and size	colourless, 0.28 × 0.10 × 0.04 mm^3
Reflections for cell refinement	3287 (θ range 2.64 to 28.20°)
Data collection method	Bruker SMART 1000 CCD diffractometer ω rotation with narrow frames
θ range for data collection	1.91 to 29.05°
Index ranges	h −14 to 15, k −26 to 28, l −11 to 11
Completeness to θ = 26.00°	99.6 %
Intensity decay	0%
Reflections collected	15467
Independent reflections	4707 (R_{int} = 0.0475)
Reflections with F^2>2σ	2978
Absorption correction	semi-empirical from equivalents
Min. and max. transmission	0.922 and 0.988
Structure solution	direct methods
Refinement method	Full-matrix least-squares on F^2
Weighting parameters a, b	0.0340, 1.9744
Data / restraints / parameters	4707 / 0 / 253
Final R indices [F^2>2σ]	R1 = 0.0464, wR2 = 0.0914
R indices (all data)	R1 = 0.0952, wR2 = 0.1124
Goodness-of-fit on F^2	1.003
Largest and mean shift/su	0.001 and 0.000
Largest diff. peak and hole	0.369 and −0.509 e Å^{-3}

Table 12: Crystal data and structure refinement for complex 79.

Identification code	pk30
Chemical formula	$C_{46}H_{36}Cl_2N_2Pd_2S_6$
Formula weight	1092.83
Temperature	150(2) K
Radiation, wavelength	MoKα, 0.71073 Å
Crystal system, space group	monoclinic, $P2_1/n$
Unit cell parameters	a = 9.986(2) Å $\quad$ α = 90°
	b = 17.072(4) Å $\quad$ β = 107.835(4)°
	c = 13.792(3) Å $\quad$ γ = 90°
Cell volume	2238.4(9) Å³
Z	2
Calculated density	1.621 g/cm³
Absorption coefficient μ	1.238 mm⁻¹
F(000)	1096
Crystal colour and size	brown, 0.13 × 0.03 × 0.03 mm³
Reflections for cell refinement	2465 (θ range 2.23 to 26.87°)
Data collection method	Bruker SMART 1000 CCD diffractometer ω rotation with narrow frames
θ range for data collection	1.96 to 25.00°
Index ranges	h −11 to 11, k −20 to 20, l −16 to 16
Completeness to θ = 25.00°	100.0 %
Intensity decay	0%
Reflections collected	16089
Independent reflections	3940 (R_{int} = 0.0901)
Reflections with $F^2 > 2\sigma$	2311
Absorption correction	semi-empirical from equivalents
Min. and max. transmission	0.856 and 0.964
Structure solution	direct methods
Refinement method	Full-matrix least-squares on F^2
Weighting parameters a, b	0.0001, 21.3230
Data / restraints / parameters	3940 / 0 / 262
Final R indices [$F^2 > 2\sigma$]	R1 = 0.0549, wR2 = 0.1012
R indices (all data)	R1 = 0.1175, wR2 = 0.1305
Goodness-of-fit on F^2	1.038
Largest and mean shift/su	0.000 and 0.000
Largest diff. peak and hole	0.948 and −1.222 e Å⁻³

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Table 13: Crystal data and structure refinement for complex 83.

Identification code	pk51
Chemical formula	$C_{34}H_{26}Cl_2CuN_2S_4$
Formula weight	725.25
Temperature	150(2) K
Radiation, wavelength	MoKα 0.71073 Å
Crystal system, space group	triclinic,
Unit cell parameters	a = 9.0546(5)Å $\quad$ α = 106.543(2)
	b = 11.3883(7) Å $\quad$ β= 92.530(2)
	c = 17.7268(10) Å $\quad$ γ= 112.615(2)
Cell volume	1592.96(16) Å^3
Z	2
Calculated density	1.512 g/cm^{-3}
Absorption coefficient μ	1.144 mm^{-1}
F(000)	742
Crystal colour and size	green, 0.39 x 0.14 x 0.11 mm^3
Reflections for cell refinement	7794 (θrange 2.43 to 28.52°)
Data collection method	Bruker SMART 1000 CCD
diffractometer	
	φ rotation with narrow frames
θ range for data collection	2.01 to 29.01°
Index ranges	h 11-12 to 12, k 15 to 15, l 24 to 23
Completeness to θ=25.00°	99.3 %
Intensity decay	0%
Reflections collected	14166
Independent reflections\tab	7366 (R_{int} = 0.0153)
Reflections with F^2>2σ	6156
Absorption correction	semi-empirical from equivalents
Min. and max. transmission	0.664 and 0.885
Structure solution	direct methods
Refinement method	Full-matrix least-squares on F^2
Weighting parameters a, b	0.0335, 1.0716
Data / restraints / parameters	7366 / 0 / 391
Final R indices [F^2>2σ]	R1 = 0.0308, wR2 = 0.0733
R indices (all data)	R1 = 0.0405, wR2 = 0.0780
Goodness-of-fit on F^2	1.043
Largest and mean shift/su	0.001 and 0.000
Largest diff. peak and hole	1.186 and 0.323 Å^{-3}

Appendix B
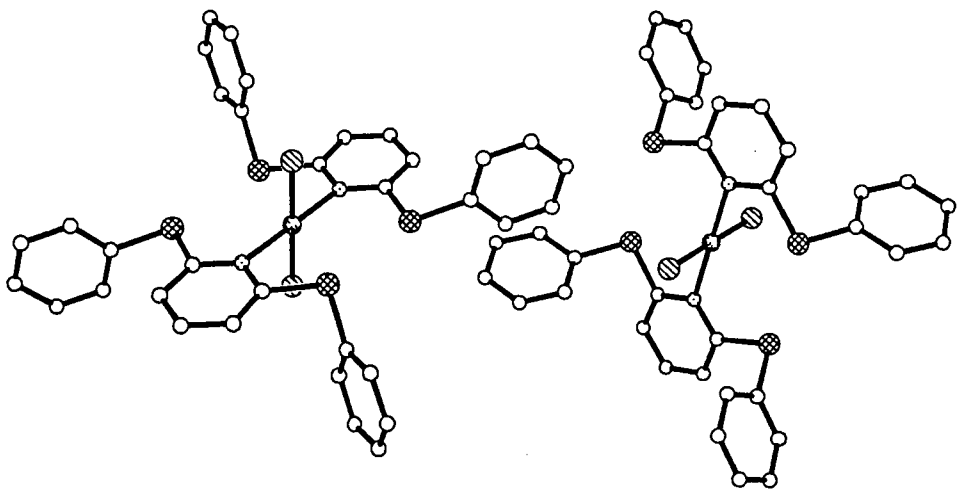
Appendix B: List of Publications

Platinum(IV)-mediated nitrile-sulfimide coupling: A route to heterodiazadienes

A. V. Makarycheva-Mikhailova, N, A, Bokach, V.Y. Kukushkin, P. F. Kelly, L. M. Gilby, M. L. Kuznetsov, K. E. Holmes, M. Haukka, J. Parr, J. M. Stonehouse, M. R. J. Elsegood and A. J. L. Pombeiro

INORGANIC CHEMISTRY

2003, **42**, 301-311

Preparation of the first complexes of bidentate sulfimides; the X-ray crystal structures of [PdBr$_2$\{1,4-(PhS\{NH\})$_2$C$_6$H$_4$\}]$_2$, [PdCl$_2$\{1,2-(PhS\{NH\})(PhS)C$_6$H$_4$\}] and trans-[PdCl$_2$\{1,2-(PhS\{NH\})(PhS)C$_6$H$_4$\}PPh$_3$]

M. R. J. Elsegood, K. E. Holmes, P. F. Kelly, E. J. MacLean, J. Parr and J. M. Stonehouse

EUROPEAN JOURNAL OF INORGANIC CHEMISTRY

2003, 120-127

The preparation and structure of novel sulfimide systems; X-ray crystal structures of 1,4-(PhS\{NH\})$_2$C$_6$H$_4$ (and dihydrate), 1,2-(PhS\{NH\})(PhS)C$_6$H$_4$H$_2$O and of [Ph$_2$SNH] and its hydrate

M. R. J. Elsegood, K. E. Holmes, P.F. Kelly, J. Parr and J. M. Stonehouse

NEW JOURNAL OF CHEMISTRY

2002, **26**, 202-206