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Copper Catalysed Aziridination Reactions

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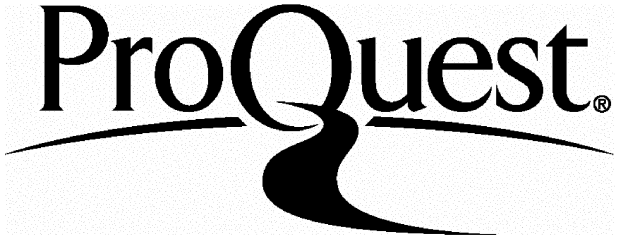

ABSTRACT

Numerous copper complexes of differing structural types, including a wide selection of poly(pyrazolyl)borate, dithiocarbamate and phosphine complexes, were synthesised and characterised. The structural and solution properties of these complexes are discussed. The ability of each of these complexes to catalyse the aziridination of styrene by PhI=NTos was assessed, the reactivities then being related to their structural and solution properties. A selected number of the more active complexes were assessed as catalysts for the aziridination of several different substrates. Nitrene sources other than PhI=NTos were also utilised, with TosNClNa being particularly effective. After a series of aziridinations using varying equivalents of substrate and quantities of catalyst, copper triphenylphosphine complexes were shown to be the most active catalysts yet employed. In contrast to the complexes $[Cu(R_2dtc)_2]ClO_4$ (R=Me, Et), the copper (III) complexes $[Cu(R_2dtc)_2][FeCl_4]$ (R=Me, Et, Pyd) were found to be active catalysts. This activity is suggested to result from reduction by Cl^- which is produced by reaction of $[FeCl_4]^-$ with PhI=NTos. Asymmetric aziridination catalysed by novel ligand-metal combinations was also investigated. Complexes of the novel amido ligands $TosNSC(NR_2)S$ and $TosNSC(NR_2)SNTos$, formed by step-wise insertion of NTos groups into metal sulfur bonds, were found to be by-products of aziridination reactions using dithiocarbamate complexes as catalysts. The crystal structures of $[Cu(TosNSC(NMe_2)SNTos)_2]$, $[Cu(TosNSC(NEt_2)S)_2]$, $[Ni(TosNSC(NEt_2)S)_2]$ and $[Co(TosNSC(NEt_2)SNTos)_2]$, as well as their reactivities and abilities as aziridination catalysts are discussed. The mechanism of copper catalysed aziridination was investigated and strong evidence for the active catalyst being a copper(I) species was obtained. Evidence for alkene precoordination was gathered and a case for the existence of a mononuclear catalytic site and for a concerted transfer of nitrene to substrate is discussed. A likely catalytic cycle is then proposed.

TABLE OF CONTENTS

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I would lastly like to thank my parents for their support, both moral and financial, and for allowing me to live in comfort while I wrote this thesis.

ABBREVIATIONS

pz	pyrazole
Tp	hydrotris(pyrazolyl)borate
Tp*	hydrotris(3,5-dimethylpyrazolyl)borate
Bp	dihydrobis(pyrazolyl)borate
Bp*	dihydrobis(3,5-dimethylpyrazolyl)borate
dtc	dithiocarbamate
dsc	diselenocarbamate
Me	methyl
Et	ethyl
Pr	propyl
Bu	butyl
Hex	hexyl
Ph	phenyl
Menth	menthyl
Tos	*para*-toluenesulfonyl
t	*tert* or tertiary
i	*iso*
M	transition metal
AzH	ethylenimine / aziridine
THF	tetrahydrofuran
Cp	cyclopentadiene
cod	cyclooctadiene
dmp	2,9-dimethyl-1,10-phenanthroline
dppe	bis(diphenylphosphino)ethane
L^1	2-methylthiomethyl-4-(*S*)-methyl-1,3-oxazoline
L^2	2-(2-cyanophenyl)-4-(*S*)-methyl-1,3-oxazoline
L^3	2-phenyl-4-(*S*)-methyl-1,3-oxazoline
Nu	nucleophile
ee	enantiomeric excess

With reference to NMR spectroscopy

NMR	nuclear magnetic resonance
δ	chemical shift
ppm	parts per million
s	singlet
d	doublet
t	triplet
q	quartet
m	multiplet

With reference to IR spectroscopy

IR	infra red
s	strong
m	medium
w	weak

With reference to mass spectrometry

EI	electron impact
FAB	fast atom bombardment
$APCI^+$	atmospheric pressure chemical ionisation

DECLARATION

The work described in this thesis was carried out in the Christopher Ingold Chemistry Laboratories, University College, London from 1st October 1994 to 30th September 1997 under the supervision of Dr Graeme Hogarth and Dr Andrea Sella.

All the work described in this thesis is my own unless stated to the contrary and has not been submitted previously for a degree in this or any other university.

Andrew G Pateman

1.0 INTRODUCTION

1.1 HOMOGENEOUS CATALYSIS

1.1.1 Introduction

A catalyst is a species that influences the rate of a reaction and that can be recovered unchanged at the end of the reaction. It can be as simple as a proton or as complicated as an enzyme. It cannot, however, change the equilibrium position of a reaction. The equilibrium point is controlled by the free energy which is in turn determined by ΔH (calculated from bond energies of reactants and products) and ΔS (the entropy of the reaction).

$$\Delta G = -RT\ln K \qquad \Delta G = \Delta H - T\Delta S$$

$$K = \frac{[\text{products}]}{[\text{reactants}]}$$

Figure 1.1.1 Thermodynamic relationships

A reaction that is thermodynamically favourable but kinetically inert can be affected by a catalyst. The addition of a catalyst provides a mechanistic pathway for the reaction which would otherwise have been unavailable. This allows a lowering of the free energy of activation of the rate determining step of the reaction. A good example of the effect of a catalyst can be seen in the thermodynamically favourable reaction between hydrogen and oxygen. Mixed together in their pure state no reaction takes place, but on the addition of a small amount of palladium as catalyst the reaction occurs at such a rate that the gases react explosively. The gas molecules are able to adsorb onto the surface of the palladium, which allows them to dissociate more easily, thereby lowering the activation energy.

Catalysts belong to one of two broad types: homogeneous and heterogeneous.[1] During heterogeneous catalysis, the catalyst is usually present as a solid and the reactants as liquids or gases. In homogeneous catalysis, by contrast, reactants

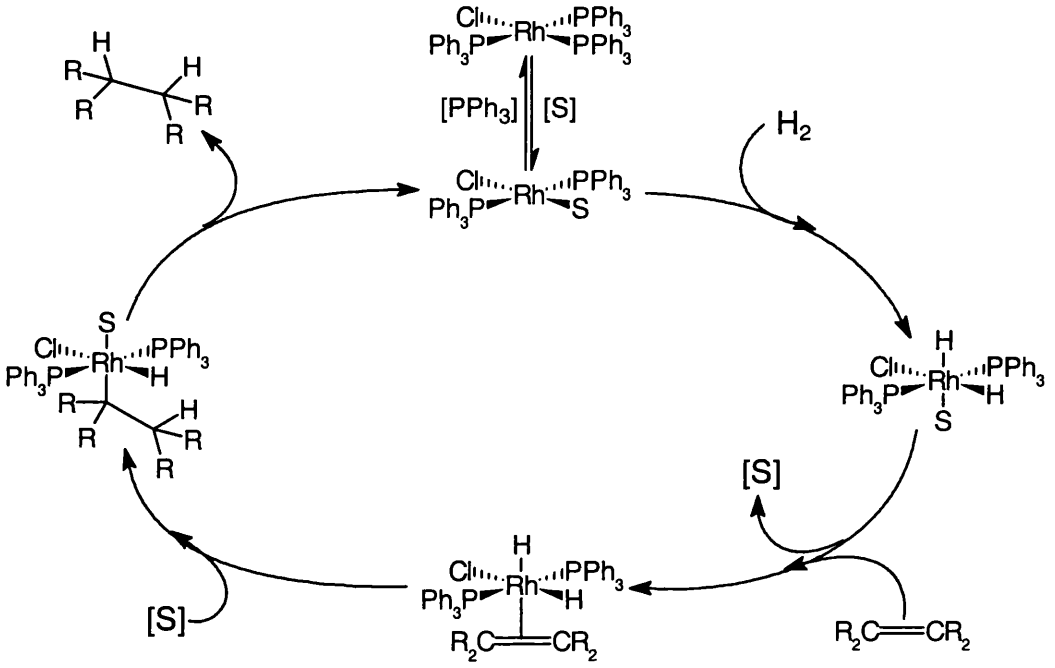
and catalyst are present in the same phase, usually in solution. There are distinct advantages and disadvantages to each type of catalyst.

Heterogeneous catalysts are the most widely used in industry since the catalyst and product are easily separated after reaction is complete.[1] In addition, heterogeneous catalysts are thermally robust, allowing them to operate under very demanding conditions without significant degradation. This may also allow the possibility of *in-situ* regeneration of poisoned catalysts. All three of these features of heterogeneous catalysts are highly desirable in industry where products are required quickly and in high purity. However, the activity per metal atom may be low, since often only one type of metal site catalyses the reaction and there may be many different types of site on the catalyst surface. This also makes the distinct molecular events involved in the catalysis very hard to identify and characterise.

Catalytic activity is often much higher with homogeneous catalysts since each catalytic centre has one, well-defined active site.[2] An advantage of homogeneous transition-metal catalysts is the very high selectivity achievable through judicious selection of ligand, including the possibility of highly enantioselective catalysis. The main disadvantage of homogeneous catalysts is that they are often difficult to remove from the reaction mixture and for this reason, it is also very difficult to regenerate poisoned or deactivated catalyst. Despite these deficiencies, the advantages of homogeneous catalysts will become more important as demand for selectivity increases, the cost of operating at high temperatures increases and as our improving understanding leads to the development of more efficient systems.

One of the best known homogeneous catalysts is Wilkinson's catalyst, $[RhCl(PPh_3)_3]$, which is used in the hydrogenation of alkenes.[1,3] The active catalytic species is produced by replacement of a phosphine ligand with a highly labile coordinated solvent molecule. This catalyst then undergoes oxidative-addition of hydrogen followed by replacement of the solvent molecule by a

coordinated alkene. This octahedral species then undergoes β-hydride migration to give a transition metal alkyl complex, again with a solvent molecule occupying the vacant coordination site. Reductive elimination of the alkane product then regenerates the active catalytic species.



[S] = coordinating solvent molecule

Figure 1.1.2 Catalytic cycle for Wilkinson's catalyst

This system is also capable of great selectivity in its reduction reactions. It directs hydrogenation towards alkene and alkyne functionalities without affecting other unsaturated groups such as aldehydes, nitriles and nitrates. Even greater selectivity can be obtained, for example, from a mixture of 1-hexyne and 1-octene. The 1-hexyne is reduced completely before either 1-octene or 1-hexene (the product of reduction) are hydrogenated.[4]

Asymmetric hydrogenation is generally achieved using chiral phosphines bound to rhodium and has already found application in industry. The synthesis of the drug *L*-DOPA, used in the treatment of Parkinson's disease, includes a step which involves asymmetric hydrogenation of a prochiral alkene (shown in Figure 1.1.3).[5] The asymmetric induction is effected by the use of the resolved

chiral ligand bis(anisyl)phenylphosphenylethane (BAPPE) which causes a differentiation in the rates of oxidative addition of a hydrogen molecule to the possible complexes obtained when the prochiral alkene coordinates in different orientations.

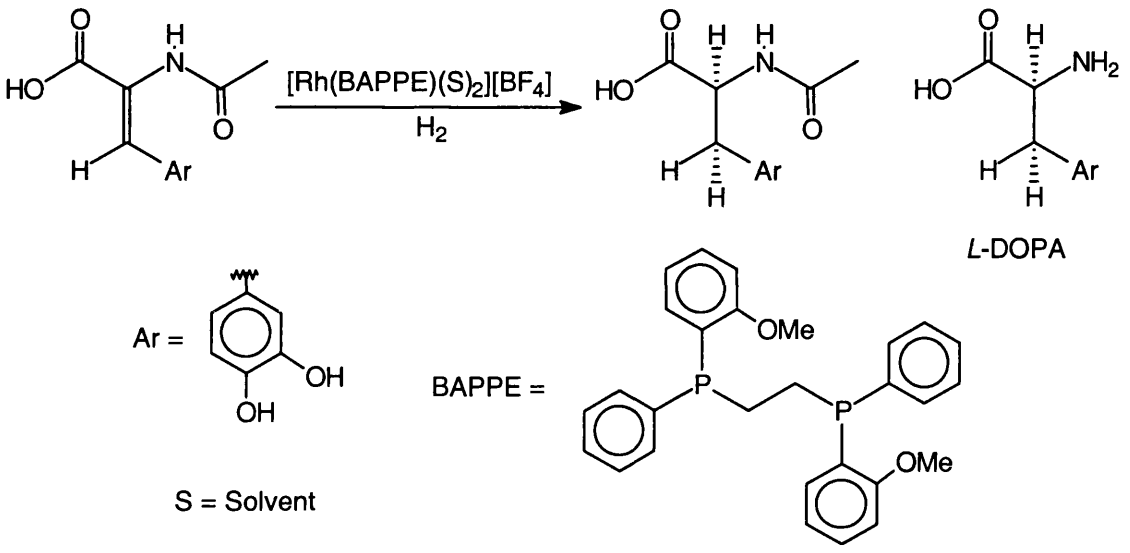


Figure 1.1.3 Synthesis of *L*-DOPA

The carbonylation of methanol to form acetic acid using a rhodium catalyst is a homogeneously catalysed reaction that has been used widely in the chemical industry since the seventies.[6] It was developed by the Monsanto Chemical company and is now known as the Monsanto process (see Figure 1.1.4 below).

The Monsanto process involves the use of HI as a co-catalyst which reacts with MeOH to produce MeI (which then goes into the main catalytic cycle) and H_2O. The product of the main catalytic cycle is acetyl iodide, which reacts with the H_2O to give acetic acid and to regenerate HI. The main catalytic cycle employs $[Rh(CO)_2I_2]^-$ as the active catalytic species which undergoes oxidative-addition of MeI followed by insertion of a carbonyl into the Rh-Me bond and then reductive-elimination of acetyl iodide.

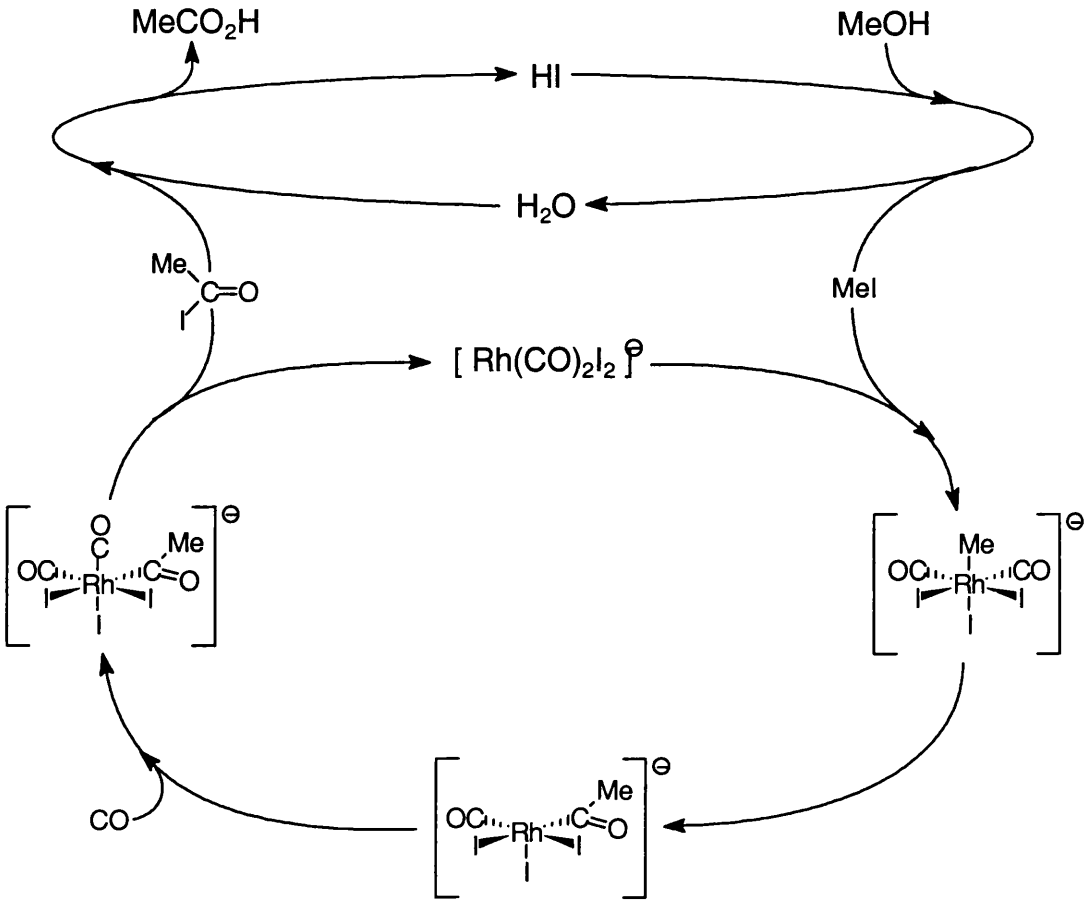


Figure 1.1.4 Catalytic cycle for the Monsanto process

The Wacker process was developed by Wacker Chemie from a stoichiometric reaction that had been known since 1894 and is now widely used in industry to produce acetaldehyde.[7] The stoichiometric reaction converts alkenes into ketones or aldehydes using aqueous $[PdCl_4]^{2-}$. This palladium(II) complex undergoes loss of chloride followed by association of an alkene. Nucleophilic attack on the alkene by OH^- generates a hydroxyalkyl complex which undergoes β-hydride elimination to give a five-coordinate hydrido palladium alkene complex. The hydride then migrates to the least substituted carbon of the alkene which reductively eliminates to give the product and palladium metal. In the late 50's, however, a team at Wacker Chemie reported that in the presence of cupric or ferric chloride, the palladium was re-oxidised to regenerate the $[PdCl_4]^{2-}$ catalyst and the reaction became catalytic.[8] The cuprous or ferrous by-products are re-oxidised by the molecular oxygen present in the system.

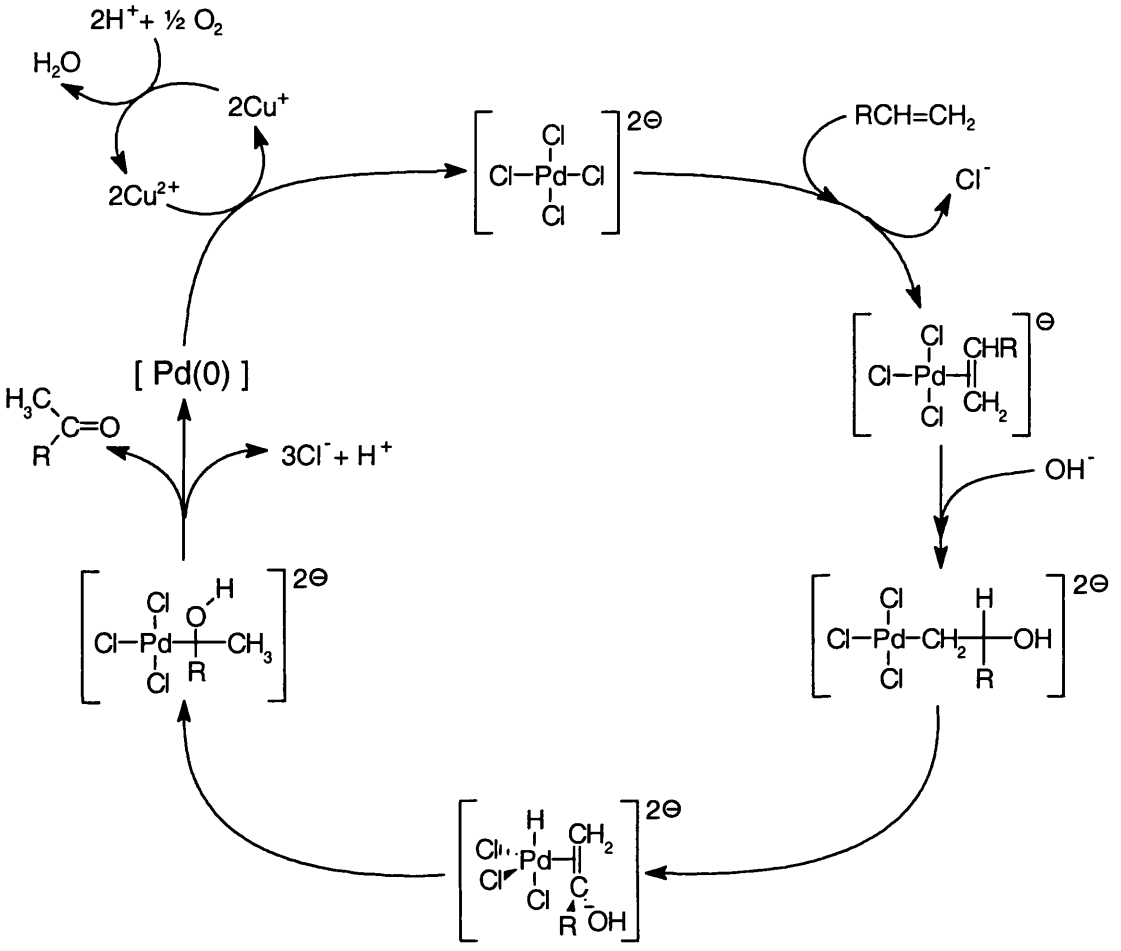


Figure 1.1.5 Catalytic cycle for the Wacker process

This catalytic process has not been limited to the conversion of alkenes to aldehydes and ketones.[2] The $PdCl_2$/Cu(II) catalyst system can also be used in the preparation of methyl acrylate from acetylene, in the oxidation of alkenes to produce many types of acetate compounds and in the oxidation of acrylonitrile, an important step in the synthesis of vitamin B_1.

1.1.2 Epoxidation [9]

Transition metal oxo and peroxo complexes have been known for a long time to catalyse this transformation, utilising a variety of oxygen sources. The most effective epoxidation catalysts such as titanium(IV), vanadium(V), molybdenum(VI) and tungsten(VI) are all classed as being either Lewis acids or metals with a low redox potential and all are labile with respect to ligand substitution. The most commonly used sources of oxygen are the alkyl

hydroperoxides such as *tert*-butylhydroperoxide (TBHP) and *meta*-chloroperbenzoic acid (MCPBA). Other sources used are molecular oxygen and iodosyl compounds such as iodosylbenzene (PhI=O).

A well known example of an epoxidation catalyst is titanium(IV) tetraisopropoxide which is used in conjunction with TBHP and (+) or (-)-diethyl tartrate to convert allylic alcohols to epoxyalcohols in an enantioselective fashion. This reaction is more commonly known as the Sharpless epoxidation (shown in Figure 1.1.6 below).[1,9]

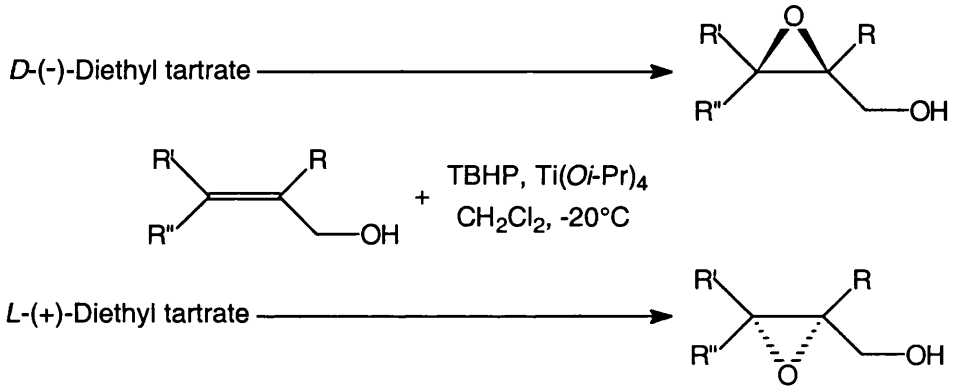


Figure 1.1.6 Sharpless epoxidation

Transition metal catalysed epoxidations are generally agreed to occur via three types of complex: transition metal peroxide or peroxo complexes, transition metal oxo complexes or, occasionally, peroxo radicals.[9] Peroxide complexes predominate with early transition metals, and the balance of mechanistic evidence points towards an interaction of the alkene with one of the electrophilic peroxygens, similar to the mechanism of the epoxidation of alkenes by peroxy acids.

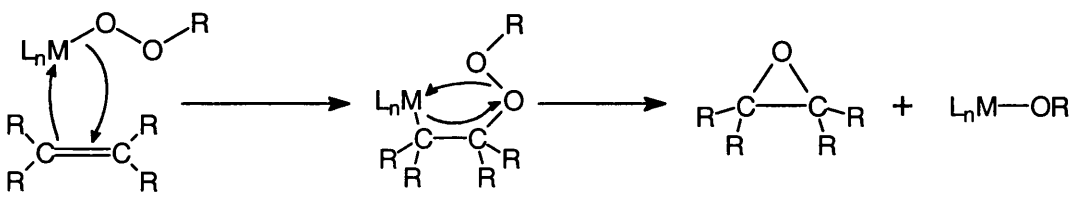


Figure 1.1.7 Mechanism for peroxide complex epoxidation

With oxo complexes, two mechanisms have been proposed. The first involves an interaction of the oxygen in the oxo complex with the alkene, and the second involves the formation of a metallacycle. However, neither mechanism is backed by strong evidence. Catalysis by metal oxo complexes occurs with the middle to late transition metals, as does the peroxo radical system. However, the peroxo radical system is only available when abstraction of an allylic hydrogen from the alkene is disfavoured.

1.1.3 Cyclopropanation [10]

The addition of a carbene fragment to an alkene is catalysed by many transition metal complexes, most notably those of copper, rhodium and palladium. It is now widely agreed that catalytic activity depends upon coordinative unsaturation at the metal centre which allows it to act as an electrophile with diazo compounds. Loss of dinitrogen occurs with formation of a transient transition metal carbene complex, which further reacts with an electron-rich substrate to complete the catalytic cycle. This cycle is shown pictorially in Figure 1.1.8 below.[10]

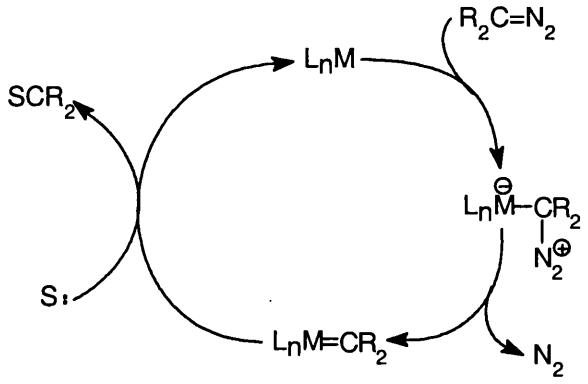


Figure 1.1.8 General catalytic cycle for cyclopropanation

Further evidence for the presence of a metal carbene complex arrives from the observation of asymmetric induction in cyclopropanation reactions using copper complexes with chiral ligands. It is highly unlikely that chirality could arise from reaction of a free carbene with a bound, prochiral alkene. It has also been

shown that stable metal carbene complexes of chromium, molybdenum and tungsten undergo stoichiometric addition of the carbene fragment to alkenes.[11]

During cyclopropanation reactions, there is always competition with dimerisation of the carbene to form alkenes. Such competition can be minimised by adding the carbene precursor (normally a diazo compound) slowly to a mixture of the catalyst and substrate, thereby keeping the concentration of active carbene to a minimum.

Acetate complexes of copper, rhodium and palladium have been shown to be some of the best catalysts for cyclopropanation, despite the availability of only one coordination site per metal atom.[9]

1.2 COPPER

1.2.1 Introduction [13,14]

Copper deposits are widely distributed in the Earth's crust and occur in many forms, from the metal itself to sulfides, chlorides and carbonates etc. and other ores such as chalcopyrite, [$CuFeS_2$], malachite, [$CuCO_3 \cdot Cu(OH)_2$] and azurite, [$2\{Cu(CO_3)_2\} \cdot Cu(OH)_2$]. It is 20th in the order of elemental abundance, occurring at a concentration of about 100 g per ton of the Earth's crust (equivalent to about 68 ppm). Copper metal is obtained from its ores by oxidative roasting and smelting, or by wet processes such as leeching and solvent extraction. Refinement is carried out electrolytically.

Copper has the electronic configuration $\{Ar\}4s^1 3d^{10}$, but despite having only one *s* electron, it has little in common with the alkali metals. The filled 3*d* orbitals do not shield the single *s* electron as well as a noble gas shell so the first ionisation energy of copper is much higher than those of the alkali metals. However, the second and third ionisation energies of copper are much lower than those of the alkali metals, which accounts in part for its transition metal character. This is also evidenced by the presence of several stable oxidation states and the facile formation of complexes from ions.

Copper forms complexes in four oxidation states: 0, +1, +2, +3 and +4, although the number of complexes known for each oxidation state varies considerably. Both copper (0) and copper (IV) are relatively unknown, although the metal is used extensively on its own and in combination with other metals in alloys. By contrast, the other three oxidation states are much more well known, with copper (II) being the most common due to its stability in aqueous solution and with copper (III) being the least common because of the high oxidation potential required to obtain it. The redox potential for Cu(I)/Cu(II) is relatively low, which accounts for its presence in some proteins and also explains its increasing use in catalysis, although the existence of Cu(III) intermediates in these systems cannot be ruled out. A more detailed description of each oxidation state is given in the following sections.

1.2.2 Copper (0) [13,14]

Copper metal was first used over 7000 years ago in the manufacture of weapons by prehistoric man. Since then it has also been used as part of the alloy bronze in coinage, weaponry and engineering. Today, it is widely used in electrical wiring due to its high conductivity and in water piping because of its corrosion resistance properties. Apart from the metal, copper does not exist as Cu(0) except in certain very reactive species such as Cu_n (n=2, 3 & 5) and $[Cu(CO)_3]$ that have been characterised using matrix isolation techniques.[15] It is possible, however, to reduce certain complexes such as $[Cu(C{\equiv}CPh)_3]^{2-}$ and $[(Ph_3P)_3CuCl]$ to produce dimeric copper(0) complexes.[16] Other copper(0) complexes involving copper-transition metal bonds have also been synthesised.[14]

1.2.3 Copper (I) [13,14]

Copper (I) complexes are diamagnetic d^{10} species and are generally colourless, except where the anionic ligand is coloured or where metal-ligand charge transfer occurs. The chemistry of Cu(I) is much less extensive than that of Cu(II) because the former is readily oxidised to the latter. The electrode potentials and the equilibrium constant shown in Figure 1.2.1 below indicate that the concentration of Cu(I) in aqueous solution is very small. However, these

potentials and thus the concentration of Cu(I) can be altered by the presence of suitable ligands, especially those that also act as a solvent (MeCN for example). The ready oxidation of Cu(I) to Cu(II) also leads to air and moisture sensitivity of the majority of Cu(I) complexes. The Cu(I) cation is a soft acid, and therefore favours complexation with soft bases. Complexes with halide ligands are common, with the exception of fluorine. With O, S, N, and P ligands, S and P ligands predominate due to their reducing properties, whilst O and N ligands are more commonly found in complex with Cu(II).

$$Cu^{+}_{(aq)} + e^{-} \longrightarrow Cu^{0}_{(aq)} \qquad E^{\circ} = 0.52\ V$$

$$Cu^{2+}_{(aq)} + e^{-} \longrightarrow Cu^{+}_{(aq)} \qquad E^{\circ} = 0.15\ V$$

therefore

$$2Cu^{+} \longrightarrow Cu^{0} + Cu^{2+} \qquad E^{\circ} = 0.37\ V$$

and $K_{eq} = \sim 10^{6}$

Figure 1.2.1 Electrode potentials and equilibrium constant for copper

The stereochemistry around Cu(I) is generally tetrahedral, although an interesting exception to this is the compound $[(PPh_3)_2Cu(\mu\text{-}Cl)_2Cu(PPh_3)]$ (shown in Figure 1.2.2), in which one copper centre is three coordinate and the other is four coordinate.[17]

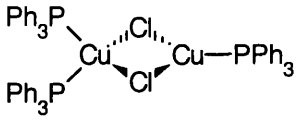


Figure 1.2.2 Structure of $[(PPh_3)_2Cu(\mu\text{-}Cl)_2Cu(PPh_3)]$

Mononuclear copper(I) species occur in coordination numbers of two, three, four and five, with four-coordinate species being by far the most common. The CuS_4 and CuP_4 choromophores are well-known and studied. In the case of monodentate ligands the four-coordinate species are generally tetrahedral, whereas polydentate ligands normally coordinate in a distorted tetrahedral fashion. Halide ligands do not form mononuclear cations of the form $[CuL_4]^{3-}$, preferring instead to bridge polynuclear copper centres.[13]

Binuclear species normally occur with bridging halide ligands, with the Cu_2L_2 unit being planar and the geometry around copper being tetrahedral. Polydentate ligands such as the trispyrazolylborates are also able to bridge dinuclear centres, although the geometry around copper is severely distorted from tetrahedral. In the case of $[CuTp]_2$ (Tp = hydrotris(1-pyrazolyl)borate), the Cu-N-Cu angle is 74°, and the Cu-Cu distance is unusually short.[18]

Tetranuclear complexes involving Cu(I) occur almost as frequently as binuclear complexes. The most common class involves the copper atoms being positioned at alternate corners of a cube, with four triply bridging halide or RS^- ligands forming the other corners. Neutral, monodentate ligands such as tertiary phosphines or pyridine cap the open coordination site on copper, leading to an overall stoichiometry of $[CuLX]_4$.

1.2.4 Copper (II) [13,14]

The +2 state is the most common oxidation state of copper because of the reasons outlined in the previous section. For these same reasons, the Cu(II) cation is stable to moisture and oxygen. The d^9 Cu(II) centre is rarely observed in regular octahedral or tetrahedral geometries due to sometimes severe Jahn-Teller distortions. On the other hand, regular square-planar geometries are quite common, although they almost invariably involve some long-range interaction along the z-axis.

Copper (II) is probably best described as a borderline hard acid, since although N is probably the best donor to Cu(II) centres, O, S and Cl^- donor ligands are also common. Fluorine is predicted to be the best ligand for hard acids, but copper(II) complexes with F^- are relatively uncommon, as are complexes of I^-. Reducing ligands such as I^- and CN^- may appear with Cu(II), but only when stabilising ligands such as 2,2'-bipyridyl (bipy) are also present. Phosphorous reacts with Cu(II) to give the corresponding phosphine oxide with concomitant reduction of copper to Cu(I). If the resulting copper phosphine oxide complex is allowed to react with atmospheric oxygen, the copper is often reoxidised to

Cu(II). The +2 oxidation state of copper is characterised by the domination of σ donor ligands to the virtual exclusion of π donor ligands.

Although mononuclear copper(II) complexes occur in a wide variety of stereochemistries and with a wide variety of coordinating ligands, chelating N-donor ligands such as ethylenediamine derivatives tend to predominate. Copper(II) complexes of the type [TpCuL], where Tp is a pyrazolylborate ligand and L is a monodentate ligand are interesting since those with pyrazolylborates of low steric bulk undergo a ligand exchange reaction to form a $[CuTp_2]$ pyrazolylborate sandwich complex and a $[CuL_2]$ species.

A widely studied class of dinuclear Cu(II) complexes are the carboxylates. These have the general form $[Cu_2(OOCR)_4 \cdot L_2]$ and the structure shown in Figure 1.2.3. They are particularly interesting because the Cu-Cu distance is quite short, allowing strong antiferromagnetic coupling of the unpaired electrons on each metal atom. The bite angle of the carboxylate ligands can easily be varied by changing the R group, thereby altering the Cu-Cu distance and thus the coupling.

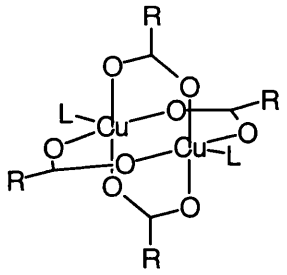


Figure 1.2.3 General structure of copper carboxylate complexes

Tetranuclear complexes are less common for copper(II) than for copper(I). In the most common class by far, four copper atoms are arranged in a tetrahedron around a central μ_4-oxygen atom, with Cl atoms bridging each edge of the tetrahedron and neutral ligands such as pyridine or phosphites capping each of the copper atoms. These complexes, of general formula $[Cu_4OCl_6L_4]$, are

obtained by atmospheric oxidation of the tetrameric Cu(I) complexes mentioned in the previous section.

1.2.5 Copper (III)

Copper (III) complexes are much less common than complexes of both Cu(I) and Cu(II). They are strong oxidising agents, and as such do not occur naturally. They are produced by oxidation of Cu(I) and Cu(II) complexes and with the exception of $K_3[CuF_6]$, they are all diamagnetic d^8 species.[19]

Chemical oxidation of Cu(II) complexes by species such as ClO^- and gaseous Cl_2 or F_2 was the first method used to produce Cu(III) and led to the isolation of many such complexes, even from aqueous solution. Electrolytic oxidation proved more useful, allowing the preparation of Cu(III) macrocyclic N_4 complexes, polypeptide complexes, borohydride complexes and carborane complexes.[13]

All Cu(III) complexes isolated so far are mononuclear and occur in relatively few stereochemistries. K_3CuF_6 is octahedral,[19] whereas $CsCuF_4$ is square planar.[20] The largest group of Cu(III) complexes, those with a CuS_4 chromophore, all have a square planar geometry.

1.2.6 Copper (IV)

Copper (IV) complexes have only been characterised in a few cases, always in the presence of very electronegative ligands such as O^{2-} and F^-. The most well characterised complex is Cs_2CuF_6,[21] but the Cu(IV) oxidation state is also believed to occur in the solid state complex $BaCuO_{2.63}$.[22] In addition, CuO_2 has been characterised by matrix isolation techniques.[23]

1.2.7 Biological Aspects of Copper [24]

Copper is an essential bioelement for all forms of life, although the required amounts vary greatly depending on the organism. Indeed, its therapeutical width (the difference in concentration between that which causes deficiency symptoms and that which causes toxicity) is very low, especially for lower organisms and

during growth periods (e.g. infancy) in higher organisms. Deficiency is often caused by the increased presence of competing (Fe, Zn) and antagonistic (S, Se) elements. Symptoms include arterial weakness, enlargement of the heart, and a reduction in the number of heat shock proteins which manage cellular stress.

The majority of the biological functions of copper involve the transport and utilisation (by oxidase and oxygenase enzymes) of molecular oxygen, as well as catalysis of the transformations of N & O containing species (nitrite reductase and amine oxidase enzymes). Complex redox processes often require the presence of more than one redox centre to facilitate the storage of several electrons and their subsequent controlled release. Examples include cytochrome C oxidase (Fe and dimeric Cu), ascorbate oxidase (trimeric Cu), and amine oxidase (Cu and quinone).

1.2.8 Copper In Catalysis [3]

Copper has played a full part in the development of homogeneous catalysis for both industrial and laboratory based systems. This section describes some of the more important processes that involve copper catalysts.

The ability of copper to bind acetylenes in both a σ- and a π- fashion has led to its use in many catalytic processes. An outdated process for the synthesis of acrylonitrile from acetylene and HCN utilised a $CuCl/NH_4Cl$ catalyst system until it was replaced by the cheaper propylene based SOHIO process. Another now obsolete system used copper catalysts in the synthesis of chloroprene, the monomer for neoprene rubber. The two steps involved were the dimerisation of acetylene followed by addition of HCl to the acetylene group of the resultant vinyl acetylene (see Figure 1.2.4). Both steps are catalysed by Cu(I) complexes.

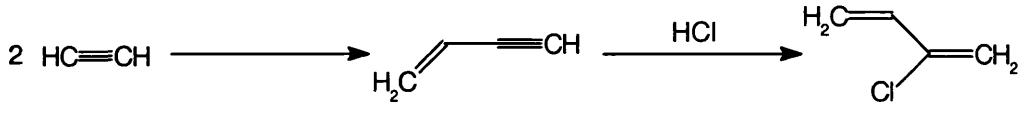


Figure 1.2.4 Synthesis of chloroprene

The addition of HCl occurs in a 1,4-manner and the resultant 4-chloro-1,2-butadiene then isomerises to chloroprene in a fashion similar to the isomerisation of dichlorobutenes (*i.e.* via a π-allyl intermediate). Acetylenes are also activated by π-bonding to copper centres and this allows nucleophilic substitution to take place, affording substituted alkenes.

Nucleophilic aromatic substitution is often very slow, especially when using poorly nucleophilic reagents. In these cases, the rate can be enhanced by the use of a copper catalyst. This class of reactions includes the addition of Grignard reagents to aryl halides and the Ullman reaction which involves the coupling of two aryl halide moieties using CuI as the catalyst.[25]

Other processes involving copper catalysis include the synthesis of 1,2-dichloroethane (DCE) from ethylene and HCl in air using $CuCl_2$ as the catalyst. DCE is an important precursor to vinyl chloride which is used in making plastics and in the synthesis of 1,1,1-trichloroethane, an industrially important solvent. The production of 1,4-butanediol and tetrahydrofuran (THF) from acetylene and formaldehyde involves the use of a copper acetylide catalyst on an inert support such as silica. The synthesis of adipic acid from cyclohexanone involves the use of $[Cu(NO_3)_2]$, although its role is limited to increasing the yield by suppression of a side reaction.

Copper has also been used as a catalyst for the three related processes of epoxidation, aziridination and cyclopropanation. Copper is a poor catalyst for epoxidation, despite its role in oxygenation and oxygen transport in nature. The mononuclear complexes $[Cu(OTf)_2]$ and $[Cu(NO_2)_2]$ are capable of catalysing the decomposition of iodosylbenzene (PhI=O) in the presence of alkenes to give epoxides, although the reaction is non-stereospecific.[26] Dinuclear copper complexes, however, have been shown to be more active than mononuclear complexes.[27] Aziridination of alkenes is a relatively new area of research and will be covered in more detail in Section 1.3.3 of this thesis.

Transition metals have been known for more than ninety years to catalyse the decomposition of diazo compounds in the presence of alkenes to give cyclopropanes and it is now recognised that copper complexes are among the most active cyclopropanation catalysts.[28] It has been concluded that Cu(I) is the active catalyst in these transformations since it has been shown that both $Cu(OTf)_2$ and $CuCl_2$ are reduced to their respective Cu(I) analogues by diazo compounds.[29] However, since Cu(I) salts are often air-sensitive and difficult to prepare, Cu(II) salts which undergo reduction *in situ* are preferentially employed in these reactions.

The utility of cyclopropanation reactions has been significantly increased since the discovery of a chiral ligand system capable of producing cyclopropanes in high enantiomeric excess. The chiral copper complex shown in Figure 1.2.5 below was first utilised by Aratani to obtain an enantiomeric excess of 68% in the reaction of ethyl diazoacetate with 2,5-dimethyl-2,4-hexadiene.[30]

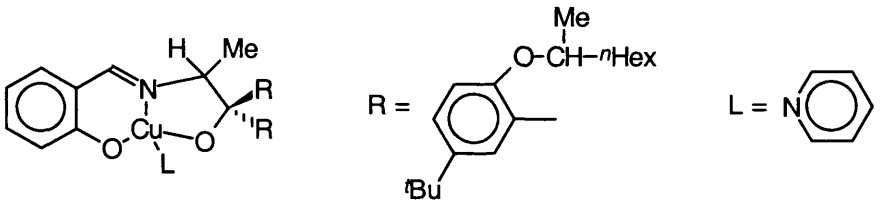


Figure 1.2.5 Aratani's chiral catalyst

It has been shown that increasing the bulk of the R group as well as the size of the substituent on the diazoacetate ester increases the enantioselectivity, allowing products with up to 90% ee to be obtained.[31]

1.3 AZIRIDINES[32]

1.3.1 General Properties

Aziridines are three-membered nitrogen heterocycles, directly analogous to epoxides and cyclopropanes. They have two main interesting chemical properties.[33] Firstly, the presence of the nitrogen atom allows similar chemical

reactions to those of aliphatic amines to take place. Secondly, and more importantly, the strain in the aziridine ring allows facile opening by nucleophiles. Ring opening reactions have a tendency to take place more readily in activated aziridines (those containing a substituent on nitrogen capable of conjugating with the lone pair of electrons), whereas the reactions of basic aziridines (those without the capability to conjugate) tend to mirror those of secondary and tertiary amines.[33] For examples of basic and activated aziridines, see Figure 1.3.1.

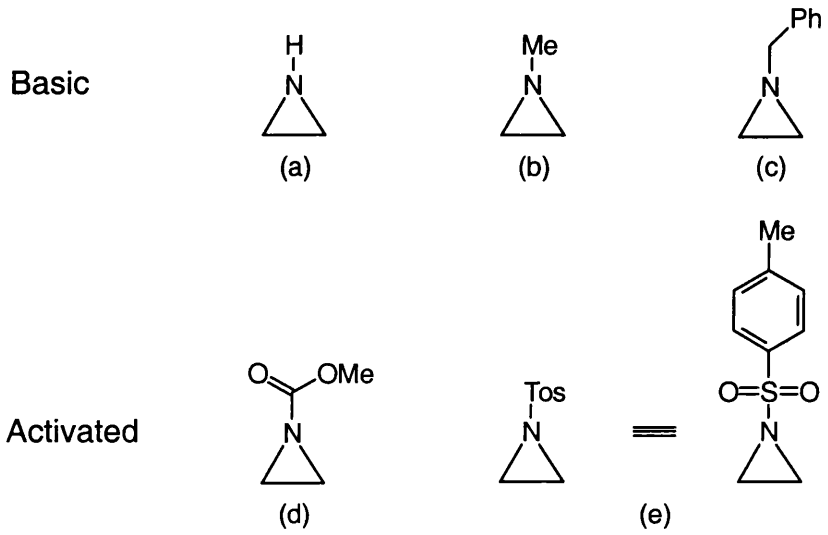


Figure 1.3.1 Basic and activated aziridines

The major difference between the reactions of basic aziridines and activated aziridines is that for the former, whose reactions often require retention of the aziridine ring, the reaction conditions must be carefully selected to avoid formation of the aziridinium ion (see Figure 1.3.2) and its subsequent ring-opening reaction with nucleophiles. Aziridinium ions are sometimes highly reactive species which will undergo ring opening reactions with any nucleophile present, including solvents or even another basic aziridine nitrogen.[33]

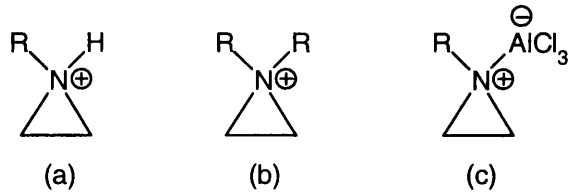


Figure 1.3.2 Cationic aziridine derivatives (aziridinium ions)

Aziridines are also known to complex with many transition metals, including copper, cobalt, nickel and rhodium.[34] Many complexes of ethylenimine (the simplest aziridine, shown in Figure 1.3.1(a)) readily lose the aziridine on exposure to air or vacuum. It has been concluded that ethylenimine behaves as a typical amine ligand, with a steric bulk somewhere between methylamine and ethylamine, although studies of formation constants have shown that the M-N bond is always weaker than that of the corresponding ammonia complex. The aziridine ring is relatively stable when bonded to a metal. Indeed, in rhodium complexes such as $[Rh(AzH)_3Cl_3]$ (where AzH is ethylenimine), the aziridine ring is stable to HCl.[33] The aziridine is stabilised to ring opening because of the coordinative saturation at the nitrogen atom when complexed.

1.3.2 Use of Aziridines

Aziridines have many and varied uses, including as fixing agents for dyes, additives in paper, plastics and as anti-cancer agents. These are in addition to the main use of aziridines - that of a key reagent in organic and natural product synthesis. This section describes a number of these uses in more detail.

1.3.2.1 Industrial Uses of Aziridines [33]

Most of the industrial applications of aziridines make use of the ease of ring-opening by nucleophiles. This property allows molecules with an attached aziridine ring to become chemically bound to a substrate, thus vastly improving the adherent qualities of any chemical additive applied.

Dyes can be attached to aziridine rings prior to application to a fabric. The reactions between activated aziridines and functional groups on fibres usually proceed rapidly and irreversibly, but competing polymerisation of the aziridines can be problematic, as can the high toxicity of aziridines. It is probably this latter property which has restricted the commercialisation of aziridines in this role.

An alternative methodology which avoids these problems and has therefore been much more widely exploited is to use aziridine precursors. When exposed to the

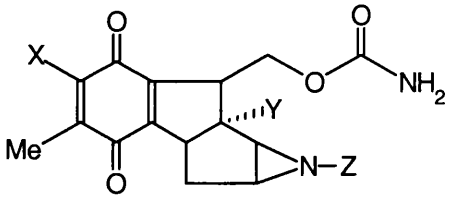
conditions used in dyeing, the aziridine ring is formed *in situ* which then reacts with the fibres. This technique - using the aziridine ring as a link between fibres and chemical additives - can also be used to introduce crease-proofing, flameproofing and water repellent properties into a fabric. In the paper industry, aziridines can be used to attach chemicals for improving wet strength and the polymeric form of aziridines can be used to cause flocculation of paper fibres.

1.3.2.2 Biological Uses of Aziridines [33]

Aziridines are generally very toxic (unlike their polymeric forms), and produce in living organisms essentially the same effect as powerful alkylating agents. This leads to changes that are very similar to those caused by ionising radiation. Ethylenimine is possibly the most toxic of the aziridines because of its high volatility, indeed its toxicity is comparable to that of chlorine or acrylonitrile. Not much is known about the mode of biological action of aziridines, but it is thought that a cross-linking effect may be a major contributor since polyfunctional aziridines often exhibit a much greater toxicity than the same amount of aziridine function administered in monofunctional form.

Aziridines are powerful mutagens, with their mode of action being to alkylate nucleic acid structures. Indeed, ethylenimine is one of the most common mutagenic compounds used by geneticists. Aziridines also produce a limited carcinogenic effect, although there is no proof of a relationship between the two effects and neither has been observed in man.

In the fifties, a group of substances with antibiotic and antitumour properties called the mitomycins were isolated from *Streptomyces caespitosus*.[35] These compounds have the general structure shown in Figure 1.3.3, and it has been established that their antibiotic properties depend on the presence of the aziridine ring.



	X	Y	Z
Mitomycin A	OMe	OMe	H
Mitomycin B	OMe	OH	Me
Mitomycin C	NH_2	OMe	H

Figure 1.3.3 Structure of mitomycins

Aziridines have also been investigated for their sexual chemosterilant properties which arise from the previously mentioned mutagenic effects on nucleic acids. Sexual chemosterilants are used to control insect populations without the use of large amounts of insecticides and hence with reduced pollution of the environment. Two of the requirements of a good chemosterilant are that it should not decrease either the life expectancy or the mating capabilities of the insect. The difficulty of meeting these two criteria along with quick reinfestation from outside the test area have been the main reasons for the lack of success with aziridine-based compounds. With regard to the mode of action of the compounds, it again appears that a cross-linking effect is in operation.

The most studied aspect of the biological functions of aziridines has been their anticancer properties which is a result of research on the use of nitrogen mustards as chemical warfare agents during the Second World War. Nitrogen mustards and aziridines tend to be associated with one another due to the spontaneous isomerisation of the mustards to aziridinium ions (see Figure 1.3.4).

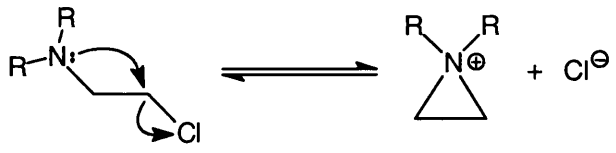


Figure 1.3.4 Isomerisation of nitrogen mustards to aziridinium ions

This tendency to cyclise has been suggested as the cause of the toxicity of nitrogen mustards. Hundreds of different aziridine derivatives have been tested for their anticancer properties but, despite their structural diversity they exhibit

similar effectiveness. As with other powerful alkylating agents, aziridines are most effective against leukemias and other lymphomas and do not tend to work well on solid tumours. Their main drawback is that they do not affect malignant tissue significantly more than normal tissue.

1.3.2.3 Reactions Of Basic Aziridines [32,33,36]

The chemistry of basic aziridines is dominated by reactions of the ring nitrogen that leave the aziridine ring intact. Basic aziridines can be ring-opened using highly nucleophilic reagents such as alkali metal salts of primary and secondary phosphines, Grignard reagents and alkoxide anions, but they generally require prior activation. Activation can be achieved by creating a positive charge on the nitrogen, forming one of the species shown in Figure 1.3.2 (see Section 1.3.1) by protonation, alkylation or reaction with Lewis acids. Thus, halogen acids and alkyl halides are good ring-opening reagents since they produce an activating cation and a nucleophilic anion. However, an excess of the alkyl or hydrogen halide is necessary since the product of ring opening will contain a basic nitrogen which will compete with the halogen in the nucleophilic attack on the activated aziridine.

Less nucleophilic reagents require prior activation of the aziridine by an acid with a weakly nucleophilic conjugate base. A stoichiometric amount of acid must be used to avoid competing ring-opening by unreacted aziridine, the activated aziridine then being ring-opened by a large excess of the nucleophile (alcohol, amine, nitrile, isocyanate or isothiocyanate). The yield of the reaction is dependent on the relative rates of reaction of the nucleophile and the ring-opened product. These in turn are dependent on both the relative nucleophilicities and the relative concentrations of the two competing reagents. If the ring-opening reagent has an acidic proton (as in carboxylic acids, phenols, thiols, imides, sulfonamides and xanthines), then activation is often not necessary since a sufficiently large proportion of the aziridine is protonated and

the conjugate base is often nucleophilic enough to compete successfully with the unreacted and ring-opened aziridines.

When using carboxylic acid derivatives such as acid halides or anhydrides, the aziridine must be added to the reagent in order to minimize polymerisation and (in the case of 1-unsubstituted aziridines) to minimize the abstraction of the proton on nitrogen by unreacted aziridine. Reactions with acid derivatives are actually examples of ring opening of activated aziridines formed *in situ*.

Reactions of basic aziridines that leave the ring intact generally involve substitution of functional groups or isomerisations.[33] Replacement of the hydrogen on the ring nitrogen is effected by nucleophilic attack of the ring nitrogen on a halogen-bearing atom in the presence of base, the latter reacting with the halogen acid formed. The base is normally chosen such that the reaction with acid is irreversible (e.g. $NaCO_3$, NaOH, NEt_3). Examples include reactions with alkyl halides and aryl halides. Reaction with phosphorus compounds such as those shown in Figure 1.3.5 (a) give rise to activated aziridines, whereas the related reaction shown in Figure 1.3.5 (b) provides basic aziridines.

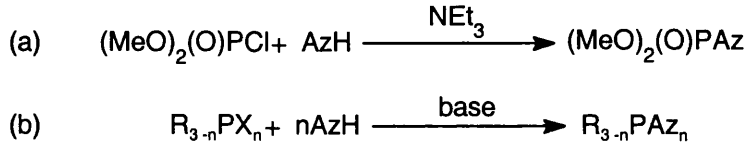


Figure 1.3.5 Reaction of aziridines with phosphorus compounds

Acylation of 1-unsubstituted aziridines occurs under the general reaction scheme outlined in Figure 1.3.6. Examples of reagents that follow this scheme are acid halides and anhydrides, esters, isocyanates, isothiocyanates and ketenes.

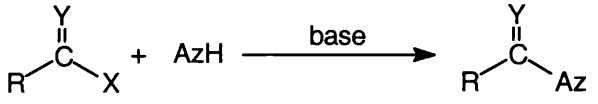


Figure 1.3.6 Acylation of aziridines

Certain substitution reactions do not require the presence of base.[33] These include reaction with epoxides and alkylene sulfides, although yields are normally low due to competition from several side reactions, often involving the successfully substituted products. Reaction with activated or protonated aziridines has been mentioned previously. Aziridines react with ketones and aldehydes in a similar way to secondary amines, forming aminohydrins of the formula RR'C(OH)Az. Reaction with alkenes can be viewed as a nucleophilic attack by the aziridine nitrogen on the β-olefinic carbon as shown in Figure 1.3.7. This is followed by proton migration to give the 1-alkylaziridine.

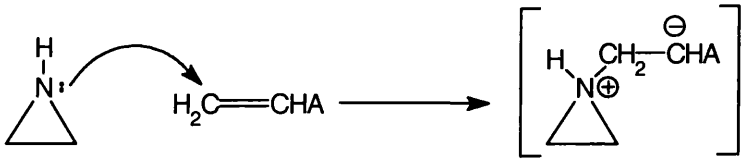


Figure 1.3.7 N-alkylation of aziridines

The replacement of groups other than the 1-hydrogen are rare and quite specific. However, replacement of the chlorine atom of 2-chloroaziridine with inversion of geometry occurs easily with a number of nucleophiles such as NaCN, NaSPh, NaOMe and LiMe.

Geometric isomerisation of 2,3-substituted aziridines is only known for aziridines where one of the substituents is an acyl group, and even then, only in a few rare cases.[37] However, isomerisation to enamine and alkylidenimine structures (as shown in Figure 1.3.8) is quite common and is catalysed by heat, light and glacial acetic acid.

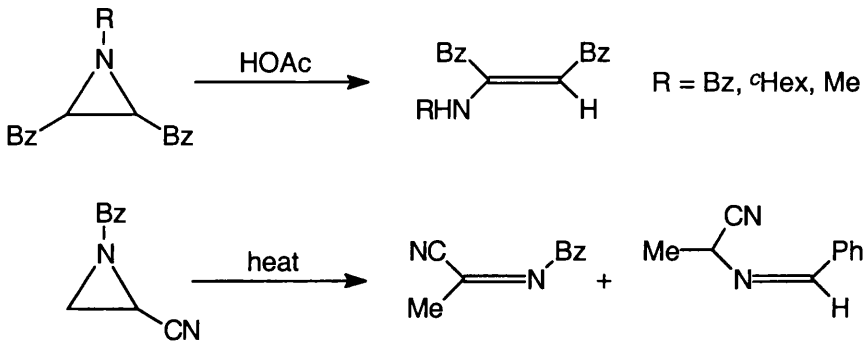


Figure 1.3.8 Isomerisation of aziridines to enamines and alkylidenimines

1.3.2.4 Reactions Of Activated Aziridines [32,33,36]

Reactions of activated aziridines are of two general types: ring-opening reactions and ring-expansion reactions. Activated aziridines undergo nucleophilic ring opening much more easily than basic aziridines and do not generally need prior activation. Thus when reacted with hydrogen halides, highly reactive species (activated equivalents of the aziridine shown in Figure 1.3.2 (a)) are formed which undergo nucleophilic ring-opening, giving high yields of products with only stoichiometric quantities of reagents. Reactions with alkyl halides are analogous to ring-opening of basic aziridines, but the yields vary greatly depending upon the nucleophilicity of the aziridine nitrogen (i.e. the relative ease of formation of the alkylated intermediate). Reaction with carboxylic acids causes ring-opening in the expected way, but also causes a large number of side reactions and isomerisations which are specific to the substituent on nitrogen. Phenols are insufficiently acidic to protonate activated aziridines, but react on addition of a catalytic amount of acid. However, they too undergo secondary reactions and isomerisations. Thiols, being highly nucleophilic, avoid many of the side reactions and isomerisations and thus give good yields of the expected product. Ring-opening by amines occurs by a simple S_N2 attack on a ring carbon, normally the least substituted carbon. Yields are often higher in hydroxylic solvents, possibly because of involvement in proton transfer from the amine to the aziridine nitrogen in the transition state. Anionic reagents react via a similar mechanism. Amides have been shown to react with activated aziridines, and indeed this property may be the cause of the

tendency for activated aziridines to polymerise since ring-opened products formed by reaction with trace impurities are often amides.

Three classes of reaction are peculiar to activated aziridines. Deamination occurs spontaneously, even at low temperatures, in unstable activated aziridines such as 1-nitrosoaziridine. These are readily prepared from the unsubstituted aziridine by reaction with nitrous acid and indeed, this is a well known method of forming alkenes from aziridines. The reaction occurs stereospecifically, with *trans* aziridines giving *trans* alkenes etc. Isomerisation of activated aziridines takes place readily and can be a competing reaction causing lowering of yields of the desired product. This occurs via two pathways (shown in Figure 1.3.9), each giving a different product. Pathway (a) is by far the most common and can be catalysed by heat, acid or most commonly nucleophiles such as halide anions. Pathway (b) only generally occurs if the R group is itself a good nucleophile.

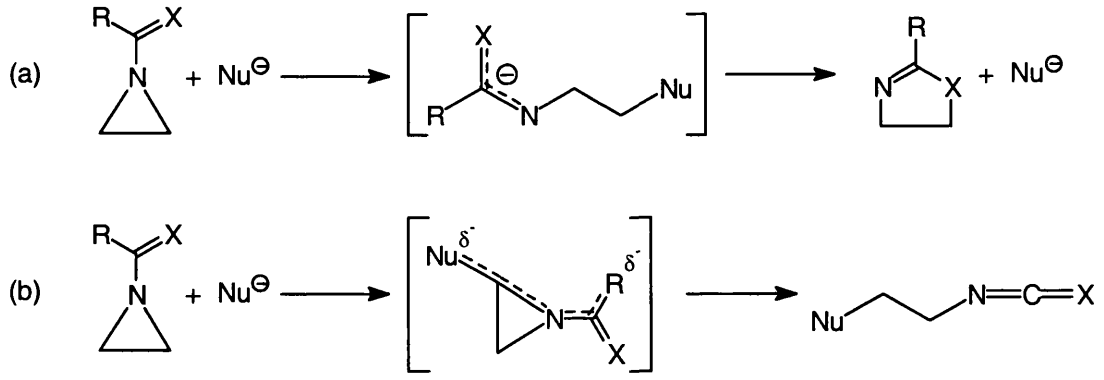


Figure 1.3.9 Isomerisation of activated aziridines

Finally, the 1-substituent can be removed (i.e. replaced by hydrogen) upon reaction in hydroxylic solvents in the presence of acid or base, or, if the substituent is a quinone derivative, reaction with alkyl amines.

1.3.3 Aziridination

Aziridines can be prepared by many different means. The traditional, organic preparations have been known for a long time but often involve several steps, especially if the process is to be asymmetric.[38] More recently, catalytic methods have been developed and it is on these that this section will concentrate.

1.3.3.1 Stoichiometric Preparation Of Aziridines [32,33,36]

Aziridines can be formed in many ways, the most general preparative route being the intramolecular displacement of a good leaving group by a vicinal amine as shown in the general scheme in Figure 1.3.10. This method can also be used for amide anions if the pH is high enough for them to form and if R is an acyl or similar group.

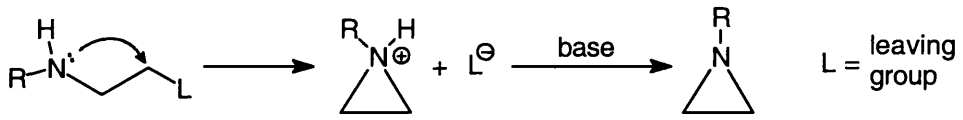
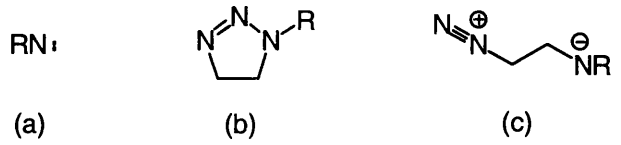


Figure 1.3.10 Intramolecular formation of aziridines

The rate of cyclisation is affected by three factors. The better the leaving group L, the higher the nucleophilicity of the nitrogen and the higher the pH, the faster the reaction. The pH must be high enough so that the nitrogen is not protonated and an alkaline medium also serves to deprotonate the resultant aziridinium ion which is highly reactive (*vide supra*). Since the reaction involves a charge separated intermediate, solvents of high dielectric constant are generally employed. A related intramolecular method is the displacement of a good leaving group on nitrogen by a vicinal carbanion.

Aziridines can also be formed by processes such as the reduction of azirines by $LiAlH_4$ and Grignard reagents. These two reducing agents can also be used in the reductive cyclisation of oximes to form aziridines.

A well known route to aziridines is the reaction of alkenes with azides. Azides may form any one of a number of intermediate structures including a nitrene, a triazoline adduct and a zwitterionic intermediate (Figures 1.3.11 (a), (b) and (c) respectively).



(a) (b) (c)

Figure 1.3.11 Intermediates formed by azides

The triazoline structures may be isolable depending on the substituents on both the azide and the alkene and, in all but a couple of cases, the nitrogen which becomes part of the aziridine ring is the substituted nitrogen from the azide.

A similar process, but one which is much less widely used, is the reaction of acyclic imines with diazo compounds. This may proceed via the triazoline intermediate shown in Figure 1.3.11(b) above or by addition of a carbene across the carbon-nitrogen double bond.

1.3.3.2 Catalytic Preparation of Aziridines

Catalysts may be used to promote the formation of aziridines in two closely related ways (Figure 1.3.12). The catalyst may promote the decomposition of diazo compounds to carbenes which then react with imines to give aziridines in much the same way that cyclopropanes are produced on reaction with alkenes. Alternatively, the catalyst can be used to induce the formation of nitrenes which then react with alkenes to give the desired aziridine.

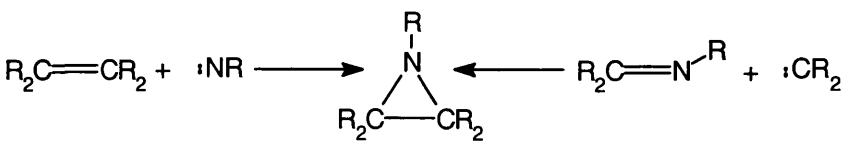


Figure 1.3.12 Formation of aziridines from alkenes and from imines

Aziridines From Imines The preparation of aziridines from imines and a carbene source (Section 1.3.3.1) is best performed in the presence of a catalyst which will promote decomposition of the diazo compound. These catalysts are generally the same as those used in the related cyclopropanation of alkenes, with copper performing most effectively. The use of a catalyst in the formation of aziridines from imines and diazo compounds has been recently studied by Jørgensen[39] and Jacobsen.[40] From substrate-screening reactions, Jørgensen has concluded that the N-substituent on the imine strongly affects the reaction yields. Bulky or electron-withdrawing substituents reduce the yield of aziridine produced, suggesting the presence of an intermediate electrophilic carbene species. Jacobsen and his group have concentrated on developing asymmetric aziridination using the bis(oxazoline) ligands favoured by Evans.[41] These chiral ligands (Figure 1.3.13) give moderate to high enantioselectivities, but in poor yield.

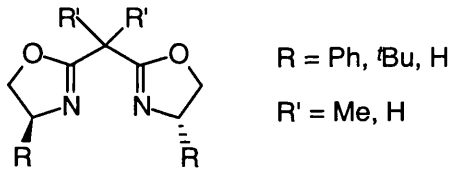
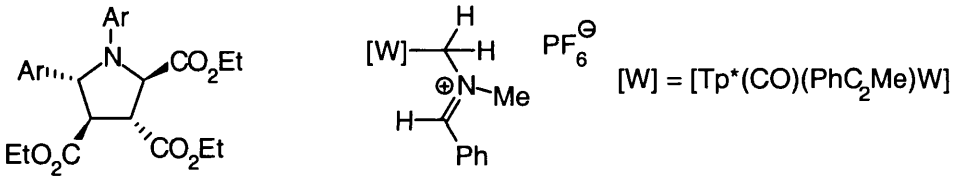


Figure 1.3.13 Bis(oxazoline) ligands

Jacobsen also notes the concomitant formation of pyrrolidine derivatives such as those shown in Figure 1.3.14(a).[40] He proposes that these are formed from the reaction of an azomethine ylide with diethyl fumarate (formed by the dimerisation of two carbene fragments). The proposal for an azomethine ylide intermediate is further supported by the isolation by Templeton of a tungsten-complexed azomethine ylide formed by the reaction of an imine with a stable tungsten carbene complex (see Figure 1.3.14 (b)).[42]



(a) (b)

Figure 1.3.14 Pyrrolidine derivatives and tungsten-complexed azomethine ylide

Aziridines From Alkenes The first catalytic transfer of a nitrene group to an alkene was reported by Kwart and Kahn using copper bronze as the catalyst.[43] In the late 80's, Mansuy reported the aziridination of several alkenes using N-tosyliminoiodobenzene (PhI=NTos) with Fe(III) and Mn(III) porphyrin complexes as catalysts, complexes which in the presence of iodosylbenzene (PhI=O) catalyse oxo transfer to alkenes to give epoxides. A characteristic of these reactions was the relatively high proportion of non-aziridine products. The PhI=NTos that did not react with alkene reacted to give $TosNH_2$ which was suggested to be the product of hydrolysis of a reactive imido intermediate, a reaction which would also produce a metal oxo complex. Epoxides were also isolated in similar ratios to those obtained in the epoxidation of alkenes using PhI=O.[44]

In the early 90's Evans published a series of papers which described the first in-depth screening of catalysts, substrates and nitrene sources for aziridination.[45,46] The screening of catalysts was based on the knowledge that Mn(III) and Fe(III) complexes are excellent catalysts for alkene epoxidation, whilst Cu(I) and Rh(II) complexes are the best transition metals for use in cyclopropanation. It was anticipated that the relationship between the three analogous products would lead to early insight into the aziridination process. Indeed, this was the case as it was found that copper complexes were significantly better at catalysing aziridination than the other metals screened. Not only did they generally give higher yields of aziridine, but the competing allylic insertion reaction did not take place. The activity of copper catalysts would suggest a correlation with cyclopropanation, but in contrast with this process, Evans found that Cu(II)

complexes were also proficient catalysts. Indeed, the yields obtained using related Cu(I) and Cu(II) complexes such as [Cu(OTf)] and [$Cu(OTf)_2$] were almost identical. This observation, as well as competition experiments led to the suggestion of a common oxidation state for the active catalyst. Since the nitrene source PhI=NTos is expected to be a two electron oxidant, Evans stated "*In view of the fact that iodine(III) reagents are oxidants, it is reasonable to conclude that these reactions are being catalysed through Cu(II) rather than Cu(I) as originally presumed.*"[46]

Evans has examined several potential nitrene sources (see Figure 1.3.15), although only PhI=NTos gave appreciable yields of aziridine at room temperature. He has also concluded that choice of solvent was an important consideration and that polar aprotic media afforded highest yields and highest reaction rates, with hydroxylic solvents only providing $TosNH_2$.

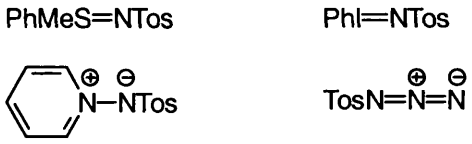


Figure 1.3.15 Nitrene sources investigated by Evans

Jacobsen too has investigated mechanistic aspects of copper-catalysed aziridination.[47] Whilst supporting the proposal for a nitrene-based mechanism, he has also offered the possibility of a Lewis acid type mechanism. He rejects this latter since it would involve an intermediate of the type shown in Figure 1.3.16. The structure of the aryl iodide moiety would in this case be expected to influence the reaction. His experiments comparing enantioselectivities obtained using the two aryl groups shown in Figure 1.3.16 show no difference between the two.

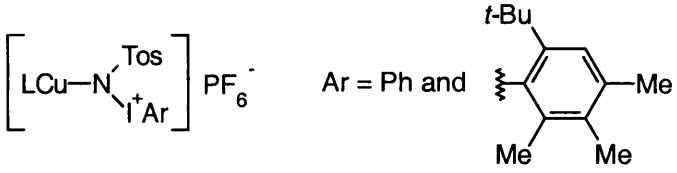


Figure 1.3.16 Possible Lewis acid intermediates

Jacobsen has also provided details of two items of evidence supporting a discrete copper nitrene species.[47] Firstly, the photochemical reaction of $TosN_3$ (which is known to produce a nitrene) in the presence of $[CuPF_6]$ and a chiral ligand gave a product with the same enantioselectivity as was obtained from the aziridination using PhI=NTos. Secondly, a series of aziridinations and cyclopropanations with different chiral diimine-based ligands showed a linear correlation between the enantioselectivities, clearly indicating a similarity between the two processes.

More recently, Perez has published work comparing the rates of both cyclopropanation and aziridination reactions using a series of substituted styrenes as substrates.[48] For both processes, styrenes possessing electron-donating substituents are found to be more reactive. However, with electron-withdrawing substituents, there ceases to be a correlation. During cyclopropanation, the rate of reaction is slowed but with aziridination reactions there is little substituent dependence, the rate even being slightly increased.

Investigation of the potential of asymmetric aziridination has been a priority for both Evans and Jacobsen.[38] Jacobsen has concentrated on the use of benzylidene derivatives of 1,2-diaminocyclohexane as chiral ligands.[49] These ligands in conjunction with [Cu(OTf)] have proved excellent asymmetric catalysts, giving enantioselectivity greater than 98% in one case. It is interesting to note that with this ligand/substrate combination (Figure 1.3.17), use of this ligand in 50% ee gave product in 50% ee. This suggests that the active catalyst is a monomeric species bearing one chiral ligand.

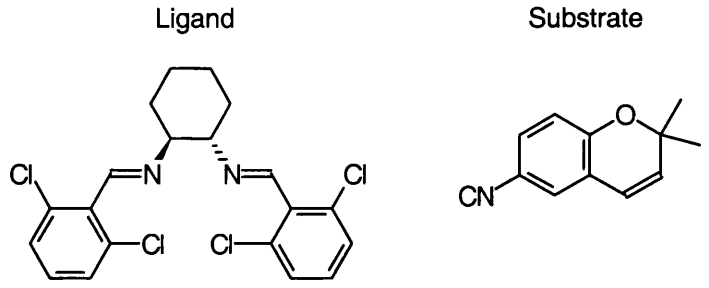


Figure 1.3.17 Highly enantioselective ligand-substrate combination

Jacobsen has also isolated and crystallographically characterised a copper styrene complex of one of his chiral ligands (Figure 1.3.18) which appears to utilise face-face and edge-face aromatic interactions to stabilise the metal-alkene interaction.[50]

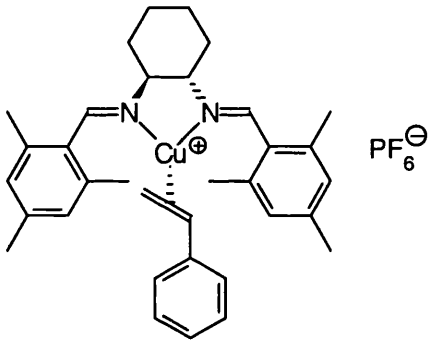


Figure 1.3.18 Copper complex crystallographically characterised by Jacobsen

The face to face interaction occurs with the distance between aromatic planes being 3.26 Å which is consistent with previously reported structures.[51] Both the aromatic ortho hydrogen and the *cis*-β-hydrogen on styrene are involved in bonding interactions with the ligand-based aromatic ring. The hydrogen to aromatic centroid distances are 2.94 Å and 2.99 Å respectively. Similar interactions are strongly indicated in several good chiral catalyst systems.[52]

Chiral bis(oxazoline) ligands (whose structure is shown in Figure 1.3.13) have been investigated by Evans and his group.[53] As mentioned previously, he has found that either Cu(I) or Cu(II) complexes can be used, with similar yields and enantioselectivities obtained with each. However, only the Cu(I) complexes were

active in cyclopropanation reactions. In common with Jacobsen, Evans chooses to use triflate complexes as he has concluded that highly electronegative counterions provide for more effective catalysis.[53] All of his ligands produce products with high enantioselectivity, but it is interesting to note that the ligand which consistently produces the highest enantioselectivity (that with R=Ph) shares a similarity to the diimine-based catalysts used by Jacobsen. Both contain pendant aromatic groups which are held close to the copper centre and it is possible to envisage, in the bis(oxazoline) system, a ligand-substrate interaction similar to that which has been shown to occur with Jacobsen's ligand system (*vide supra*).

1.4 SUMMARY

This introduction has given a general overview of copper chemistry and homogeneous catalysis, with particular reference to cyclopropanation and epoxidation which are both analogous to aziridination. The industrial, biological and synthetic potential of aziridines has been discussed and the traditional synthetic routes towards aziridines detailed. The catalytic synthesis of aziridines is a relatively new area of chemistry and it has only been in the last few years that the potential of this system has begun to be realised. This thesis aims to increase our knowledge of copper catalysed aziridination reactions and in particular to gain insights into the mechanism of catalysis which would aid development of new catalysts capable of higher turnover and increased enantioselectivity. Chapter Two details the synthesis of a number of copper complexes within several different classes. Structural details of potential interest to the catalytic process will be discussed. Chapter Three then describes the use of these complexes as aziridination catalysts under a variety of conditions. Information gained from these reactions, along with structural data from Chapter Two are then brought together to provide insights into the mechanism of catalysis. A catalytic cycle based on the conclusions reached is proposed.

2.0 PREPARATION OF COPPER CATALYSTS

This chapter describes the synthesis as well as the solution and structural properties of a variety of copper complexes. These complexes can be classified into four broad groups, the synthesis of each group being described after a brief introduction. The four groups are pyrazolylborate complexes, dithiocarbamate complexes, phosphine complexes and a group of novel amido complexes formed by the insertion of a nitrene functionality into the Cu-S bond of dithiocarbamate complexes. The aziridination capability of all of the complexes described in this chapter will be discussed in chapter three. Any exceptions to this will be noted alongside the description of the complex below.

2.1 PYRAZOLYLBORATE COMPLEXES

2.1.1 Introduction

Pyrazolylborate ligands were first reported in 1966 by Trofimenko and consist of a borohydride anion that has two, three, or four of the hydrogen atoms replaced by pyrazoles or pyrazole derivatives.[54] Synthesis of this class of ligand is achieved by heating the desired borohydride with an excess of the pyrazole, the degree of substitution being controlled by the temperature of the melt. The B-N bond is usually formed adjacent to the carbon atom bearing the least bulky substituent.[55]

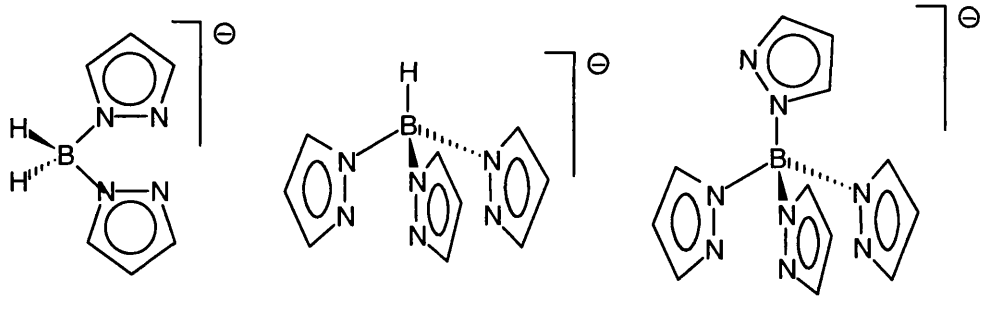


Figure 2.1.1 Poly(pyrazolyl)borate ligands

Pyrazolylborate ligands can coordinate to transition metals in either a bidentate or tridentate fashion. Bidentate coordination, which occurs with bispyrazolylborates and in certain circumstances with tris- and

tetrakispyrazolylborates, can be considered as analogous to the coordination of β-diketonates such as acac (acetylacetonate).[56] Both are uninegative four-electron donors, but whereas acac is a planar ligand, the six-membered ring formed with pyrazolylborate ligands forms a 'boat' structure. The tridentate coordination found with tris- and tetrakispyrazolylborates can be considered analogous to the coordination of cyclopentadiene, since both are uninegative six-electron donors that occupy three coordination sites on the metal. However, pyrazolylborates have several advantages over their more well known analogues due to the high level of substitution possible.

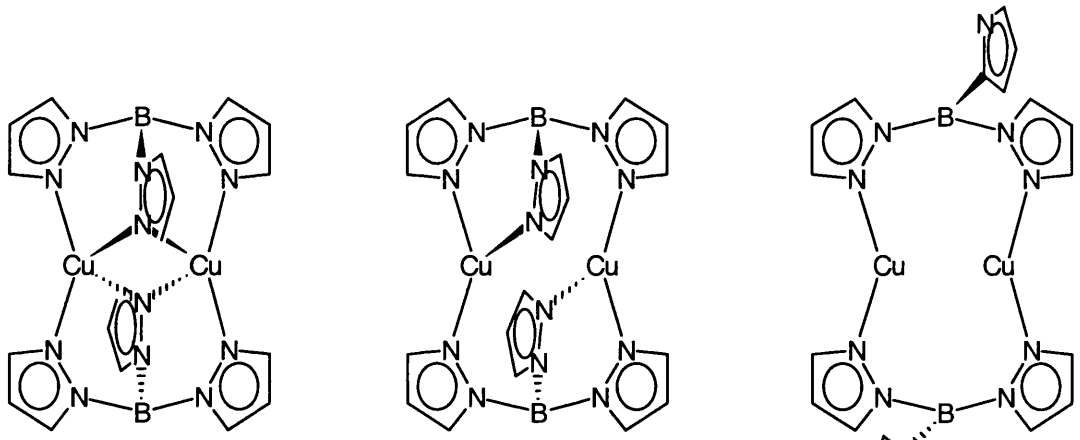
Varying the substituents on the pyrazole ring allows the tailoring of both the steric and electronic nature of the ligand. Bulky substituents in the 3- position of the pyrazole ring increase the steric crowding around the complexed metal, whereas in the 5- position, they decrease the 'bite angle' at the metal centre as well as providing a measure of protection for the reactive B-H bond. Substituents in the 4- position can be used to alter the packing of complexes in the solid-state. Substituents in all three positions have an effect on the electronic properties of the ligand, as well as altering the solubility of a complex.

The names of pyrazolylborates are usually abbreviated, "Tp" for trispyrazolylborates, and "Bp" for bispyrazolylborates. Any substitution on the pyrazole ring is indicated in superscript, with the assumption that single substitutions are at the 3- position, and double substitutions are at the 3- and 5-positions. The bulkier of two substituents is assumed to be in the 3- position. Thus, a trispyrazolylborate with a methyl substituent in the 5- position and a *tert*-butyl substituent in the 3- position is abbreviated to $Tp^{Me,t\text{-}Bu}$. The only exception to these abbreviations is for the widely used hydrotris(3,5-dimethylpyrazolyl)borate and dihydrobis(3,5-dimethylpyrazolyl)borate which are abbreviated Tp* and Bp* respectively.

Complexes involving pyrazolylborate ligands are generally obtained by metathesis reactions with metal halides, although metal carbonyl complexes are

sometimes also used.[57] Reactions with metal halides are driven by precipitation of either the complex (in aqueous solution) or the halide salt (in organic media). In the latter, thallium salts of the pyrazolylborate ligand are often employed since, unlike alkali metal halides, thallium halide salts are completely insoluble in organic solvents. With unusual pyrazolylborate ligands and especially those susceptible to decomposition, complexation with thallium also conveys the benefit of increased stability and thus a longer shelf-life.

Univalent complexes of trispyrazolylborates are usually associated with coordinative unsaturation which is relieved either by the use of ancillary ligands such as CO or PPh_3 or by dimerisation. The mode of bonding in such dimers is affected by the steric bulk of the trispyrazolylborate ligand and is most clearly shown in the coordination spheres of the series of dimers $[(CuHB(3\text{-}R,5\text{-}R'\text{-}pz)_3)_2]$ shown in Figure 2.1.2.



(all substituents and protons omitted for clarity)

Figure 2.1.2 Dimeric copper tris(pyrazolyl)borate complexes

When R=R'=H, each copper is four coordinate, with one of the pyrazole rings in an unusual bridging mode.[18] If R=R'=Me or Ph, the copper atoms are three coordinate [18,58] but if R=^{t}Bu & R'=H or Me, the copper atoms are two coordinate,

with the third pyrazole being uncoordinated.[58,59] In all but one of these complexes the pyrazole groups are fluxional on the NMR timescale at room temperature. For [(CuHB(3-^{t}Bu, 5-Me-pz)$_3$)$_2$], the rings are static even at a temperature of 90°C, which serves to outline the effect that substituents far removed from the metal centre can have on structure.[59]

The well documented ability of copper to coordinate small molecules such as CO and ethylene in the +1 oxidation state is advantageously shown in trispyrazolylborate complexes. The pyrazolylborate ligands are able to coordinate to the copper leaving a small, and adjustable (by the use of different pyrazole substituents) 'pocket' for the coordination of small molecules. Copper(I) complexes of CO, C_2H_4 and PPh_3 have all been synthesised in the presence of Tp*.[60-62] The complex [Tp*Cu(C_2H_4)] has also recently been shown to be good catalyst for olefin cyclopropanation and aziridination.[63] The effect of introducing electron-withdrawing and electron-donating substituents on the trispyrazolylborate ligand can be shown clearly by comparing the CO stretching frequency of [Tp*Cu(CO)] (2066 cm^{-1}) with that of [HB(3,5-(CF_3)$_2$pz)$_3$Cu(CO)] (2132 cm^{-1}), its polyfluorinated analogue. This difference results from a much reduced level of Cu to CO π-back-bonding.[64] Indeed in the latter, the higher frequency is very close to that of free carbon monoxide (2143 cm^{-1}).

Divalent complexes containing trispyrazolylborate ligands are much more numerous than their univalent counterparts due to the large number of possible combinations of neutral and anionic auxiliary ligands. Complexes of molybdenum form the largest of such groups of complexes and serve to illustrate the many different properties of pyrazolylborate ligands.[57]

Divalent trispyrazolylborate complexes of copper have two general structures depending on the size of the substituent in the 3- position on the pyrazole rings. The chemistry of copper (II) in the presence of either Tp or Tp* is dominated by the formation of the sandwich complexes [CuTp$_2$] and [CuTp*$_2$] since complexes of the type [TpCuL] (where L is an anionic ligand) decompose readily to give

[CuL_2] and [$CuTp_2$]. Sandwich complexes of the type [$CuTp^*_2$] are relatively stable and unreactive due to the methyl groups providing a protective covering round the copper atom.

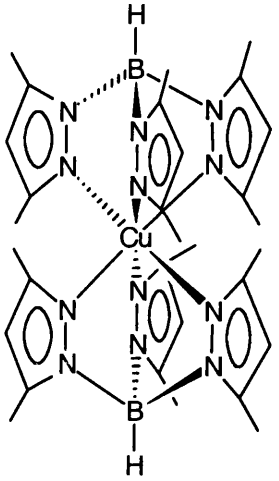


Figure 2.1.3 Structure of [$CuTp^*_2$]

Larger ligands inhibit this redistribution, and complexes such as [$Tp^{t\text{-}Bu}CuCl$] are stable.[59]

Trofimenko has reported the synthesis of a complex [CuL_2] where L=3-neopentylpyrazolylborate, although characterisation was by comparison of the IR spectrum with that of the cobalt analogue.[65] Due to the extra CH_2 unit in the neopentyl group compared to the *t*-butyl group, the substituents arrange themselves in a 'propeller'-like fashion about the metal centre. This allows the possibility of the isolation of optical isomers if the barrier to rotation can be increased sufficiently. More recently, examples of chiral trispyrazolylborate ligands derived from menthone have been synthesised by Tolman.[66]

Trivalent complexes containing only trispyrazolylborate ligands are restricted, due to the large size of the ligands, to the lanthanides and even in these cases some, or all, of the ligands are forced to coordinate in a bidentate fashion. Despite the often quoted analogy between bispyrazolylborates and β-diketonates, only one analogous trivalent transition metal complex containing

only bispyrazolylborate ligands has been synthesised,[67] despite there existing many acac analogues.[57]

For the purposes of this project, it was decided to concentrate initially on copper complexes of Tp and Tp* since these ligands have been extensively studied and are readily available. The difference in steric bulk, their cone angles being 198.5° and 236° respectively, would hopefully allow the effect on the aziridination process of altering the size of the coordination environment to be studied. In addition, asymmetric catalysis may be possible using a copper complex of a chiral pyrazolylborate ligand.

2.1.2 Results and Discussion

Preparation of NaTp* and KTp* Both NaTp* and KTp* have equal reactivity towards metal centres, although the sodium salt is preferentially employed with metal iodides in metathesis reactions since NaI has a high lattice energy and therefore precipitates from organic solution more easily. The two pyrazolylborate ligands were synthesised according to a modification of the procedure developed by Trofimenko.[68] The relevant alkali metal borohydride was heated at over 200°C in the presence of six equivalents of 3,5-dimethylpyrazole, the resultant white crystalline solid being separated from the excess pyrazole by sublimation. The two products were characterised by ^{1}H NMR spectroscopy. Both salts were used in the synthesis of the copper pyrazolylborate complexes described herein.

Initial synthesis and investigation was centred on a series of copper trispyrazolylborate complexes [Tp*CuL]. Changing the bulk of the pyrazolylborate was necessary to investigate the effect of changing the reactive "pocket" created at the copper centre by the pyrazolylborate ligand. The most obvious choice of alternative pyrazolylborate ligand is the unsubstituted Tp ligand since it has been widely studied and is commercially available. Since only a limited amount of this ligand was available, it was decided to prepare only the

dimer and PPh_3 complex since these syntheses were the simplest and gave the highest yields of product.

2.1.2.1 Complexes Of Tp and Tp*

Synthesis Of [Tp*Cu(PPh_3)] And [TpCu(PPh_3)] Pyrazolylborate copper phosphine complexes have previously been reported and investigated, although crystallographic studies have been limited to unsubstituted pyrazolylborates.[69,70] [Tp*Cu(PPh_3)] is air-stable both in the solid-state and in solution, although it has been reported that this is not the case above room temperature.[70] This Cu(I) phosphine complex was prepared according to the method utilised by Kitajima.[62] CuCl, KTp* and PPh_3 were stirred together in CH_2Cl_2, the desired product being isolated as a white crystalline solid by filtration and recrystallisation from CH_2Cl_2. [Tp*Cu(PPh_3)] also appeared to be light sensitive in the crystalline form under nitrogen. Exposure to light caused the crystals to turn orange, with partial reversal of this phenomenon appearing to occur on subsequent exposure to air. However, since this effect did not appear to be relevant to aziridination, it was not investigated further. The unsubstituted pyrazolylborate analogue is structurally similar to the Tp* complex and is prepared in an identical manner. However, this complex did not appear to show the light-sensitivity observed in the Tp* analogue.

Synthesis Of $[Tp^*Cu]_2$ And $[TpCu]_2$ These colourless crystalline solids were synthesised by stirring KTp* or NaTp and CuCl together in THF, with purification being effected by extraction into benzene followed by recrystallisation from CH_2Cl_2. It is interesting to note that it has been shown that $[Tp^*Cu]_2$ is extensively dissociated in benzene solution and with the ^1H NMR spectrum showing only three resonances, it is possible to suggest that dissociation and association are relatively rapid on the NMR timescale.[18] However, the solid state structure shows that the pyrazolylborate group bridges the two copper atoms with two pyrazoles coordinating to one copper centre and the third pyrazole coordinating to the other copper centre (see Figure 2.1.2 (b)). In contrast to $[Tp^*Cu]_2$, however, $[TpCu]_2$ is dimeric both in solution and in the solid state.[60]

There are significant differences between the Tp and Tp* analogues of $[TpCu]_2$ and $[TpCu(PPh_3)]$ which will make the cause of any difference in aziridination capability difficult to ascribe. In the case of the dimeric species, the Tp complex remains dimeric in solution, whereas the Tp* complex dissociates. The large difference between the two B-H frequencies (2510 cm^{-1} for $[TpCu]_2$ compared with 2441 cm^{-1} for $[Tp^*Cu]_2$) also suggests that the electron density on the latter is likely to be higher, consistent with the introduction of electron-donating substituents on the ligand. For the phosphine complexes, the steric demand at copper will be greater for $[Tp^*Cu(PPh_3)]$ than for $[TpCu(PPh_3)]$. The B-H stretching frequencies, however, suggest that there is also an electronic difference between the two complexes. The effect on the B-H frequency of coordination to a $CuPPh_3$ unit for Tp* is almost double that for Tp. This suggests greater σ-donation from PPh_3 in the latter complex as evidenced by a shorter Cu-P bond.[62,70]

Synthesis of [Tp*Cu(CO)] Pyrazolylborate complexes were the first copper complexes to be able to bind carbon monoxide in a stable fashion and to be isolated in a pure state.[60] [CpCu(CO)] had previously been synthesised, but it co-distilled with pentane.[71] Many copper pyrazolylborate carbonyl complexes have since been synthesised using variously substituted pyrazolylborate ligands.[72] [Tp*Cu(CO)] was synthesised by bubbling CO through a THF solution of CuCl and KTp* and was purified by recrystallisation from CH_2Cl_2 and 40/60 petrol. The product was characterised by IR and ^1H NMR spectroscopy, FAB mass spectrometry and elemental analysis.

Attempted Synthesis of [Tp*Cu(C_2H_4)] Synthesis of $[Tp^*Cu(C_2H_4)]$ was attempted according to the procedure outlined by Brookhart and Templeton, which involved adding KTp* slowly to a slurry of CuCl in CH_2Cl_2 under a saturated atmosphere of ethylene.[61] Although the complex could be identified from it's ^1H NMR spectrum and its B-H stretch in the IR spectrum, it could not be isolated. The ethylene appears to be so weakly bound that exposure to either heat or vacuum causes dissociation of the ethylene followed by formation of the

dimeric complex $[Tp^*Cu]_2$ mentioned above, and it is for these reasons that all attempts at recrystallisation failed. The ethylene complex $[Tp^*Cu(C_2H_4)]$ could also not be identified by ^1H NMR after bubbling ethylene through a solution of $[Tp^*Cu]_2$. From this and observations by others on the relative reactivities of the $[Tp^*CuL]$ complexes ($L=PPh_3$, CO, $CuTp^*$, C_2H_4), an order of Cu-L bond strength can be proposed (Figure 2.1.4).[18,60,62,63]

$$PPh_3 < CO \sim CuTp^* < C_2H_4$$

Figure 2.1.4 Relative stabilities of copper Tp* complexes

Preparations of all Cu(I) trispyrazolylborate complexes were performed under an atmosphere of nitrogen since oxidation by atmospheric oxygen occurs easily, $[Tp^*Cu(PPh_3)]$ apart. The relative air-sensitivity of the complexes can be used empirically to support the order of bond strength proposed above. At room temperature in solution, $[Tp^*Cu(PPh_3)]$ is air-stable whereas a solution of 50% $[Tp^*Cu(C_2H_4)]$, 50% $[Tp^*Cu]_2$ became coloured almost instantaneously on exposure to air. The oxidation products included an unidentified green complex, thought possibly to be $[Tp^*Cu(CO_3)CuTp^*]$, and $[CuTp^*_2]$. Both $[Tp^*Cu(CO)]$ and $[Tp^*Cu]_2$ have intermediate air-sensitivity.

Synthesis Of $[CuTp^*_2]$ This Cu(II) sandwich complex is readily formed when air-sensitive Cu(I) pyrazolylborate complexes are exposed to atmospheric oxygen, as noted in the introduction to this section. A rational synthesis was effected by reacting $CuCl_2$ and $NaTp^*$ in CH_2Cl_2, crystallisation occurring on slow cooling of the reaction mixture. The large blue crystals thus isolated were characterised by IR spectroscopy, EI mass spectrometry and elemental analysis. The complex is described as an elongated rhombic octahedron, with the steric bulk of Tp* also causing distortions of the natural threefold symmetry of the ligands.[73] Similar complexes with bulkier pyrazolylborate ligands are very rare and this steric saturation is often cited as the cause of the low reactivity at copper of this complex.[65]

2.1.2.2 Complexes Of Bp And Bp*

Complexes of the bispyrazolylborate ligands Bp and Bp* are of interest since it is known that in certain circumstances trispyrazolylborate ligands are able to coordinate in a bidentate fashion.[57] As well as the steric information gained from comparing the catalytic activities of the two bispyrazolylborate ligands, it may also be possible to gain insight into the bonding mode of the pyrazolylborate ligand during the catalytic cycle by comparison with the trispyrazolylborates.

As with the trispyrazolylborates, the best known bispyrazolylborate ligands are the unsubstituted and dimethyl substituted versions, Bp and Bp* respectively. It was decided to concentrate on the two Cu(II) complexes [$CuBp_2$] and [$CuBp^*_2$] since they are known, although they had not yet been crystallographically characterised. No Cu(I) bispyrazolylborate complexes are known, although [$(pz)_2B(\mu\text{-}pz)_2Cu(PPh_3)_2$], which contains a tetrakispyrazolylborate ligand chelating in a bidentate fashion, has recently been synthesised and crystallographically characterised.[69]

Synthesis Of [$CuBp_2$] And [$CuBp^*_2$] Synthesis of [$CuBp^*_2$] by a modified version of Trofimenko's procedure for the preparation of transition metal complexes of substituted bispyrazolylborates was initially attempted.[75] This involved reaction of KBp* and $CuSO_4 \cdot 5H_2O$ in DMF, but no product could be isolated. Therefore, the procedure given by Trofimenko as a general preparation of transition metal Bp complexes, which involved reaction of the ligand salt with [$CuCl_2$] in aqueous solution, was used to synthesise both [$CuBp_2$] and [$CuBp^*_2$].[74] [$CuBp^*_2$], which is a salmon coloured precipitate, was poorly soluble in CH_2Cl_2, even at reflux. At room temperature it was insoluble in toluene, but at reflux it completely dissolved. Recrystallisation was thus effected by slow cooling of a refluxing toluene solution, from which large reddish brown crystals were isolated. Desolvation over the course of an hour prevented crystallographic structure determination. Purification of [$CuBp_2$] was considerably easier due to its higher solubility. The lilac precipitate was recrystallised from CH_2Cl_2 to give large dark

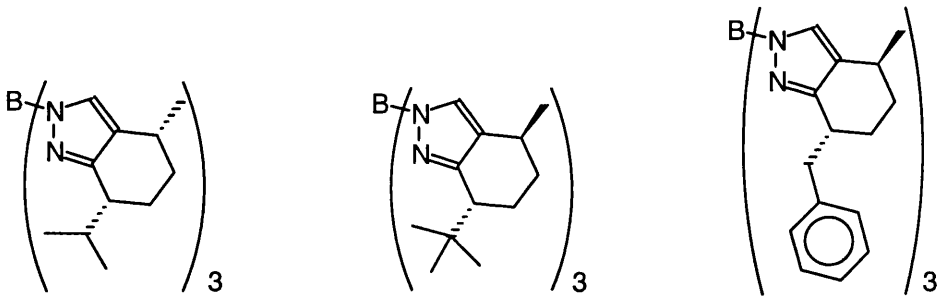
purple crystals suitable for diffraction (see Appendix 1.1 for significant crystallographic data).

The copper(II) centre has an essentially square planar geometry (sum of angles around copper is 360.0°) and the bispyrazolylborate ligands form two six-membered rings which adopt a boat conformation.

There also exist long-range intermolecular interactions between the copper centre and pyrazole hydrogens on adjacent molecules. The Cu-N distances (1.976(2) Å and 1.987(2) Å) are common for nitrogen donors to copper and in most other respects, the complex is similar to other transition metal bispyrazolylborate complexes.[13,57]

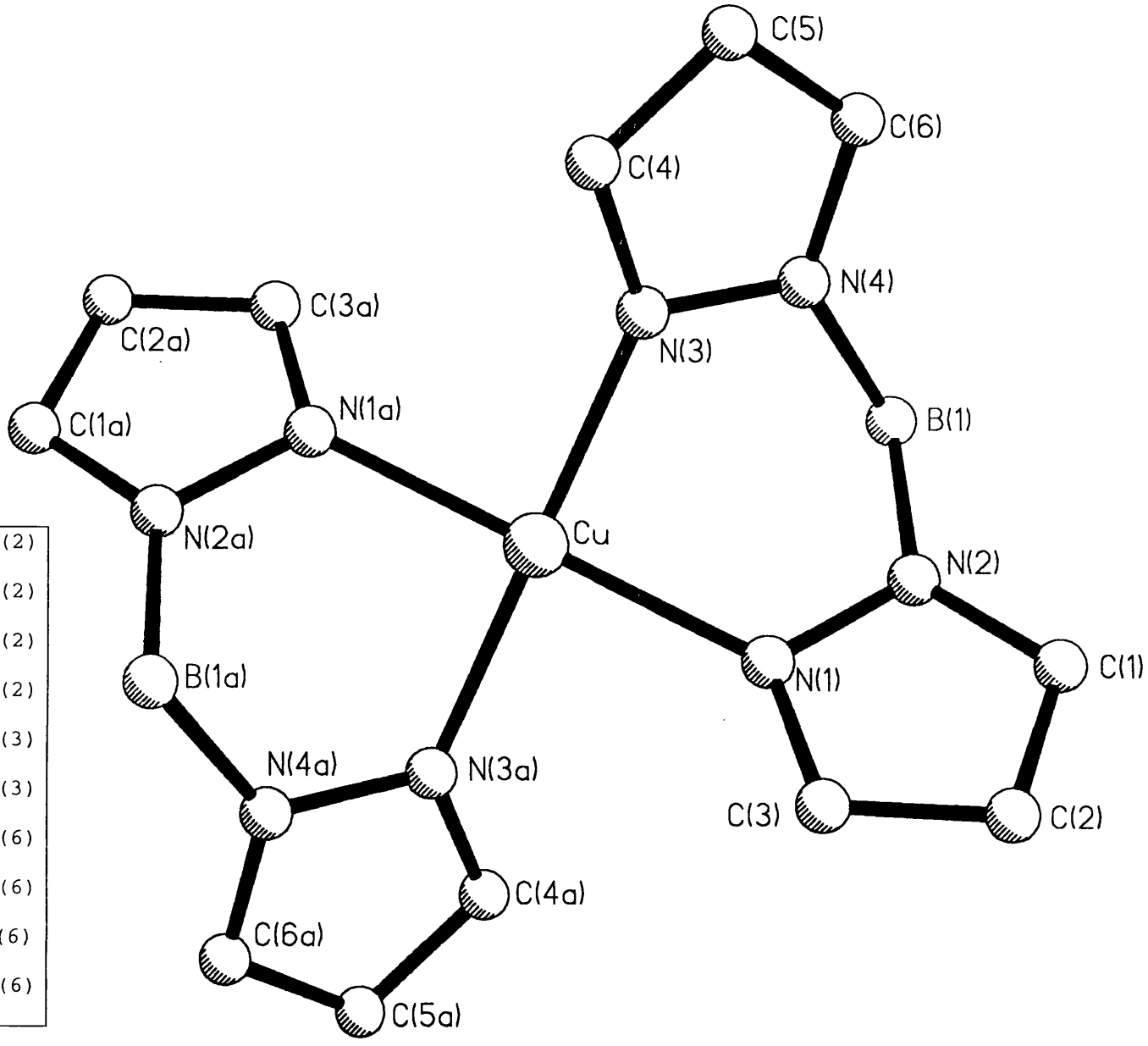
2.1.2.3 Chiral Pyrazolylborate Complexes

It has not been possible to synthesise chiral pyrazolylborate ligands where the chiral centre is on boron (i.e. a ligand with four different pyrazole groups). However, some progress has been made in attaching chiral substituents to the pyrazole rings, affording chiral C_3-symmetric ligands. Only those derived from menthone have thus far been synthesised and these form a C_3-symmetric "pocket" close to the coordinated metal atom (Figure 2.1.6).[76,77]



(a) Tp^{Menth} (b) $Tp^{Mementh}$ (c) *trans*-Tp^{pm}

Figure 2.1.6 Chiral tris(pyrazolyl)borate ligands



Cu(1)-N(3)	1.976(2)
Cu(1)-N(1)	1.987(2)
N(1)-N(2)	1.355(2)
N(3)-N(4)	1.351(2)
N(2)-B(1)	1.541(3)
N(4)-B(1)	1.552(3)
N(3)-Cu(1)-N(1)	90.93(6)
N(3)-Cu(1)-N(1)#1	89.07(6)
N(3)#1-Cu(1)-N(1)#1	90.93(6)
N(3)#1-Cu(1)-N(1)	89.07(6)

Figure 2.1.5 Crystal Structure of [$CuBp_2$] with selected bond lengths (Å) and angles (°)

Copper complexes of the chiral ligands (a) and (b) have been Cu(II) derivatives - no Cu(I) complexes have yet been prepared. However, recently, a copper(I) acetonitrile complex of the chiral ligand (c) has been synthesised and utilised in asymmetric catalytic cyclopropanation reactions.[77]

Attempted Synthesis Of [$Tp^{Menth}Cu(PPh_3)$] The synthesis of this complex was attempted using the same procedure as that used for the Tp* analogue (*vide supra*). On mixing $TlTp^{Menth}$ with CuCl and PPh_3 in CH_2Cl_2, a bright white precipitate was formed, believed to be TlCl.[78] After filtration and removal of solvent, a white solid was obtained. Whilst the mass spectrum of this product had as base peak the fragment $[CuHB(Menthpz)_2]^+$, the molecular ion was very small (~3%) and there were four unidentified peaks at higher values of m/e - at 933, 1277, 1366 and 1801. In addition, the ^1H NMR spectrum was inconclusive and no satisfactory elemental analyses were obtained. It is possible that the two ligands Tp^{Menth} and PPh_3 are too bulky to coordinate around the copper centre at the same time. However, both have C_3 symmetry allowing the possibility of the two ligands 'interlocking'. Also, in severely crowded environments, trispyrazolylborates have been known to relieve strain by coordinating in a bidentate fashion.[57] Since no pure complex was isolated from this reaction, the product was not used in aziridination reactions.

2.1.3 Summary

Several pyrazolylborate complexes of both copper(I) and copper(II) were synthesised and the relative labilities of ligands L in the complexes [Tp*CuL] (L=PPh_3, CO, Tp*Cu and C_2H_4) were compared. [Tp*Cu(PPh_3)] appeared to undergo an unusual reversible photochemical reaction, the crystals becoming orange on exposure to sunlight. The crystal structure of [$CuBp_2$] has been discussed. The synthesis of the complex [$Tp^{Menth}Cu(PPh_3)$] was unsuccessful, probably due to steric interaction between the bulky chiral pyrazolylborate and the triphenylphosphine ligand.

2.2 DITHIOCARBAMATE COMPLEXES

2.2.1 Introduction

Dithiocarbamates belong to a group of ligands called dithioacids which are formed by the action of nucleophiles X^- on carbon disulfide according to the reaction scheme shown in Figure 2.2.1(a). When the nucleophile is R_2N^-, the resultant ligand is a dithiocarbamate, shown in Figure 2.2.1(b).

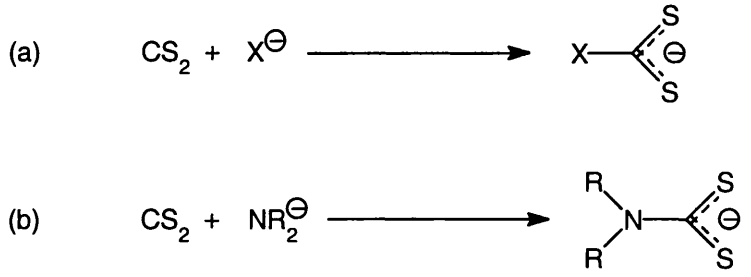


Figure 2.2.1 Formation of dithioacids and dithiocarbamates

Dithiocarbamates can be formed using an excess of the amine giving salts of general formula $[R_2NH_2]^+[R_2dtc]^-$. Alternatively, in the presence of an alkali metal hydroxide MOH, $[M]^+[R_2dtc]^-$ is produced. If secondary amines are used, however, the resultant dithiocarbamates are much more stable and thus it is this group of ligands that have been most thoroughly investigated. They do, however, readily react with acid to regenerate the amine and carbon disulfide.

The structure of the dithiocarbamates is such that three resonance structures are possible. The resonance structures shown in Figures 2.2.2(a) and (b) are equivalent and result in the overall structure shown in Figure 2.2.2(c). The alternative resonance structure shown in Figure 2.2.2(d) results in greater donation to the metal atom, and is thus more predominant in high-valent metal complexes.

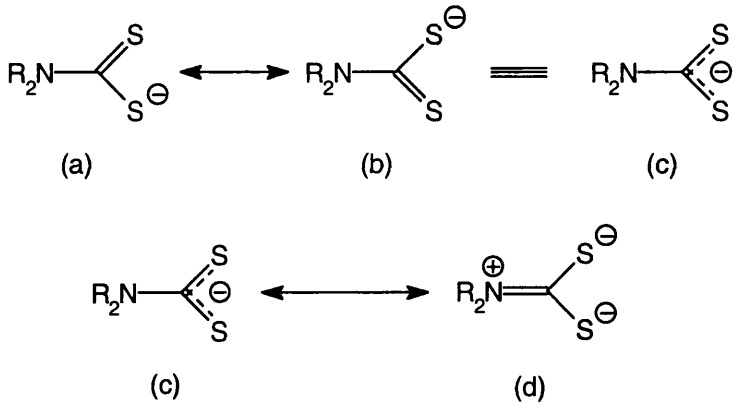


Figure 2.2.2 Resonance structures of dithiocarbamate anions

The substituents on nitrogen affect the ligand in two ways. Firstly, it has been shown that the greater the bulk of the substituent, the higher the solubility of the alkali metal salt of the ligand in organic solvents.[79] Secondly, the electron withdrawing or donating properties of the substituent affect the relative contributions of the resonance forms shown in Figure 2.2.2(c) and (d) and thus the relative ability of the ligand to stabilise low or high oxidation states. Of particular interest is pyrrole dithiocarbamate, where the tendency of the pyrrole ring to acquire aromaticity means that there is little contribution from the resonance form shown in Figure 2.2.2(d).[80]

Dithiocarbamate complexes can be prepared by two methods. If the dithiocarbamate is stable as the alkali metal salt, then this can be isolated before reaction with the appropriate transition metal salt in aqueous solution. If, however, the dithiocarbamate is unstable, the complex can also be prepared *in situ* by adding the transition metal salt to the ligand reaction mixture. In both cases, the resultant complex appears as a precipitate which can be filtered, washed and recrystallised.

Dithiocarbamate complexes of copper have been synthesised in the +1, +2 and +3 oxidation states. Studying the aziridination capabilities of analogous complexes in all three major oxidation states should allow information to be gained as to the oxidation state of the active catalyst in aziridination reactions. It was decided to begin by concentrating on copper complexes of Et_2dtc and

Me_2dtc since these were cheap and readily available, were the most widely studied and produced stable complexes. It would also be of interest to prepare a copper complex of a chiral dithiocarbamate. The simplest way to introduce chirality on a dithiocarbamate ligand that might have an effect near a coordinated metal is to introduce a substituent in the 2- position on a cyclic alkyl backbone (see Figure 2.2.3). Asymmetric induction from such a dithiocarbamate complex would depend on preventing rotation around the C-N bond, thus a high contribution of the resonance form shown in Figure 2.2.2(d) would be necessary.

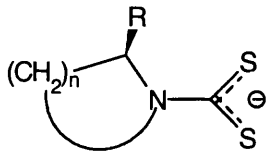


Figure 2.2.3 Dithiocarbamate ligands derived from chiral cyclic amines

Pyrrolidine (Pyd) is a simple and stable cyclic secondary amine and the simplest and cheapest chiral pyrrolidine derivative was *S*-2-pyrrolidinemethanol (Pydm). Both amines and their related dithiocarbamate structures are shown in Figure 2.2.4.

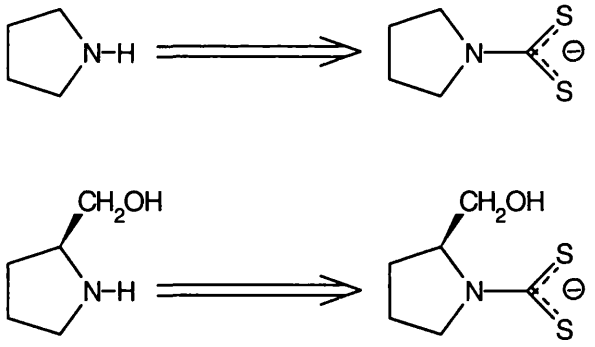


Figure 2.2.4 Formation of pyrrolidine-based dithiocarbamates

It was decided to try to synthesise a copper complex of the pyrrolidine dithiocarbamate as a preparation has been reported in the literature and it would hopefully provide an indication of any synthetic or purification problems that might be encountered whilst attempting the synthesis of the chiral derivative.[81]

2.2.2 Synthesis Of Complexes

The copper complexes reported in the literature for Me_2dtc are almost identical to those of Et_2dtc. The major difference in the physical properties of the two types of complex is that in general the complexes of Me_2dtc are less soluble than their diethyl analogues. The synthetic strategy utilised was to synthesise the Cu(I) and Cu(III) species by reducing and oxidising the previously prepared Cu(II) complex.

2.2.2.1 Copper (I) Dithiocarbamate Complexes

These complexes can be prepared in a number of different ways. Both reaction of a Cu(I) compound with the dithiocarbamate salt and oxidation of metallic copper with tetraalkyl thiuram disulfide give the desired complex.[82,83] However, a third method of preparation reported by Martin was utilised.[84]

A conproportionation reaction between the Cu(II) complex and freshly prepared copper powder in CS_2 gave, in the case of Et_2dtc, a pale yellow product which was recrystallised from CS_2/Et_2O. $[Cu(Et_2dtc)]_4$ appears to be indefinitely air stable in the solid state. The ^1H NMR spectrum shows two resonances, a triplet and a quartet, indicating that all ethyl groups are equivalent on the NMR timescale. The mass spectrum is very unusual, with the molecular ion peak at a height of about 2 % and a large proportion of the significant peaks being at a higher m/e value. The base peak occurs at 1122, which could correspond to a $[Cu_6(Et_2dtc)_5]^+$ fragment. Other peaks can also be correlated with combinations of Cu (mw = 63.5) and Et_2dtc (mw = 148), with the largest being at 1333 (57 %) which corresponds to a $[Cu_7(Et_2dtc)_6]^+$ fragment. Interestingly, there is also a peak at 356 corresponding to $[Cu(Et_2dtc)_2]^+$ which may be present as a result of atmospheric oxidation of the product, or could have been produced in the spectrometer. However, since the elemental analysis was good and the ^1H NMR spectrum only shows two resonances, it is believed that formation of these high molecular weight fragments occurs during ionisation in the spectrometer.

$[Cu(Et_2dtc)]_4$ has been shown to be tetrameric in both the solid state and in solution, with the four copper atoms arranged in a slightly distorted tetrahedron.[85] Each dithiocarbamate ligand attaches to a face of the tetrahedron with one sulfur bonding to one copper atom and the other sulfur bridging the remaining two copper atoms.[86] It is interesting to note, however, that analogous complexes with larger alkyl substituents appear to be slightly dissociated in solution.[85]

An identical protocol was used for the attempted preparation of the dimethyl analogue. However, instead of a pale yellow solution, a dark brown solution and a dark brown precipitate were obtained. After filtration no products were identified in the filtrate. This was expected since Åkerström has already reported the extreme insolubility of the product.[85] The mass spectrum and elemental analysis of the solid also gave no indication of the identity of the product. Since this complex could not be characterised, it was not used as a catalyst in aziridination reactions.

The complex $[Cu(Et_2dtc)_2]^-$, formed by reaction of $[Cu(Et_2dtc)]_4$ with $NaEt_2dtc$, would be expected to be a tetrahedral species in which the copper centre would be less hindered than in $[Cu(Et_2dtc)]_4$. Although being identified by ^1H NMR, this species could not be isolated. Oxidation to $[Cu(Et_2dtc)_2]$ occurred almost instantaneously on exposure to air and under an inert atmosphere, $[Cu(Et_2dtc)]_4$ was the major product of attempted isolation. Since $[Cu(Et_2dtc)_2]^-$ could not be isolated, the reaction mixture was used as the catalyst in aziridination and cyclopropanation reactions.

2.2.2.2 Copper(II) Dithiocarbamate Complexes

Both $[Cu(Et_2dtc)_2]$ and $[Cu(Me_2dtc)_2]$ were synthesised using the same protocol. They were prepared by reaction of the dithiocarbamate salt with $[CuCl_2]$ in aqueous solution.[87] The resultant chocolate brown precipitate was filtered, washed several times with water and then recrystallised by slow evaporation of a CH_2Cl_2 solution to give large, very dark brown, almost black crystals. If very dilute aqueous solutions are used and the precipitate is washed thoroughly,

recrystallisation is unnecessary. In the solid state, the diethyl complex can be considered to be dimeric and the dimethyl complex exists as polymeric chains of molecules linked by intermolecular Cu-S interactions.[88,89] In solution, however, both complexes are monomeric.[82] Research by Khodzhaeva and Kissin has also been published reporting that $[Cu(Et_2dtc)_2]$ shows almost instantaneous exchange with ^{35}S enriched tetraethyl thiuram disulfide, the authors proposing that exchange occurs via a six-coordinate copper species.[90]

Since salts of Pyddtc and Pydmdtc were not commercially available, their respective copper(II) complexes were prepared directly to avoid the necessity of isolation and purification of the ligand. The dithiocarbamate reaction mixture of amine, NaOH and CS_2 in MeOH was added to a dilute aqueous solution of $CuCl_2$, immediately producing a dark brown precipitate. $[Cu(Pyddtc)_2]$ was crystallised by repeated dissolution in CH_2Cl_2 and separation from an insoluble yellow solid by filtration followed by slow evaporation of solvent. Although elemental analysis and the crystalline nature of the product indicate that it was pure, the mass spectrum of $[Cu(Pyddtc)_2]$ also contained peaks at 566 (possibly corresponding to a $[Cu_2(Pyddtc)_3]^+$ fragment) and at 921 (possibly corresponding to a $[Cu_3(Pyddtc)_4]^+$ fragment). It is suggested that, as with $[Cu(Et_2dtc)]_4$ (Section 2.2.2.1), these fragments were produced in the spectrometer.

$[Cu(Pydmdtc)_2]$ could not be isolated by the same purification method, only a weak brown solution and a mixture of brown and yellow solids being obtained. Layering and vapour diffusion techniques also failed, despite a wide range of solvent combinations being utilised. Although the elemental analysis of the brown solid was not compatible with any combinations of the chiral ligand and copper, the mass spectrum gave the molecular ion, but also with another peak at 782. This second peak was consistent with a $[Cu_4(Pydmdtc)_3]^+$ fragment which could be due to impurities or could have been formed in the spectrometer (as proposed with the mass spectrum of $[Cu(Et_2dtc)]_4$, Section 2.2.2.1). Despite being unable to obtain $[Cu(Pydmdtc)_2]$ as a pure solid, it was used in

aziridination reactions since it was probable that the brown solid contained some of the desired product.

2.2.2.3 Copper(III) Dithiocarbamate Complexes

Copper(III) complexes containing a CuS_4 chromophore are generally synthesised by oxidising the relevant copper(II) complex. The synthesis of many complexes of the type $[Cu(R_2dtc)_2]^+X^-$ have been reported, with $X^- = I_3^-$, I_5^-, $[FeCl_4^-]$, ClO_4^-, BF_4^- and PF_6^-. The synthesis of both dimethyl and diethyl analogues of $[Cu(R_2dtc)_2]BF_4$ and $[Cu(R_2dtc)_2]I_3$ were attempted, but none of the products could be sufficiently purified or characterised. The BF_4^- complexes tended to decompose quickly in solution and it was believed that the I_3^- complexes were contaminated with the I_5^- analogue. Two types of copper(III) complexes could be synthesised and characterised, these being tne ClO_4^- and $[FeCl_4]^-$ complexes.

The dimethyl, diethyl and pyrrolidyl analogues of $[Cu(R_2dtc)_2][FeCl_4]$ were prepared according to the procedure described by Golding which involved the oxidation of $[Cu(Et_2dtc)_2]$ with $[FeCl_3]$ in Me_2CO/C_6H_6 solution.[87] The product was purified by layering a CH_2Cl_2 solution with toluene or C_6H_6, affording dark green needle crystals.

The dark green crystals of $[Cu(Et_2dtc)_2][FeCl_4]$ obtained by this method were suitable for diffraction and contained half a molecule of C_6H_6 per molecule of complex in the crystal lattice. Significant crystallographic data are summarised in Appendix 2. The copper centre is square planar with the ligand bite angle being approximately 79°. The $((CH_2)_2NCS_2)_2Cu$ unit is planar and the C-N distance is short at 1.296(7) Å, features that are similar to those found in other copper(III) dithiocarbamate complexes.[91-93] These facts suggest sp^2 hybridisation of each atom in the backbone and the ligand can therefore be best described by the resonance structure shown in Figure 2.2.2(d) (*vide supra*). There exist long-range intermolecular Cu-S contacts leading to infinite polymeric chains of copper dithiocarbamate units.

Cu(1)-S(1)	2.2067(14)
Cu(1)-S(2)	2.210(2)
N(1)-C(1)	1.296(7)
S(1)-C(1)	1.715(6)
S(2)-C(1)	1.729(6)
Cu(2)-S(4)	2.2027(14)
Cu(2)-S(3)	2.213(2)
N(2)-C(6)	1.302(7)
S(3)-C(6)	1.732(6)
S(4)-C(6)	1.724(6)
S(1)-Cu(1)-S(2)	78.77(5)
S(4)-Cu(2)-S(3)	78.83(6)
S(1)-C(1)-S(2)	108.9(3)
S(4)-C(6)-S(3)	108.4(3)

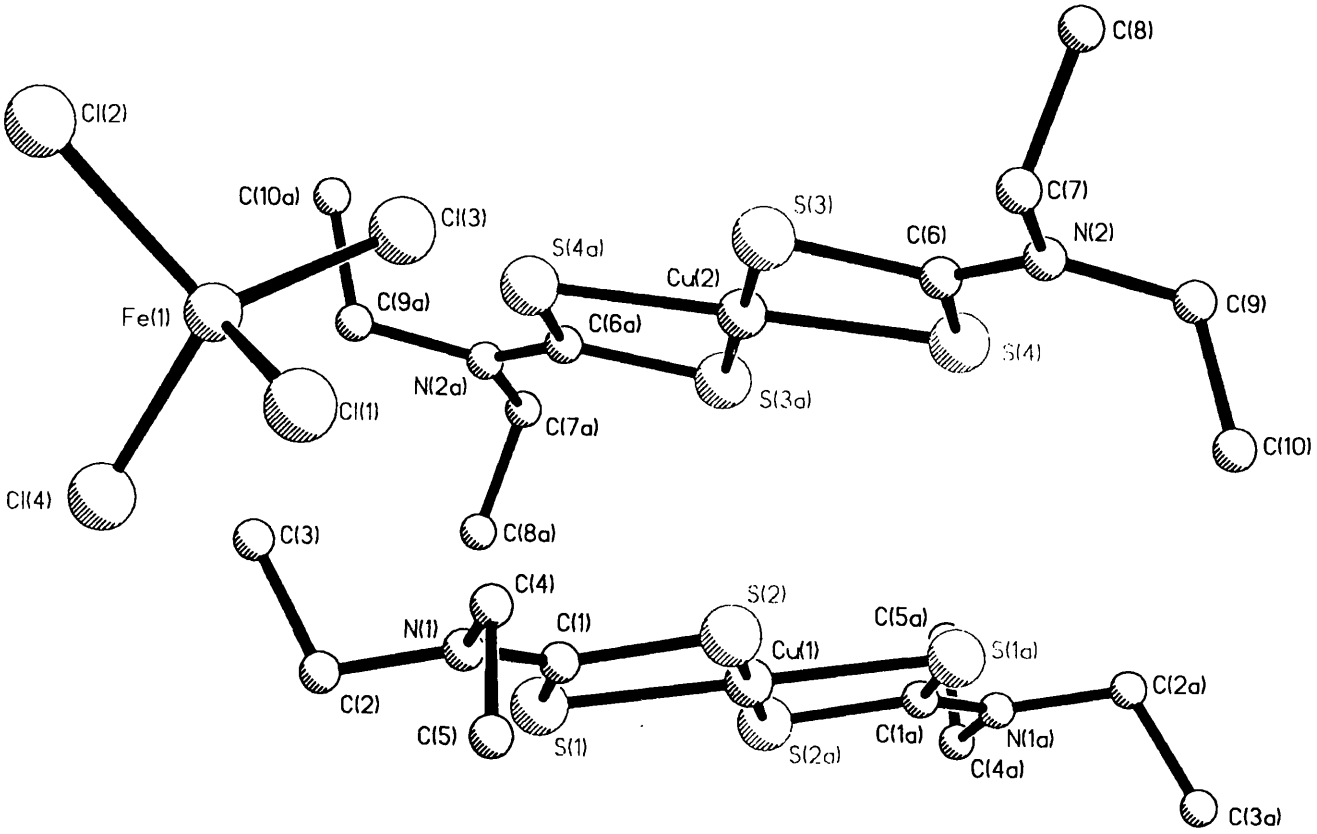


Figure 2.2.5 Crystal Structure of $[Cu(Et_2dtc)_2][FeCl_4]\cdot\frac{1}{2}C_6H_6$ with selected bond lengths (Å) and angles (°)

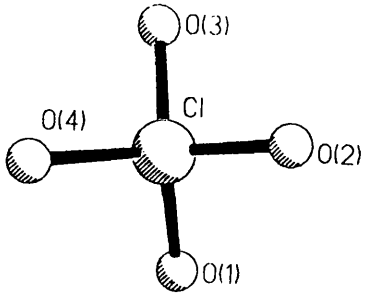
Although there is an interaction between the copper atoms of individual molecules, the $[FeCl_4]^-$ anion is discrete and does not show any interaction with the copper dithiocarbamate unit (see Figure 2.2.5).

The complexes $[Cu(R_2dtc)_2]ClO_4$ (R = Et and Me) were both prepared according to Golding's procedure which involved oxidation of $[Cu(R_2dtc)_2]$ in $CHCl_3$ solution with $[Cu(ClO_4)_2]\cdot 6H_2O$ in Me_2CO solution.[87] Isolation, however, was achieved by two different methods. To isolate $[Cu(Et_2dtc)_2]ClO_4$ the reaction mixture was filtered, the filtrate concentrated and then layered with C_6H_6 giving dark green needle crystals. Isolation of $[Cu(Me_2dtc)_2]ClO_4$ was achieved by removal of solvent under vacuum, dissolution in CH_2Cl_2 followed by filtration, crystals being obtained by slow cooling and evaporation of solvent. The two complexes were sensitive to heat and friction, both causing detonation. The ^1H NMR spectrum of $[Cu(Et_2dtc)_2]ClO_4$ showed two resonances as expected, but the resonance for the CH_2 groups was very broad, indicating either a fluxional system or a certain amount of paramagnetism at the copper centre. Indeed magnetic measurements on this complex by Golding *et al.* have given a magnetic moment of 0.42 BM,[87] similar to the 0.5 BM reported for $[Br_2Cu(^nBu_2dtc)]$.[94] This effect has been attributed to the existence of stable oxidised forms of the dithiocarbamate ligand, causing the actual copper oxidation state to be slightly lower than formally proposed.[95]

The crystals of $[Cu(Me_2dtc)_2][ClO_4]$ obtained were suitable for diffraction. Significant crystallographic data are summarised in Appendix 3.

The copper adopts a square planar geometry with respect to the sulfur atoms. However, there is also a long range (3.649 Å) intermolecular Cu-S interaction and the sixth coordination site is occupied by an oxygen atom from the perchlorate anion to give an overall distorted octahedral geometry. As with the $[FeCl_4]^-$ analogue described above, the $((CH_3)_2NCS_2)_2Cu$ unit is planar and the C-N bond length is 1.320(5) Å, both indicating sp^2 hybridisation and the dominance of the resonance structure shown in Figure 2.2.2(d).

Cu(1)-S(1)	2.231(2)
Cu(1)-S(2)	2.2308(14)
Cu(1)-S(4)	2.2372(14)
Cu(1)-S(3)	2.237(2)
C(1)-N(1)	1.320(5)
C(4)-N(2)	1.327(5)
S(1)-Cu(1)-S(2)	79.03(6)
S(4)-Cu(1)-S(3)	79.01(6)
S(1)-C(1)-S(2)	109.3(2)
S(3)-C(4)-S(4)	109.8(2)



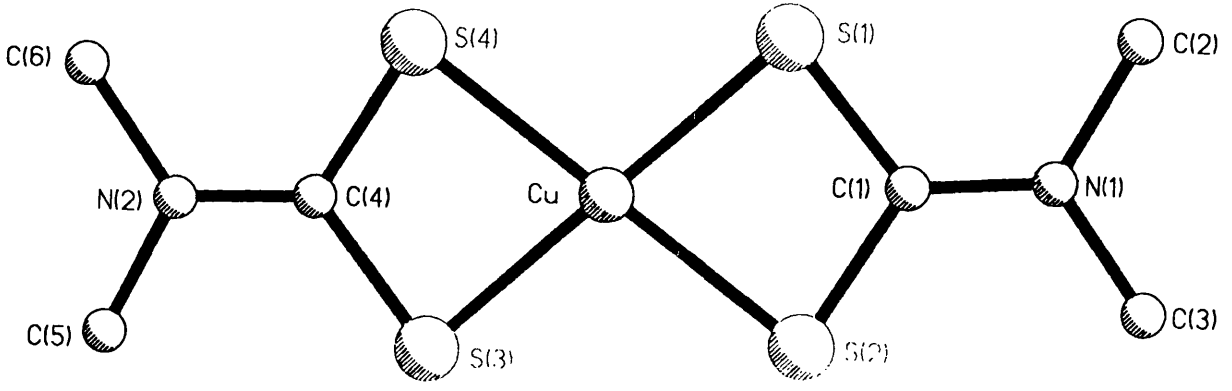


Figure 2.2.6 Crystal Structure of $[Cu(Et_2dtc)_2]ClO_4$ with selected bond lengths (Å) and angles (°)

These structural aspects of two different copper(III) dithiocarbamate complexes indicate that the environment at the copper centre, both steric and electronic, effectively remains independent of the anion.

2.2.3 Summary

Diethyl dithiocarbamate complexes of all three major oxidation states of copper have been synthesised and characterised and the crystal structure of $[Cu(Et_2dtc)_2][FeCl_4]$ was discussed. Copper(II) and copper(III) complexes of dimethyl dithiocarbamate have been synthesised and the crystal structure of $[Cu(Me_2dtc)_2][ClO_4]$ was discussed. The synthesis of complexes of dithiocarbamate ligands derived from pyrrolidine and *S*-2-pyrrolidinemethanol was attempted, although only $[Cu(Pyddtc)_2]$ and $[Cu(Pyddtc)_2][FeCl_4]$ could be successfully characterised. Attempts to synthesise copper(III) dithiocarbamate complexes with I_3^- and BF_4^- anions were unsuccessful.

2.3 PRODUCTS OF NITRENE INSERTION

2.3.1 Introduction

Although migratory insertion has been known to take place in several catalytic systems, including the Monsanto process discussed in Section 1.1.1, insertion of a functional group into a bond between a metal and a spectator ligand is less common. The insertion of a carbene unit into a metal porphyrin bond was reported to occur upon one-electron oxidation of $[Fe^{II}(TPP)(C{=}C(C_6H_4Cl)_2)]$ (TPP is the dianion of *meso*-tetraphenylporphyrin).[96] Insertion of a carbene into ruthenium-sulfur and ruthenium-oxygen bonds has been shown to occur in several cases [97] and more recently, insertion of a carbene into a ruthenium-dithiocarbamate bond has been reported in the reaction between $[Ru(\equiv CC_6H_4OMe\text{-}4)Cl(CO)(PPh_3)_2]$ and $[NH_4][S_2C^nC_4H_8]$.[98] In addition, a tosyl nitrene moiety has been shown by Mansuy to insert into a metal-nitrogen bond of an iron porphyrin complex.[99] This reaction is particularly interesting in that the insertion takes place during the aziridination of olefins by PhI=NTos and iron(III) tetra-arylporphyrin complexes. Mansuy also proposes the involvement of an

iron(V) nitrene complex as an intermediate in the aziridination cycle (see Figure 2.3.1). During the aziridination, all of the starting porphyrin complex was converted to the insertion product and the insertion was also shown to take place in the absence of olefinic substrate.

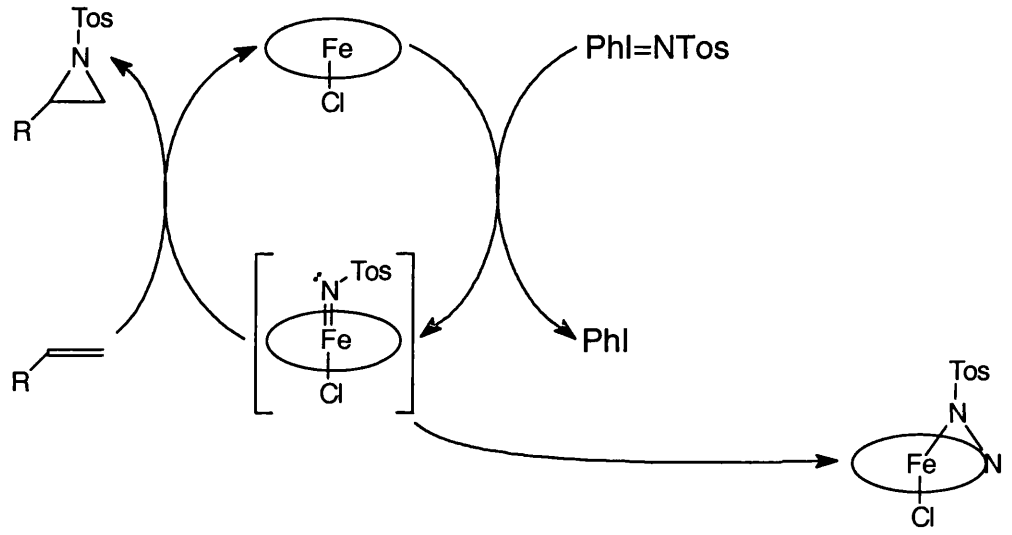


Figure 2.3.1 Iron-porphyrin catalysed aziridination

Although the nitrene moiety did not show any evidence of transfer to olefins, the insertion product was shown to be an active aziridination catalyst.[99]

Our research into copper-catalysed aziridination has shown a similar insertion taking place during aziridination reactions catalysed by copper dithiocarbamate complexes. For a complete description of aziridination reactions performed, see Chapter 3.

2.3.2 Insertion Into Copper Dimethyl Dithiocarbamate Complexes

An aziridination reaction involving styrene, PhI=NTos and $[Cu(Me_2dtc)_2][FeCl_4]$ was performed and after reaction was complete and the yield of aziridine had been calculated, the reaction mixture was left for several days in order for the solvent to evaporate. The mass spectrum of the green crystals thus formed gave a peak at a molecular weight of 980 which corresponds to combination of a $[Cu(Me_2dtc)_2]$ unit with four equivalents of NTos. The elemental analysis

supported this proposed stoichiometry. The structure of this new complex was determined crystallographically (see Appendix 4 for a summary of significant crystallographic data) and showed that the four nitrene groups had inserted into the four Cu-S bonds of the catalyst forming a novel tetra-amido complex [$Cu(TosNSC(NMe_2)SNTos)_2$] (see Figure 2.3.2).[100] This complex was presumed to have formed by interaction of a copper nitrene species with the dithiocarbamate ligand in the absence of any olefin with which to form aziridines.

The copper is in the +2 oxidation state, indicating a reduction of the initial copper(III) complex during the aziridination reaction which is unexpected since PhI=NTos is a two-electron oxidant. This suggests that there must be a mechanism for reduction of the copper(III) species that is available even in the presence of an oxidising agent, a topic which will be discussed further in Section 3.1.2.2. The complex has overall D_{2d} symmetry with the copper centre having a compressed tetrahedral geometry and the six-membered ring, formed by each ligand and the metal, is severely puckered.

As with dithiocarbamate ligands, it is possible to envisage three resonance forms contributing towards the overall structure (see Figure 2.3.3).

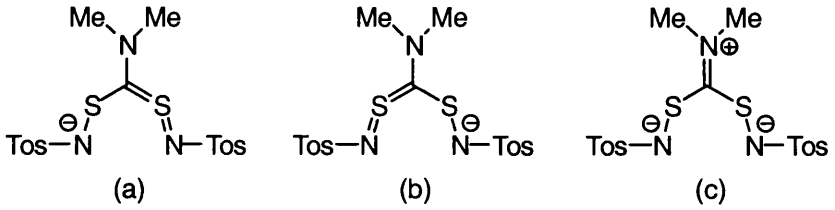


Figure 2.3.3 Resonance structures of novel diamido ligands

Cu(1)-N(1)	2.005(4)
Cu(1)-N(2)	2.016(4)
S(3)-N(1)	1.687(4)
S(4)-N(2)	1.694(4)
S(3)-C(30)	1.759(5)
S(4)-C(30)	1.781(5)
N(3)-C(30)	1.330(6)
N(1)-Cu(1)-N(2)	87.4(2)
S(1)-N(1)-Cu(1)	119.6(2)
S(1)-N(1)-S(3)	115.4(2)
S(3)-N(1)-Cu(1)	124.3(2)
S(3)-C(30)-S(4)	119.3(3)

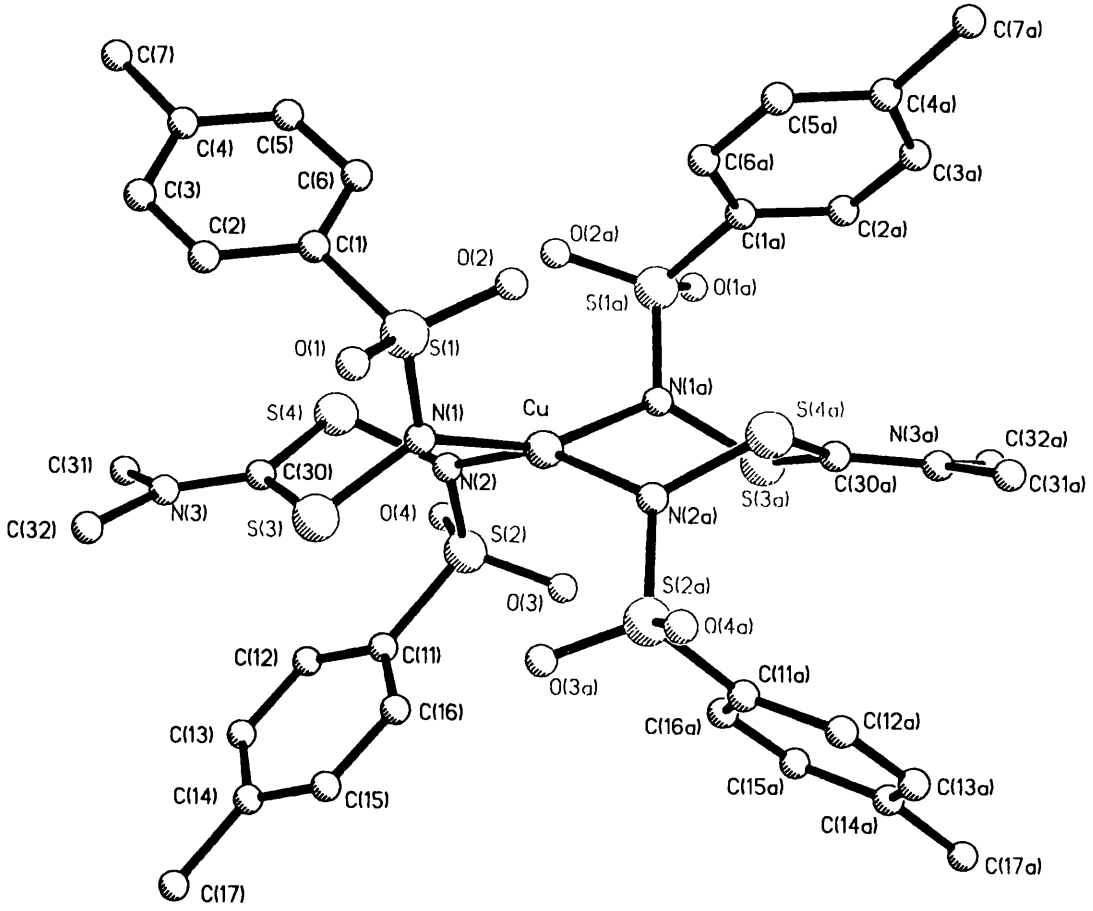


Figure 2.3.2 Crystal Structure of $[Cu(TosNSC(NMe_2)SNTos)_2]\cdot 2CH_2Cl_2$ with selected bond lengths (Å) and angles (°)

That resonance form (c) provides the major contribution to ligand structure is shown by the dithiocarbamate unit being planar, with the C-N bond length being 1.330(6) Å. The most accurate description of the structure is therefore given by the zwitterionic formulation shown in Figure 2.3.4.

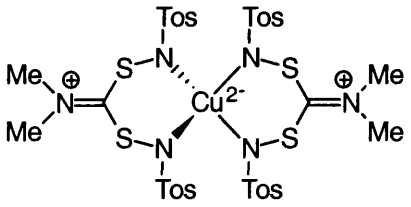


Figure 2.3.4 Structure of $[Cu(TosNSC(NMe_2)SNTos)_2]$

In addition, the Cu-N bond lengths (2.016(4) Å and 2.005(4) Å) are similar to those found in other copper amide complexes [101] and the C-S bond lengths, at 1.759(5) Å and 1.781(5) Å, are somewhat longer than those in both $[Cu(Me_2dtc)_2]$ (1.716(8) Å and 1.726(9) Å) [89] and $[Cu(Et_2dtc)_2]$ (1.711(8) Å, 1.713(8) Å, 1.708(7) Å and 1.736(7) Å).[88]

Although formed during an aziridination reaction, $[Cu(TosNSC(NMe_2)SNTos)_2]$ results from reaction of the copper dithiocarbamate centre with nitrene. Thus the formation of $[Cu(TosNSC(NMe_2)SNTos)_2]$ in the absence of olefin was investigated. Since four equivalents of nitrene are required to form $[Cu(TosNSC(NMe_2)SNTos)_2]$, reaction between $[Cu(Me_2dtc)_2][FeCl_4]$ and four equivalents of PhI=NTos in CH_2Cl_2 was investigated. On addition of PhI=NTos to the copper complex under N_2, the green solution became dark red and all the insoluble PhI=NTos appeared to react. This red solution could indicate the formation of a reactive intermediate, possibly a copper(III) imido species. However, on exposure to air, the red solution turned green. After removal of solvent under vacuum, extraction into $CHCl_3$ and slow evaporation, green and colourless crystals were obtained. The colourless crystals were identified as $TosNH_2$ by ^1H NMR spectroscopy, whilst the elemental analysis and mass spectrum of the green crystals suggested the presence of the starting material $[Cu(Me_2dtc)_2][FeCl_4]$. A reaction involving ten equivalents of PhI=NTos, the

amount used during aziridination reactions, was also performed. The presence of $[Cu(TosNSC(NMe_2)SNTos)_2]$ was detected by mass spectrometry, although none could be isolated.

Since the insertion of NTos into copper dithiocarbamate complexes affords a novel class of tetra-amido ligands, the scope of the reaction was investigated further. Initially, other complexes based on the dimethyl dithiocarbamate ligand were screened. Aziridination reactions using $[Cu(Me_2dtc)_2][ClO_4]$ showed no sign of insertion taking place and thus the direct reaction between the catalyst and PhI=NTos was not investigated. However, reaction of four equivalents of PhI=NTos with $[Cu(Me_2dtc)_2]$ afforded a good yield of $[Cu(TosNSC(NMe_2)SNTos)_2]$ which was characterised by mass spectrometry and elemental analysis.

2.3.3 Insertion Into Copper Diethyl Dithiocarbamate Complexes

$[Cu(Et_2dtc)_2]$ was reacted with several different quantities of PhI=NTos. With only two equivalents of PhI=NTos, a green solution was obtained, but no product could be isolated, presumably due to the low concentration of $[Cu(TosNSC(NEt_2)SNTos)_2]$ in the mother liquor. Reaction with ten equivalents of PhI=NTos again led to a green CH_2Cl_2 solution, but on attempted crystallisation by layering with toluene, the solution became brown and a brown, unidentified precipitate was formed. The lack of isolated product was presumed to be due to decomposition in the presence of excess PhI=NTos. As with $[Cu(Me_2dtc)_2][FeCl_4]$, reaction with four equivalents of PhI=NTos gave the most promising results. Reaction overnight followed by concentration of the solution and layering with toluene afforded both green and dark brown crystals. The green crystals were characterised by mass spectrometry and elemental analysis and were identified as the tetra-amido complex $[Cu(TosNSC(NEt_2)SNTos)_2]$. However, the crystals obtained were unsuitable for diffraction, being either too small or being multiple crystals. An interesting feature of the IR spectrum of $[Cu(TosNSC(NEt_2)SNTos)_2]$ is that the absorption assigned to the C=N stretching frequency was observed at 1532 cm^{-1}. This is noticeably higher in frequency

than the absorption in the related copper(II) dithiocarbamate complex $[Cu(Et_2dtc)_2]$ (1505 cm^{-1}), whereas the crystal structure of $[Cu(TosNSC(NMe_2)SNTos)_2]$ suggests that the C-N distances of the two complexes are likely to be comparable (1.33 Å for $[Cu(TosNSC(NMe_2)SNTos)_2]$ and 1.31 Å for $[Cu(Me_2dtc)_2]$).[89]

The mass spectrum of the dark brown crystals suggested a product derived from reaction of $[Cu(Et_2dtc)_2]$ with two equivalents of PhI=NTos. Indeed, the IR spectrum of the brown crystals was very similar to that of $[Cu(TosNSC(NEt_2)SNTos)_2]$, with the exception of the C=N stretch being shifted to 1518 cm^{-1}, almost exactly halfway between the C=N stretches of $[Cu(Et_2dtc)_2]$ and $[Cu(TosNSC(NEt_2)SNTos)_2]$ (1505 cm^{-1} and 1532 cm^{-1} respectively). The elemental analysis of the brown crystals, which slowly desolvated over the course of one week, also suggested a complex combining a $[Cu(Et_2dtc)_2]$ unit with two equivalents of NTos. However, there are three possible structures for this complex, assuming that it is derived from insertion of NTos into Cu-S bonds (see Figure 2.3.5). The *cis* isomer (a) would result if initial insertion of NTos resulted in a deactivation of the Cu-S bond *trans* to the one already reacted. If insertion resulted in activation of the *trans* Cu-S bond, the *trans* isomer (b) would be formed. Steric factors would also favour the formation of the *trans* isomer. The structure derived from insertion of both NTos groups into the same dithiocarbamate ligand (c) was discounted since if that were the case, the IR spectrum would be expected to show two distinct C=N stretches.

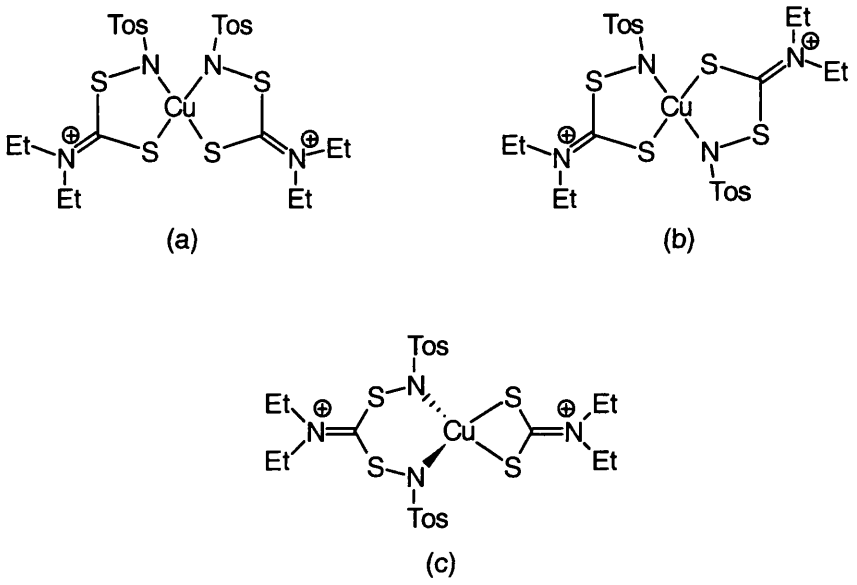


Figure 2.3.5 Possible structures resulting from two NTos insertions

A crystal structure determination (see Figure 2.3.6) on the brown crystals showed that the complex was the *trans* isomer described by Figure 2.3.5(b), with one molecule of CH_2Cl_2 per molecule of copper complex in the unit cell (significant crystallographic data are summarised in Appendix 5).[102] The geometry around copper can best be described as a compressed tetrahedron, with the two tosyl groups positioned on the same face of the copper dithiocarbamate plane. The dichloromethane molecule resides in the cleft between the two dithiocarbamate units.

As with $[Cu(TosNSC(NMe_2)SNTos)_2]$, the dithiocarbamate unit is planar and the C-N bond length is short at 1.310(5) Å, indicating the dominance of the contribution from the resonance structure shown in Figure 2.3.7(a) towards the ligand structure.

Cu(1)-N(1)	1.949(3)
Cu(1)-S(3)	2.2969(11)
S(2)-N(1)	1.680(3)
S(2)-C(8)	1.768(4)
S(3)-C(8)	1.691(4)
N(2)-C(8)	1.313(5)
N(1)-Cu(1)-S(3)	88.97 (9)
S(2)-N(1)-Cu(1)	116.72(17)
N(1)-S(2)-C(8)	101.93(17)
S(3)-C(8)-S(2)	119.3 (2)
C(8)-S(3)-Cu(1)	101.31(14)

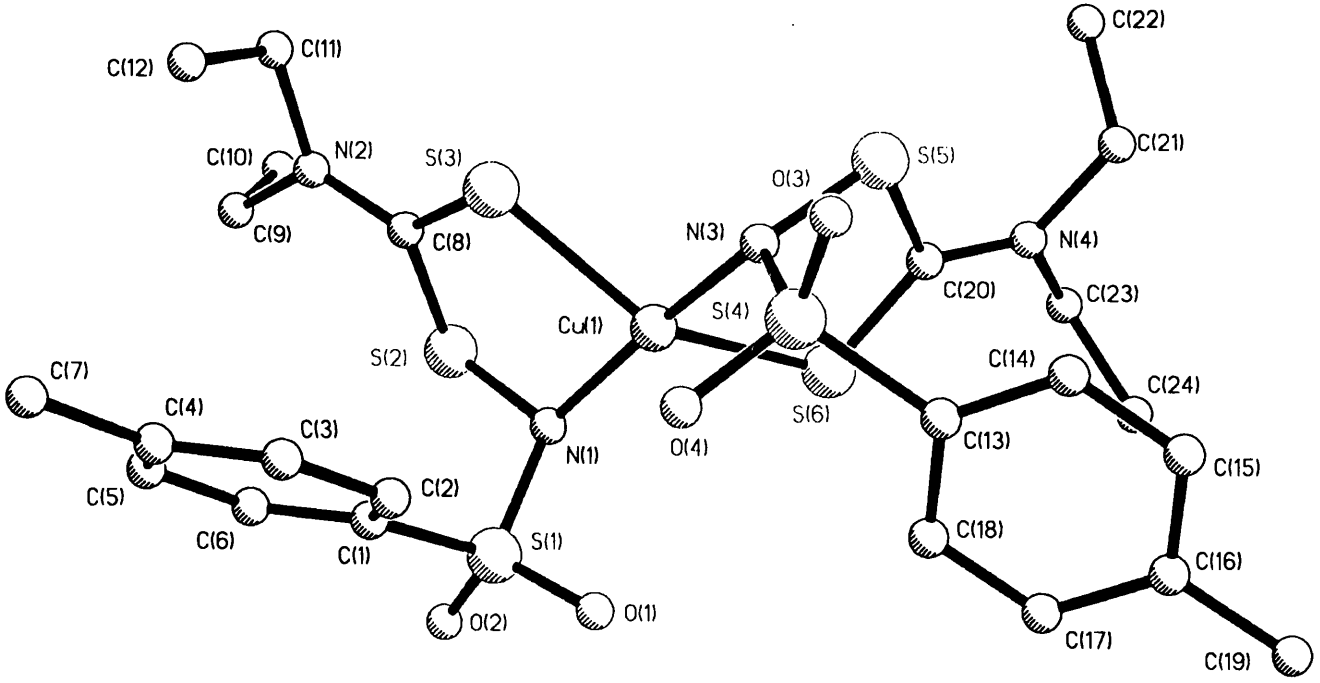


Figure 2.3.6 Crystal Structure of $[Cu(TosNSC(NEt_2)S)_2]\cdot CH_2Cl_2$ with selected bond lengths (Å) and angles (°)

Figure 2.3.7 Resonance structures of amido ligands

The Cu-N bond lengths (1.949(3) Å and 1.954(3) Å) are slightly shorter than those in $[Cu(TosNSC(NMe_2)SNTos)_2]$ (*vide supra*), whilst the Cu-S bond lengths remain similar to those in $[Cu(Et_2dtc)_2]$.[88] In addition, the dithiocarbamate S-N bond lengths (1.680(3) Å and 1.670(3) Å) are considerably shorter than those found in $[Cu(TosNSC(NMe_2)SNTos)_2]$.

$[Cu(Et_2dtc)]_4$ was also reacted with four equivalents of PhI=NTos. After a colour change from yellow to dark brown to green, 6% yield of $[Cu(TosNSC(NEt_2)SNTos)_2]$ was isolated upon recrystallisation from CH_2Cl_2 and toluene.

The formation of both novel ligands, $[TosNSC(NEt_2)S]$ and $[TosNSC(NEt_2)SNTos]$, appears to occur via a stepwise process, with initial insertion of one equivalent of NTos activating the *trans* Cu-S bond towards further insertion. However, the reaction of the second equivalent of NTos occurs so readily that the presence of a product of one insertion of NTos cannot be detected in the mass spectra of any of the reaction mixtures discussed thus far.

2.3.4 Insertion Into Other Dithiocarbamate Compiexes

In addition to those already discussed, three other copper dithiocarbamate complexes were reacted with PhI=NTos in order to generate insertion products. Although signals corresponding to both the amido and diamido products of insertion into $[Cu(Me,^nHexdtc)_2]$ were identified in the mass spectrum of a reaction with four equivalents of PhI=NTos, neither product could be isolated. In

addition, neither $[Cu(Pyddtc)_2]$ nor $[Cu(Pydmdtc)_2]$ showed any evidence of insertion in the mass spectra of their reactions with five equivalents of PhI=NTos.

It was decided to investigate the generality of this insertion reaction with respect to other transition metal dithiocarbamate complexes. The complexes $[MCl_2 \cdot 6H_2O]$ (M = Co, Ni) were therefore reacted with two equivalents of $NaEt_2dtc \cdot 3H_2O$ in aqueous solution, in both cases affording a green precipitate. In the nickel reaction, filtration and recrystallisation gave pure crystalline $[Ni(Et_2dtc)_2]$. However, the desired cobalt(II) dithiocarbamate complex is highly air-sensitive and oxidises readily to the related cobalt(III) complex. Thus, pure crystalline $[Co(Et_2dtc)_3]$ was obtained after filtration and recrystallisation of the crude reaction mixture.

As with the copper dithiocarbamate complexes, reaction of $[Ni(Et_2dtc)_2]$ with ten equivalents of PhI=NTos gave no evidence of insertion in the mass spectrum of the reaction mixture. However, reaction with both six and four equivalents of PhI=NTos allowed the isolation, by slow evaporation of a CH_2Cl_2 solution, of blue crystals of $[Ni(TosNSC(NEt_2)S)_2]$ (see Figure 2.3.8). This complex was characterised crystallographically, as well as by IR and ^1H NMR spectroscopy, mass spectrometry and elemental analysis (significant crystallographic data are summarised in Appendix 6).[102]

The geometry, as expected for a nickel(II) complex, is square planar, with the sum of angles around nickel being 362.0°. The Ni-S bond lengths, at 1.897(4) Å and 1.904(4) Å, and the Ni-N bond lengths, at 2.1977(15) Å and 2.2183(15) Å, are shorter than the related bonds in $[Cu(TosNSC(NEt_2)S)_2]$, a trend also seen in the dithiocarbamate complexes of the two metals.[81,88,89,103,104] In contrast to $[Cu(TosNSC(NEt_2)S)_2]$, however, the Ni-S bonds are shorter than those found in $[Ni(Et_2dtc)_2]$ (2.202(1) Å and 2.196(1) Å).[103] In all other structural aspects, the nickel complex is similar to its copper analogue, including the dithiocarbamate C-N bond length. The C=N stretch in the IR spectrum, at 1520 cm^{-1} is also similar to that of the copper analogue.

Ni(1)-N(1)	1.897(4)
Ni(1)-S(3)	2.2183(15)
S(2)-C(8)	1.764(6)
S(3)-C(8)	1.703(5)
N(2)-C(8)	1.318(7)
N(1)-Ni(1)-S(3)	89.33(14)
S(2)-N(1)-Ni(1)	115.4(3)
N(1)-S(2)-C(8)	100.1(2)
S(3)-C(8)-S(2)	118.2(3)
C(8)-S(3)-Ni(1)	100.77(19)

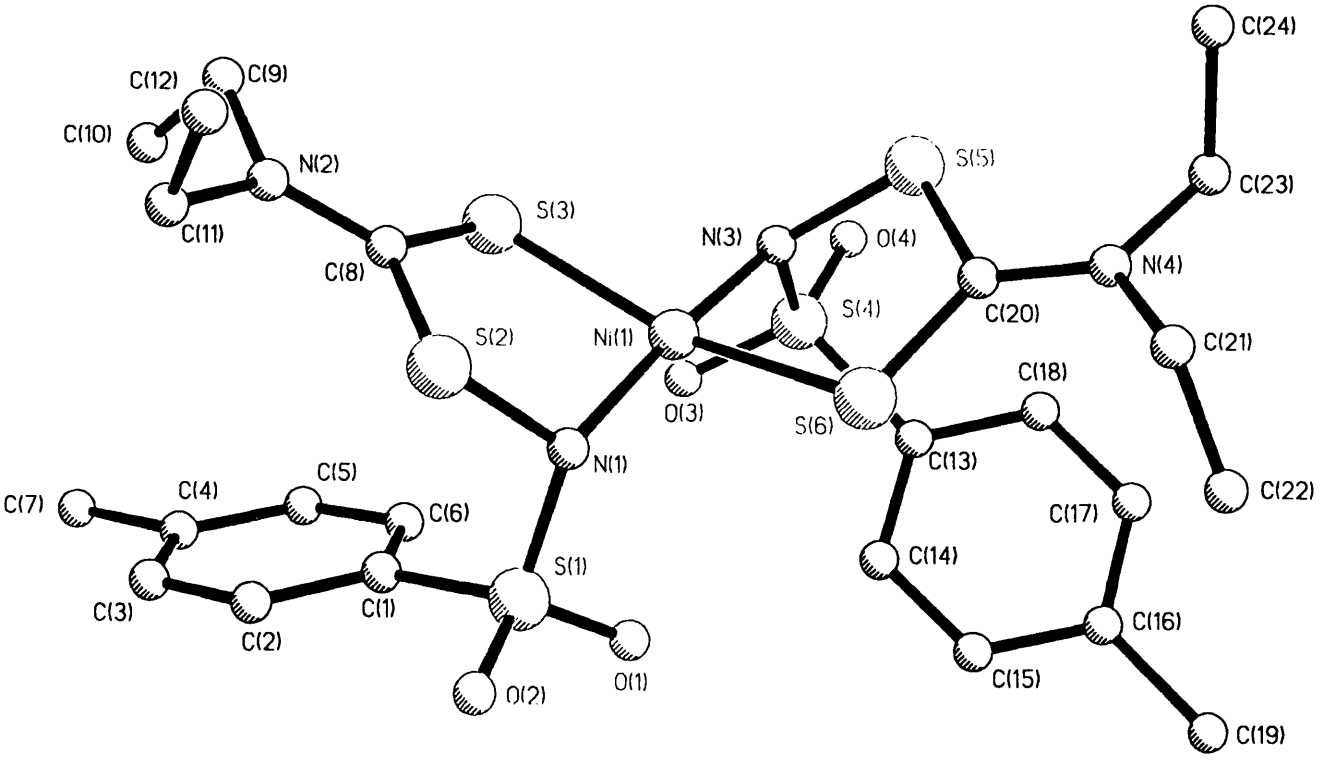


Figure 2.3.8 Crystal Structure of $[Ni(TosNSC(NEt_2)S)_2]\cdot CHCl_3$ with selected bond lengths (Å) and angles (°)

Direct reaction of $[Co(Et_2dtc)_3]$ with PhI=NTos did not result in formation of any insertion product, independent of the excess of PhI=NTos utilised. However, aziridination reactions (see Section 3.1.2) involving $[Co(Et_2dtc)_3]$ consistently produced a pale blue solid characterised by IR spectroscopy, mass spectrometry and elemental analysis as $[Co(TosNSC(NEt_2)SNTos)_2]$. This product is a cobalt(II) complex, indicating that reduction from cobalt(III) has taken place at some point during the aziridination reaction, despite the presence of PhI=NTos which is expected to be a strong oxidant. Slow evaporation of a CH_2Cl_2 solution of the product afforded blue crystals suitable for diffraction (see Appendix 7 for a summary of significant crystallographic data).[102]

By contrast with the copper analogue $[Cu(TosNSC(NEt_2)SNTos)_2]$, no solvent appears in the crystal lattice of $[Co(TosNSC(NEt_2)SNTos)_2]$. However, this new cobalt(II) complex appears to be similar in many respects to the copper(II) analogue, all of the bond lengths being slightly shorter. The dithiocarbamate C-N distances are very short at 1.311(6) Å and 1.310(6) Å, although the C=N stretch, at 1527 cm^{-1}, is actually lower in energy than in the copper complex (C-N 1.330(6) Å and C=N 1532 cm^{-1}, *vide supra*). Another similarity with $[Cu(TosNSC(NEt_2)SNTos)_2]$ is that the dithiocarbamate unit of $[Co(TosNSC(NEt_2)SNTos)_2]$ is planar, as are the inserted nitrogens (sum of angles are 358.3° and 360.0°).

Aziridination reactions (see Section 3.1.2) involving the dithiocarbamate complexes $[Cd(Me,^nPrdtc)_2]$ and $[Zn(Me,C_{18}H_{37}dtc)_2]$ are of particular interest since the mass spectra of both reaction mixtures showed evidence for the presence of a product formed by insertion of three equivalents of NTos. This appears to support the proposal for a stepwise insertion process, although no firmer evidence could be obtained and no product could be isolated.

Co(1)-N(1)	2.003(4)
Co(1)-N(2)	1.985(4)
S(3)-N(1)	1.673(4)
S(3)-C(15)	1.751(6)
N(3)-C(15)	1.311(6)
N(2)-Co(1)-N(1)	92.89(16)
S(3)-N(1)-Co(1)	121.1(2)
N(1)-S(3)-C(15)	105.4(2)
S(4)-C(15)-S(3)	120.3(3)
N(2)-S(4)-C(15)	104.4(2)
S(4)-N(2)-Co(1)	118.3(2)

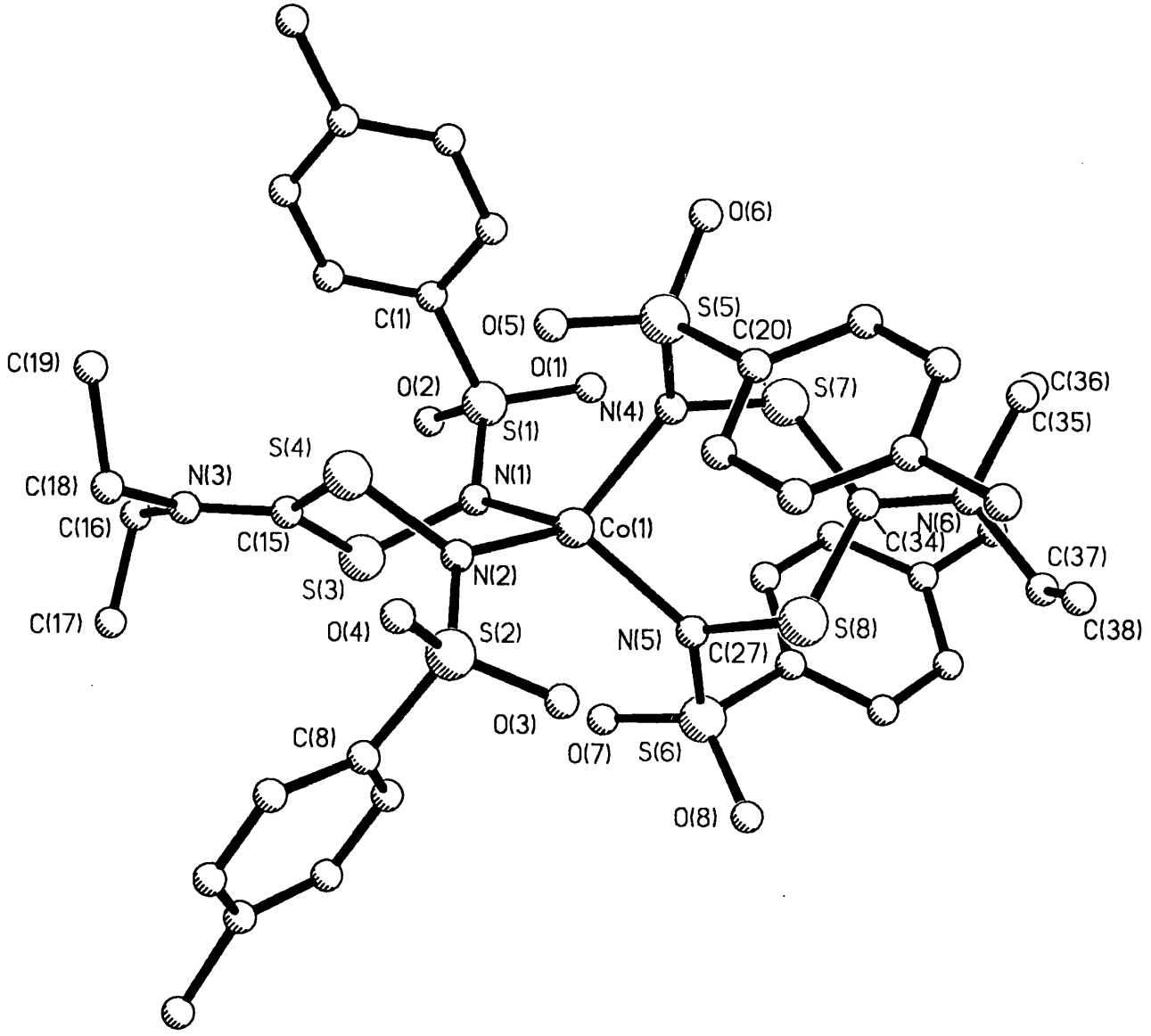


Figure 2.3.9 Crystal Structure of [Co(TosNSC(NEt$_2$)SNTos)$_2$] with selected bond lengths (Å) and angles (°)

2.3.5 Other Insertion Reactions

Whilst PhI=NTos has been shown to insert an NTos group readily into a wide variety of dithiocarbamate complexes, attempts at insertion using other reagents were not so successful.[105]

Chloramine-T (TosNClNa) has been shown to be a proficient source of nitrene in aziridination reactions (see Section 3.1.5). Equally, in direct reactions with copper dimethyl dithiocarbamate complexes, $[Cu(TosNSC(NMe_2)SNTos)_2]$ was produced, although the yield could not be calculated since the product was difficult to isolate from the reaction mixture. In addition, no evidence for the presence of the amido complex $[Cu(TosNSC(NEt_2)S)_2]$ was detected in the mass spectra of the reactions.

As these novel complexes were first detected in aziridination reaction mixtures, it was thought that the related processes of cyclopropanation and epoxidation might yield similar insertion products (see Figure 2.3.10).

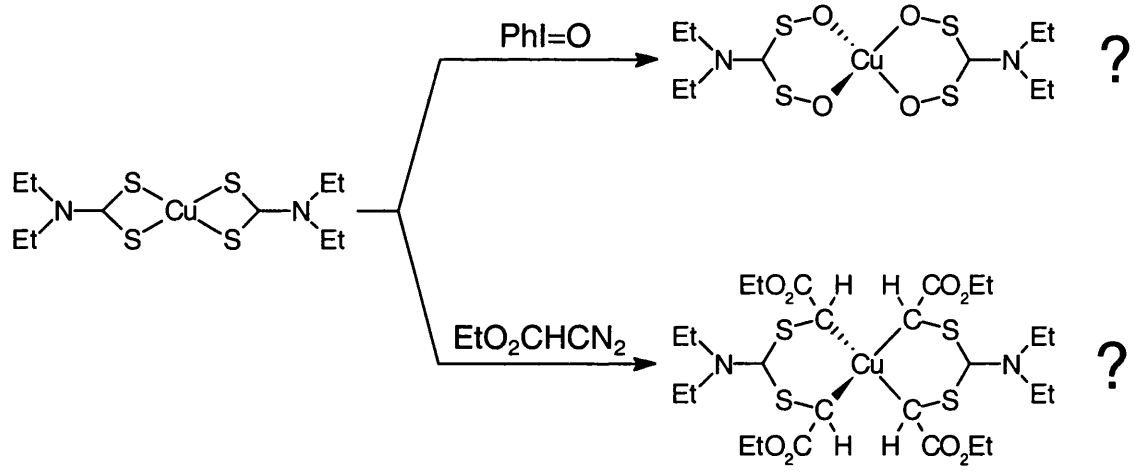


Figure 2.3.10 Other possible insertion reactions

Reaction of $[Cu(Et_2dtc)_2]$ with six equivalents of PhI=O in CH_2Cl_2 under N_2 gave a green solution which, when exposed to air became brown.[106] The mass spectrum of this brown product showed no evidence of insertion, possibly because of the reaction that occurred on exposure to atmospheric oxygen and

moisture. The reaction was repeated under strict exclusion of oxygen and moisture and the reaction mixture remained green. However, this unidentified product also showed no evidence for insertion from its mass spectrum. Reaction of both $[Cu(Et_2dtc)_2]$ and $[Cu(Et_2dtc)]_4$ with excess ethyl diazoacetate gave no evidence of insertion, the solution of each not changing colour during overnight reaction.

The fact that neither insertion of an oxo species nor a carbene species appeared to take place is not entirely unexpected. Copper dithiocarbamate complexes are proficient aziridination catalysts and insertion of a nitrene group takes place readily, facts which appear to link the two processes (see Section 3.1.2). However, by contrast, copper dithiocarbamate complexes do not catalyse either cyclopropanation (see Section 3.2.2) or epoxidation and there is therefore no evidence that copper oxo or copper carbene species are easily formed.

2.3.6 Reactivity Of Insertion Products

The apparent stepwise nature of the insertion process should permit generation of $[Cu(TosNSC(NEt_2)SNTos)_2]$ by further reaction of $[Cu(TosNSC(NEt_2)S)_2]$ with PhI=NTos. Indeed, an experiment reacting $[Cu(TosNSC(NEt_2)S)_2]$ with four equivalents of PhI=NTos gave $[Cu(TosNSC(NEt_2)SNTos)_2]$ in 7% isolated yield, the low yield presumably being due to reaction with excess PhI=NTos. However, as with all previous reactions involving insertion into copper dithiocarbamate complexes, no evidence was found for the presence of a product from insertion of three equivalents of NTos.

The only previously known insertion of a nitrene into a metal-ligand bond during catalysis (see Section 2.3.1) proved to be irreversible, with reaction of the insertion complex and 100 equivalents of cyclooctene providing no aziridine after 20 hours.[99] The copper insertion products $[Cu(TosNSC(NEt_2)S)_2]$ and $[Cu(TosNSC(NEt_2)SNTos)_2]$ were both stirred in CH_2Cl_2 with a large excess of styrene. Initially, the reactions were performed under an atmosphere of N_2, but after reaction for one week, a small aliquot was removed from each for analysis

by ^{1}H NMR spectroscopy and the reactions were then opened to the atmosphere and a small quantity of water added. The reactions were allowed to continue stirring for a further week after which time the solvent was allowed to evaporate and the resultant crystals of the starting complexes were removed manually. The reaction mixtures were then analysed by ^{1}H NMR spectroscopy and mass spectrometry. The reaction with [Cu(TosNSC(NEt$_2$)S)$_2$] showed no evidence of aziridine in either of the two ^{1}H NMR spectra or the mass spectrum. However, the reaction between [Cu(TosNSC(NEt$_2$)SNTos)$_2$] and styrene showed small but clear signals for the expected aziridine in the ^{1}H NMR spectrum of the final reaction mixture, as well as a small peak in the mass spectrum corresponding to a molecular weight of 271 (the molecular weight of the styrene aziridine is 273). This is evidence that the insertion process is at least partly reversible, with perhaps the last two nitrene groups less strongly bound to the copper and sulfur atoms.

The ability of the two copper insertion products to act as aziridination catalysts was also investigated (see Section 3.1.2) and the results obtained appear to correlate with the reversibility of insertion discussed here. [Cu(TosNSC(NEt$_2$)SNTos)$_2$] was shown to be a proficient aziridination catalyst, whilst [Cu(TosNSC(NEt$_2$)S)$_2$] was inactive, results which are in contrast with those of Mansuy.[99]

2.3.7 Summary

The insertion of a nitrene group into the metal-sulfur bonds of dithiocarbamate complexes has been shown to be applicable to different dithiocarbamate ligands and different transition metals and has given rise to several novel amido and diamido complexes. The crystal structures of four of these complexes have been discussed. Insertion products have been found in aziridination reaction mixtures, suggesting that they result from the decomposition of a copper imido complex in the absence of a substrate.

2.4 PHOSPHINE COMPLEXES

2.4.1 The Phosphine Ligand

Phosphines have been known for over 150 years, and have found widespread use as ligands in inorganic chemistry.[107] Phosphorus forms stable compounds in both the +3 and +5 oxidation states, although the trivalent state has a lone pair of electrons available for coordination to transition metals. Primary, secondary and tertiary phosphines are known, although the scope of this thesis is limited to tertiary phosphines only.

Tertiary phosphines can be synthesised in a number of ways, although the simplest is to react PCl_3 with either Grignard or organolithium reagents. This procedure almost always provides the tertiary phosphine, except when using alkyl groups that are very bulky (e.g. cyclohexyl or *t*-butyl) when the product is the secondary phosphine chloride. It is also possible to prepare tertiary phosphines with different alkyl groups by reacting primary and secondary phosphine halides with the required Grignard or organolithium reagent. Due to the sp^3 hybridised nature of the phosphorus atom, the three substituents and the lone pair are arranged in a tetrahedral fashion, leading to optical activity when all three substituents are different.

Phosphine ligands need not be restricted to monodentate species and indeed diphosphine ligands are very common. Among the most widely used are bis(diphenylphosphino)methane (dppm) which tends to bridge dinuclear metal centres, bis(diphenylphosphino)ethane (dppe) which chelates in a *cis* fashion and bis(diphenylphosphino)propane (dppp) which is also capable of chelating in a *trans* fashion. More recently, macrocyclic phosphine ligands have also been developed.[107]

2.4.2 Phosphine Complexes

Phosphines are soft base ligands and therefore are most commonly found in complex with soft acid metal centres such as Pt(II), Cu(I) etc. Copper complexes of phosphines are generally limited to those of Cu(I) due to the reducing

properties of the ligand. Some Cu(II) complexes are known, but only also in the presence of stabilising ligands, as in $[Cu_2(O_2CMe)_4(PPh_3)_2]$.[108] Monophosphines generally ligate in a monodentate fashion and when monophosphines exist in polynuclear complexes, the bridging ligands are usually halides or oxygen or sulfur donors. Mononuclear copper phosphine complexes are quite rare, polynuclear structures such as tetramers or hexamers being preferred. The CuP_4 chromophore has been crystallographically characterised in $[Cu(PPh_3)_4]ClO_4$.[109]

Phosphine complexes have been extensively used in homogeneous catalysis (see Section 1.1) and as such are natural choices for catalyst screening exercises. Phosphine complexes of copper also have the added advantage, due to their reducing ability, of restricting the metal to its univalent state. Of particular interest is the series of complexes $[(Ph_3P)_nCuCl]$ where n=1-3, since the steric demand at the copper centre along the homologous series changes considerably.[17]

2.4.3 Copper Triphenylphosphine Complexes

The syntheses of the three complexes $[(Ph_3P)_nCuCl]$ where n=1, 2 and 3 were all effected via a similar methodology.[17] The required stoichiometric amount of triphenylphosphine was refluxed with [CuCl] in THF under an atmosphere of N_2, more solvent being added if the refluxing solution became cloudy. After reaction for five hours, the hot solution was filtered under N_2, the volume of the solution was reduced and the reaction mixture was placed in a freezer at -15°C overnight. The crystalline $[(Ph_3P)_2CuCl]$ and $[(Ph_3P)_3CuCl]$ were then separated from the mother liquor by filtration. $[(Ph_3P)CuCl]_4$ appeared as a white solid which was separated from the supernatant by filtration and was then recrystallised by slow cooling of a warm CH_2Cl_2 solution. The crystalline product in each case appeared to be stable, in the short to medium term, to oxidation by atmospheric oxygen and was characterised by ^1H NMR spectroscopy, mass spectrometry and elemental analysis. The solubility of the copper phosphine complexes in CH_2Cl_2 solution varies considerably, with $[(Ph_3P)_3CuCl]$ being easily soluble at room

temperature and $[(Ph_3P)CuCl]_4$ only being soluble after a considerable time at reflux. This is presumably due to the tetrameric nature of the complex in the solid state,[110] which has been shown to dissociate into two dimeric $[(Ph_3P)CuCl]_2$ species in solution.[111] The tetrameric complex $[(Ph_3P)CuCl]_4$ also appears to share the light sensitivity property observed in $[Tp^*Cu(PPh_3)]$ (see Section 2.1.2.1), whereby in the crystalline state under N_2, the colourless crystals become orange upon exposure to light.

2.4.4 Copper Bis(diphenylphosphino)ethane Complexes

Copper complexes of the ligand dppe (bis(diphenylphosphino)ethane) generally tend to be dinuclear in nature, with the two copper centres being bridged by a diphosphine unit. Another diphosphine ligand chelates to each of the copper centres and a uninegative ancillary ligand occupies the remaining coordination site, giving an overall stoichiometry of [(dppe)LCu(μ-dppe)CuL(dppe)]. The solution chemistry of these complexes has recently been studied. It was suggested that dissociation of the complex plays a major role, the $[Cu(dppe)_2]^+$ cation, although not isolated, being detected by ^1H NMR.[112]

It was decided that the preparation of a $[Cu(dppe)_2]X$ complex would allow investigation of the aziridination capabilities of a copper diphosphine complex without the complications caused by the presence of two copper centres. A common strategy utilised in the synthesis of copper diphosphine complexes is to react a copper salt of a poorly ligating ligand with the diphosphine ligand, although reaction of an excess of the ligand leads to formation of the dinuclear complexes described above.[112]

The complex $[Cu(MeCN)_4]ClO_4$ was synthesised by first allowing an MeCN solution of $[Cu(H_2O)_4](ClO_4)_2$ to evaporate slowly to produce crystals of $[Cu(MeCN)_4](ClO_4)_2$. This was then reduced to $[Cu(MeCN)_4]ClO_4$ by reflux in MeCN with copper powder under an atmosphere of N_2 until the solution became colourless. Hot filtration followed by slow cooling overnight gave a white

microcrystalline solid that is highly moisture sensitive and was characterised by ^{1}H NMR spectroscopy and elemental analysis.

The synthesis of $[Cu(dppe)_2]ClO_4$ was effected by stirring $[Cu(MeCN)_4][ClO_4]$ with two equivalents of dppe in MeCN. The crude product appeared to be air-stable, since no colouration of a CH_2Cl_2 solution occurred after several days exposed to the atmosphere. The product was purified by slow reduction in the polarity of the solvent until precipitation of the impurities occurred followed by filtration and removal of solvent under vacuum. The mass spectrum of the product showed a large peak at a molecular weight of 859 which corresponds to the $[Cu(dppe)_2]^+$ cation and the ^{1}H NMR spectrum showed an aromatic resonance along with a smaller multiplet at δ 2.46 which was assigned to the CH_2 protons.

2.5 SUMMARY

This chapter has described the synthesis, characterisation and properties of a wide range of complexes of copper in all three common oxidation states, as well as several complexes of other metals. A series of novel complexes of the ligands $TosNSC(NR_2)S$ and $TosNSC(NR_2)SNTos$, formed by the insertion of two and four equivalents of NTos into dithiocarbamate complexes has been described, four of the complexes being crystallographically characterised. The following chapter will initially describe the ability of all of these complexes to catalyse aziridination of olefins. Observations during these aziridination reactions along with results from other experiments will lead to a discussion on aspects of the catalytic mechanism.

3.0 AZIRIDINATION AND MECHANISM

3.1 COPPER CATALYSED AZIRIDINATION REACTIONS

3.1.1 General Reaction Conditions

The reaction conditions utilised by Evans,[45,46,53] Jacobsen[47,49] and others[48,63,113,114] were analysed and our general reaction conditions derived from their observations. It was felt that reactions would provide superior results if a larger amount of catalyst and a greater excess of substrate were utilised. Thus, it was decided to use 10 mol% of catalyst and 10 equivalents of substrate, with the nitrene source as the limiting reagent. Although Evans states that reactions occur more quickly and in higher yield when performed in MeCN, CH_2Cl_2 was chosen since, whilst it too affords high yields of aziridine, it is generally more convenient. Also for reasons of convenience and at little expense to reaction yield, it was decided to perform the reactions at room temperature. PhI=NTos was chosen as the nitrene source since Evans has reported that, of four potential nitrene sources examined, it was the only one that provided aziridine in good yield.[46,115] In addition, PhI=NTos is insoluble in a number of common organic solvents, allowing the course of the aziridination reaction to be followed by monitoring the reduction in the opacity of the reaction mixture. Styrene was the substrate of choice because of low cost, simplicity of structure, relatively high volatility and the fact that it gives good yields in aziridination reactions.[46]

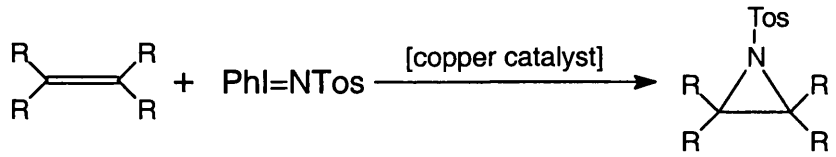


Figure 3.1.1 Aziridination of alkenes

An aziridination reaction was performed using $[Cu(Et_2dtc)_2]$ as catalyst in the presence of 10 ml of water. A yield of 57% was obtained, only 23% lower than that obtained under anhydrous conditions, which suggests that performing the reaction in the presence of molecular sieves, as Brookhart and Templeton have done, would not significantly reduce the yield.[63] Nevertheless, it was decided

that reactions would be performed under anhydrous conditions in order to negate any effect caused by atmospheric variation. A series of aziridinations assessing the effect of reaction time were performed using $[Cu(MeCN)_4]ClO_4$ in MeCN. One reaction was worked-up (by removal of solvent under vacuum, opening to air and re-dissolution in GPR solvent) as soon as the solution had become clear (*i.e.* all the PhI=NTos had reacted), a second was left to react overnight and the third was left for one week. The first reaction gave no aziridine whilst the other two both gave 25% yield, indicating that reaction was complete after approximately 16 hours. Thus, all reactions were allowed to stir overnight before work-up.

3.1.2 Aziridinations Using The General Aziridination Reaction Procedure

The general aziridination procedure involves placing the nitrene source and the substrate together in one Schlenk tube, with the catalyst placed in a separate Schlenk tube. Solvent was added to both and once the catalyst has dissolved, it was transferred to the Schlenk tube containing the nitrene source and the substrate and stirring is commenced.

Initially, reactions designed to test the suitability of the general aziridination procedure were performed. Any PhI=NTos not converted to aziridine is reduced to $TosNH_2$ and PhI, Evans having suggested that this arises from solvent trapping.[45] However, reaction with moisture during work-up could also be a contributing factor. An aziridination reaction using $[Tp^*Cu]_2$ as catalyst and $TosNH_2$ as the nitrene source showed that $TosNH_2$ does not transfer the TosN species to alkenes and is thus an inactive component of aziridination reaction mixtures. In addition, a reaction was performed in which the catalyst, $[Tp^*Cu]_2$ / $[Tp^*Cu(C_2H_4)]$ (1:1), was reacted with PhI=NTos prior to the addition of styrene. No aziridination occurred, a result which could be caused either because reaction with nitrene precursor rendered the catalyst inactive, or because all the PhI=NTos had reduced to $TosNH_2$ and PhI (*vide supra*) before the styrene was added. It was also discovered, after several aziridinations using a reverse procedure in which the styrene was initially placed with the catalyst

(see Section 4.6), that the yield was essentially unaffected by the change in protocol.

3.1.2.1 Pyrazolylborate Complexes As Catalysts

All pyrazolylborate complexes synthesised and described in Section 2.1 were utilised in aziridination reactions and the yields obtained are summarised in Table 3.1. The three Cu(I) complexes of Tp* all gave high yields of aziridine, with [Tp*Cu(CO)] giving 100% conversion. Interestingly, the lowest yield of the three complexes was obtained with $[Tp^*Cu]_2$ as the catalyst, a complex reported to be extensively dissociated in benzene solution.[18] Very different yields of aziridine were obtained with the two phosphine complexes $[Tp^*Cu(PPh_3)]$ and $[TpCu(PPh_3)]$ with the former giving 80% yield and the latter giving a yield that is 51% lower. This effect could be due greater steric crowding in the Tp* complex, reflected in the longer Cu-P bond length.[62,70] This may lead to a greater tendency to relieve the strain, either by dissociation of the phosphine ligand or by one arm of the tridentate pyrazolylborate ligand releasing, thus opening a coordination site for reaction to occur.

The copper(II) complexes $[CuTp^*_2]$, $[CuBp_2]$ and $[CuBp^*_2]$ also produced differing yields. $[CuTp^*_2]$ gave 5% yield, a result most probably caused by the steric saturation at copper. The two bispyrazolylborate complexes gave 40% and 42% respectively, the greater yield compared with that of $[CuTp^*_2]$ being ascribed to the lower steric demand at the square-planar copper centre. However, the difference in steric bulk between Bp and Bp* appears to have little effect on the yield of aziridine obtained.

Catalyst	Yield (%)
[TpCu(PPh$_3$)]	29
[TpCu]$_2$	77
*[Tp*Cu(PPh$_3$)]*	80
*[Tp*Cu]$_2$*	63
*[Tp*Cu(CO)]*	100
[CuTp$_2$]*	5
[CuBp$_2$]	40
[CuBp$_2$]*	42

Table 3.1 Yields of aziridinations using copper pyrazolylborate catalysts

3.1.2.2 Dithiocarbamate Complexes As Catalysts

A wide range of copper dithiocarbamate complexes were synthesised and assessed as aziridination catalysts (see Table 3.2), all three major oxidation states of copper being represented.

Catalyst	Yield (%)
[Cu(Et$_2$dtc)$_2$] *	69
[Cu(Et$_2$dtc)]$_4$	78
[Cu(Me$_2$dtc)$_2$]	70
[Cu(Et$_2$dtc)$_2$]	80
[Cu(Pyddtc)$_2$]	82
[Cu(S-Pydmdtc)$_2$]	71
[Cu(Me,^{n}Hexdtc)$_2$]	83
[Cu(Me$_2$dtc)$_2$][FeCl$_4$]	55
[Cu(Et$_2$dtc)$_2$][FeCl$_4$]	76
[Cu(Pyddtc)$_2$][FeCl$_4$]	51
[Cu(Me$_2$dtc)$_2$]ClO$_4$	0
[Cu(Et$_2$dtc)$_2$]ClO$_4$	5

* Mixture of 25% $[Cu(Et_2dtc)_2]^-$ and 75% $[Cu(Et_2dtc)]_4$

Table 3.2 Yields of aziridinations using copper dithiocarbamate catalysts

A mixture of 25% $[Cu(Et_2dtc)_2]^-$, 75% $[Cu(Et_2dtc)]_4$ gave a 9% lower yield than $[Cu(Et_2dtc)]_4$ alone, suggesting that the monomeric $[Cu(Et_2dtc)_2]^-$ species has a

lower activity than the tetrameric copper(I) species. In $[Cu(Et_2dtc)]_4$, whilst one sulfur of the dithiocarbamate ligand coordinates directly to a copper atom, the second bridges two copper atoms, possibly allowing for easier dissociation and thus reducing the steric crowding around the copper centre during aziridination.[86] This suggests that vacant coordination sites are necessary for efficient catalysis.

Yields of two distinct types were obtained with the five copper(II) complexes assessed, the more soluble complexes $[Cu(Et_2dtc)_2]$, $[Cu(Pyddtc)_2]$ and $[Cu(Me,{}^{n}Hexdtc)_2]$ giving yields of aziridine approximately 10% higher than those of the less soluble complexes $[Cu(Me_2dtc)_2]$ and $[Cu(Pydmdtc)_2]$.

Formation of a copper nitrene complex would be expected to involve a two electron oxidation process and therefore it was thought that copper(III) dithiocarbamate complexes would be inactive as catalysts. The copper(III) complexes $[Cu(Me_2dtc)_2]ClO_4$ and $[Cu(Et_2dtc)_2]ClO_4$ supported this hypothesis since they showed no catalytic activity. However, all three copper(III) complexes with an $[FeCl_4]^-$ anion showed an appreciable ability to catalyse aziridination, with $[Cu(Et_2dtc)_2][FeCl_4]$ giving 76% yield, a level of activity only 6% lower than with $[Cu(Et_2dtc)_2]$. Initially it was supposed that the catalytic activity of these copper(III) complexes was caused by the iron centre in the anion, but this was ruled out after an aziridination reaction using $NEt_4[FeCl_4]$ as the catalyst showed no activity. However, an aziridination reaction using the inactive catalyst $[Cu(Et_2dtc)_2]ClO_4$ in the presence of one equivalent of $NEt_4[FeCl_4]$ gave 43% yield of aziridine, suggesting that it is some property of the $[FeCl_4]^-$ anion that is causing the activity. A further possible explanation was the interaction of the copper complex with Cl^- released from the $[FeCl_4]^-$ anion. An aziridination reaction performed using the inactive complex $[Cu(Et_2dtc)_2]ClO_4$ as catalyst in the presence of one equivalent of NEt_4Cl gave 72% yield of aziridine, essentially the same yield as $[Cu(Et_2dtc)_2][FeCl_4]$, which strongly suggests that it is the presence of the Cl^- that is causing the activity. An explanation for this could be that the Cl^- reduces the copper(III) centre to copper(II) thus allowing further oxidation during the catalytic process, a hypothesis supported by the observation

that the only isolated product of the reaction of equimolar amounts of $[Cu(Et_2dtc)_2]ClO_4$ and NEt_4Cl was $[Cu(Et_2dtc)_2]$.

The colour changes observed during each of these aziridination reactions were informative. Both the ClO_4^- and the $[FeCl_4]^-$ copper(III) complexes were green, all the copper(II) complexes were dark brown and the copper(I) complex was pale yellow. When the copper(I) complex was used in an aziridination reaction, the solution immediately became dark brown, swiftly followed by a change to green. This suggests a step-wise increase in oxidation state from +1 to +2 and then to +3, but the ^1H NMR spectra of the reaction mixtures showed no signals assignable to copper complexes, implying that the final oxidation state is likely to be the paramagnetic copper(II). In a similar fashion, the copper(II) catalysts utilised changed from dark brown to green during the reaction and the ^1H NMR spectra showed no evidence for the presence of a copper(III) species. The copper(III) catalysts used remained green throughout the reaction period.

The green end-product of the catalytic process was isolated by slow evaporation of the reaction mixture to give green crystals which were washed quickly with $CHCl_3$. Elemental analysis and the IR and mass spectra of the green crystals were consistent with $[Cu(TosNSC(NR_2)SNTos)_2]$, the product of insertion of four equivalents of nitrene into the copper dithiocarbamate complex (see Section 2.3 for a description of insertion products). This product was identified by mass spectrometry in all reactions using copper dithiocarbamate complexes, except those of $[Cu(R_2dtc)_2]ClO_4$. These results appear to link the two processes of insertion and aziridination, since only those copper dithiocarbamate complexes that are active catalysts show any tendency towards insertion.

Dithiocarbamate complexes of cobalt(III) and nickel(II) were also synthesised and assessed as aziridination catalysts, along with the more unusual complexes $[Zn(Me,C_{18}H_{37}dtc)_2]$, $[In(Me,Etdsc)_2]$ and $[Cd(Me,^nPrdtc)_2]$.[116] $[Co(Et_2dtc)_3]$ and $[Cd(Me,^nPrdtc)_2]$ gave 13% and 10% yield of aziridine respectively, with all the other complexes effectively showing no activity. Insertion products were

detected by mass spectrometry in the reaction mixtures of $[Co(Et_2dtc)_3]$, $[Ni(Et_2dtc)_2]$, $[Zn(Me,C_{18}H_{37}dtc)_2]$ and $[Cd(Me,^nPrdtc)_2]$ catalysed reactions, with $[Co(TosNSC(NEt_2)SNTos)_2]$ and $[Ni(TosNSC(NEt_2)S)_2]$ being isolated (see Section 2.3.4). The identification of $[Ni(TosNSC(NEt_2)S)_2]$ indicates that insertion does not, contrary to evidence previously obtained, arise directly from aziridination since $[Ni(Et_2dtc)_2]$ is not an active aziridination catalyst.

3.1.2.3 Insertion Products As Catalysts

$[Cu(TosNSC(NEt_2)S)_2]$ and $[Cu(TosNSC(NEt_2)SNTos)_2]$ were assessed as aziridination catalysts, with the former appearing to be inactive and the latter giving 25% yield. The difference in activity between these two complexes can be related to the tendency in each complex for the insertion process to be reversible (see Section 2.3.6).

3.1.2.4 Phosphine Complexes As Catalysts

Since $[Cu(dppe)_2]ClO_4$ is synthesised from $[Cu(MeCN)_4]ClO_4$ and dppe, it was decided initially to assess the ability of $[Cu(MeCN)_4]ClO_4$ as an aziridination catalyst in the presence of dppe, knowing that $[Cu(MeCN)_4][ClO_4]$ alone gives 25% yield in MeCN (see Section 3.1.2.5). Reactions were performed in MeCN using one and two equivalents of dppe and the yields of aziridine obtained were 10% and 5% respectively, suggesting that the dppe inhibits the aziridination process. It is, however, more likely that the phosphine ligand is relatively slow to react with the copper ion and will therefore react preferentially with the nitrene fragment forming a phosphorus imine. The formation of phosphorus imine would reduce the amount of PhI=NTos present in the system, thereby making the conditions for catalysis more demanding and consequently reducing the yield. The phosphine complex $[Cu(dppe)_2]ClO_4$ gave 86% yield of aziridine, indicating that the poor yields in the previous experiments were not due to a copper phosphine complex.

The three triphenylphosphine complexes synthesised all gave yields of aziridine in the region of 90%. The change in steric crowding around the copper centre

moving from $[(Ph_3P)CuCl]_4$ through $[(Ph_3P)_2CuCl]$ to $[(Ph_3P)_3CuCl]$ leads to a lowering of only 5% in the aziridination yield.

Catalyst	Yield (%)
$[Cu(MeCN)_4]ClO_4$ + 1 eq. dppe	10
$[Cu(MeCN)_4]ClO_4$ + 2 eq. dppe	5
$[(Ph_3P)CuCl]_4$	90
$[(Ph_3P)_2CuCl]$	91
$[(Ph_3P)_3CuCl]$	85
$[Cu(dppe)_2]ClO_4$	86

Table 3.3 Yields of aziridinations using copper phosphine catalysts

3.1.2.5 Other Copper Complexes As Catalysts

Several copper complexes that cannot be classified as being part of the four previous groups were assessed as aziridination catalysts. The starting materials for many of the complexes prepared in this study were [CuCl] and $[CuCl_2]$, but after assessing their aziridination ability it was found that they were both inactive as catalysts.

Catalyst	Yield (%)
[CuCl]	0
$[CuCl_2]$	0
$[Cu(OTf)_2]$	0
$[Cu(MeCN)_4]ClO_4$	0
$[Cu_2(MeCO_2)_4]\cdot 2H_2O$	80
$[Cu(TosNSC(NEt_2)S)_2]$	0
$[Cu(TosNSC(NEt_2)SNTos)_2]$	25
$[Cu(dmp)_2]ClO_4$	68

Table 3.4 Yields of aziridinations using miscellaneous copper catalysts

$[Cu(OTf)_2]$ was extensively utilised by Evans who reported 92% yield when the reaction was performed in MeCN.[46] However, using the general reaction

procedure, $[Cu(OTf)_2]$ showed no activity in either CH_2Cl_2 or MeCN. A similar conflict with the results of Evans occurred when using $[Cu(MeCN)_4]ClO_4$ as catalyst. The general reaction procedure was performed using $[Cu(MeCN)_4]ClO_4$, but no activity was observed in CH_2Cl_2 and only 25% yield was obtained in MeCN. This is in contrast with Evans' report of 90% yield in CH_2Cl_2.[46] Although the reaction conditions employed by Evans were slightly different from those of the general reaction procedure, this was not the cause of the disparity in results since a reaction performed using Evans' reaction conditions gave a yield only 6% higher than that obtained using the general procedure. The cause of this difference in results is unknown, but could be due several factors including length of reaction, purity of reagents and the amount of water present in the system.

The dimeric copper(II) complex $[Cu_2(MeCO_2)_4]\cdot 2H_2O$ only has one vacant coordination site per copper atom and is very poorly soluble in CH_2Cl_2, a very slight blue colouration of the solvent being detectable after reflux. Despite this, 80% yield was obtained from an aziridination reaction. Similar activity has been noted in catalytic reactions with diazo compounds (see Section 1.1.3), whereby despite being in the +2 oxidation state and only having one vacant coordination site, high yields were obtained.[117]

3.1.2.6 Summary

Of all the complexes employed as aziridination catalysts, those including a coordinating phosphine ligand generally give higher yields than those without. Copper dithiocarbamate complexes are also highly proficient catalysts, all oxidation states of copper being active, although the activity of copper(III) complexes is thought to be due to *in situ* reduction to copper(II). Although copper(I) trispyrazolylborate complexes were highly active catalysts, the air sensitivity of the complexes assessed, $[Tp^*Cu(PPh_3)]$ apart, restricts their utility. The results reported by Evans for $[Cu(OTf)_2]$ and $[Cu(MeCN)_4][ClO_4]$ could not be reproduced, the yields obtained being significantly lower in both cases.[46]

3.1.3 Reactions Using Different Stoichiometries

In order for a catalyst to be useful in organic synthesis, where substrates are often expensive or are the product of a long sequence of reactions, it must be able to produce aziridines in high yield using only one equivalent of the substrate, preferably also using the minimum amount of catalyst in order to avoid contamination and possible side-reactions. Three suitable catalysts were assessed in reactions using less substrate and less catalyst than in the general procedure in order to gauge their ability to aziridinate under more demanding conditions.

Reactions Using [Tp*Cu(PPh$_3$)] Using the general reaction procedure, an 80% yield of aziridine is obtained. However, on lowering the quantity of catalyst used to 5% and then to 1%, the yield is reduced to 66% in both cases. Upon reducing the quantity of styrene to one equivalent but still using 10% catalyst, the yield is reduced to 60%. These results indicate that the effectiveness of the catalyst is reduced significantly upon reduction of the quantity of catalyst or substrate present and therefore experiments combining both reductions were not performed.

Ratio of Reagents			Yield (%)
Substrate	PhI=NTos	Catalyst	
10	*1*	*0.1*	80
10	*1*	*0.05*	66
10	*1*	*0.01*	66
5	*1*	*0.1*	86
1	*1*	*0.1*	60

Table 3.5 Yields of aziridinations using [Tp*Cu(PPh$_3$)] as catalyst

Reactions Using [Cu(Et$_2$dtc)$_2$] Again, 80% yield of aziridine is obtained when using the general reaction procedure. However, upon reduction of the quantity of catalyst to 5% and then to 1%, the yield increased to 83% and 86% respectively. This is possibly due to a reduction in the amount of the competing

insertion reaction that is taking place (see Sections 2.3.4 and 3.2.4). However, when a reaction was performed using one equivalent of styrene and 10% catalyst, the yield obtained was 64%, suggesting that the use of $[Cu(Et_2dtc)_2]$ under more demanding conditions would not provide useful yields of aziridine.

Ratio of Reagents			Yield (%)
Substrate	**PhI=NTos**	**Catalyst**	
10	*1*	*0.1*	80
10	*1*	*0.05*	83
10	*1*	*0.01*	86
5	*1*	*0.1*	89
1	*1*	*0.1*	64

Table 3.6 Yields of aziridinations using $[Cu(Et_2dtc)_2]$ as catalyst

Reactions Using $[(Ph_3P)CuCl]_4$ The general reaction procedure gave 90% yield of aziridine, with reduction in the amount of catalyst to 5% resulting in an increase in yield to 93%, a result which could possibly be due to a reduction in the competing formation of phosphorous imine. A reduction in the quantity of styrene used to one equivalent resulted in no loss of activity. These two results suggest that $[(Ph_3P)CuCl]_4$ works well under more demanding conditions and the two reductions were therefore combined. With one equivalent of styrene and 5% catalyst the yield was 88% and with one equivalent of styrene and 1% catalyst 67% yield was obtained. The performance of $[(Ph_3P)CuCl]_4$ under these conditions is still significant, proving it to be the most active aziridination catalyst yet reported. Evans,[45,46,53] Jacobsen[47,49] and others[48,63,113,114] have not assessed their catalysts under similar conditions, each of them using their own respective standard conditions. The most demanding of these standard conditions were those of Shi who used 1.5% catalyst with 4 equivalents of substrate, yields as high as 85% being obtained with styrene as substrate.[113]

Ratio of Reagents			Yield (%)
Substrate	PhI=NTos	Catalyst	
10	*1*	*0.1*	90
10	*1*	*0.05*	93
5	*1*	*0.1*	96
1	*1*	*0.1*	90
1	*1*	*0.05*	88
1	*1*	*0.01*	67

Table 3.7 Yields of aziridinations using $[(Ph_3P)CuCl]_4$ as catalyst

In summary, although all three of the complexes assessed gave excellent yields of aziridine under the general reaction conditions, only $[(Ph_3P)CuCl]_4$ maintained this performance when more demanding conditions were employed. Despite being the most active catalyst used in the course of this research, $[(Ph_3P)CuCl]_4$ is very slow to dissolve in CH_2Cl_2, a problem which may be solved by altering the substituents on the phosphine.

3.1.4 Reactions Using Different Substrates

Another requirement of a catalyst that is to be used in organic synthesis is the ability to aziridinate many different substrates. In addition, the yields obtained may provide information as to the nature of the reactive species involved.

Much of the research into aziridination substrates has been directed towards the stereospecificity and regiospecificity of reactions. It has been reported by Evans that *trans* alkenes react stereospecifically to give *trans* aziridines, but *cis* alkenes give varying ratios of the two possible aziridine products depending upon the catalyst used.[46] However, Knight notes that in certain circumstances, small amounts of *cis* aziridines can be obtained from *trans* dienes.[114]

All of the aziridination reactions discussed in this and the following two sections were performed using the general aziridination procedure under standard conditions (see Section 4.5) unless otherwise stated.

Aziridination Of Alkenes After styrene, the second most studied substrate is cyclohexene, the former being an activated alkene and the latter being a deactivated alkene. Generally, cyclohexene gives lower yields of aziridine than styrene, but this effect is very much dependent upon the catalyst used. For instance, using [Tp*Cu(PPh_3)] as catalyst, the yield of aziridine with cyclohexene as substrate is 14%, 66% lower than the corresponding yield with styrene. However, with [Tp*Cu(CO)] as catalyst, the yield of cyclohexene aziridine is 3%, 97% lower than the equivalent yield using styrene. A summary of the results obtained in these reactions is given in Table 3.8 below, with the yields given as a percentage. It can be seen that none of the three alternative alkenes give the high yields commonly obtained with styrene.

Catalyst	Yields (%)			
	Styrene	Acrylonitrile	Cyclohexene	Methyl Methacrylate
*[Tp*Cu(PPh_3)]*	80	24	14	15
*[Tp*Cu(CO)]*	100	31	3	26
[$CuTp^*_2$]	5			3
[$Cu(Et_2dtc)]_4$	78	39		
[$Cu(Et_2dtc)_2$]	80		14	19
[$Cu(Et_2dtc)_2$][$FeCl_4$]	76	24		
[$Cu(Et_2dtc)_2$]ClO_4	5	4		
[(Ph_3P)CuCl]$_4$	90	60	29	

Table 3.8 Yields of aziridinations of alkenes

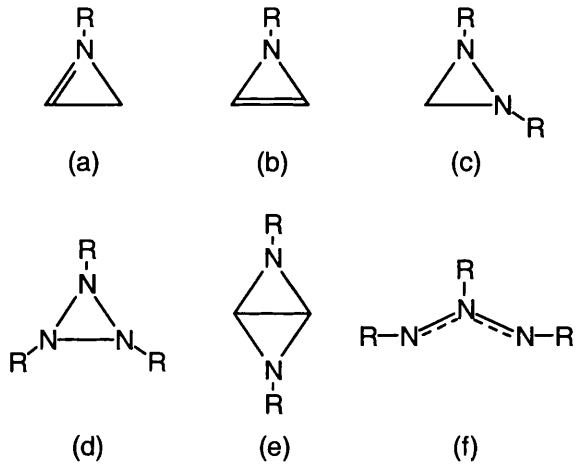
Aziridination Of Dienes And Trienes The aziridination of several dienes was attempted in order to examine the regioselectivity of the aziridination reaction as well as the possibility of more than one aziridination taking place on one molecule of substrate. The substrates investigated included a bicyclic diene (bicyclo-[2.2.1]-1,5-heptadiene), a long-chain aliphatic diene (2,5-dimethylhexa-1,5-diene), cycloheptatriene and the cyclic dienes 1,3-cyclooctadiene and 1,5-cyclooctadiene.

When 1,5-cyclooctadiene was added to PhI=NTos, a vigorous exothermic reaction took place, the only product identified being $TosNH_2$. The aziridination of 1,5-cyclooctadiene was therefore performed according to the reverse procedure (see Section 4.6) using $[Tp^*Cu(C_2H_4)]$ / $[Tp^*Cu]_2$ (1:1) as catalyst. The ^1H NMR spectrum of the reaction mixture showed some small peaks between 3 ppm and 4 ppm, a region where aziridine ring proton signals are normally found. However, no product could be unambiguously identified and the mass spectrum showed no evidence of aziridination.

The reactions involving 1,3-cyclooctadiene, cycloheptatriene and 2,5-dimethylhexa-1,5-diene gave similar results, with the major product being $TosNH_2$ and the ^1H NMR spectra also showing small peaks that could possibly be due to aziridine. No products other than $TosNH_2$ could be identified in any of the reaction mixtures and the low yields obtained prevented isolation by column chromatography.

However, the aziridination of bicyclo-[2.2.1]-1,5-heptadiene gave a high yield of an unidentified product which, from evidence obtained from the mass spectrum, appeared to result in the reaction of the substrate with one equivalent of NTos. The major product was then isolated by column chromatography. A ^1H NMR spectrum of the white solid thus obtained showed many peaks, including those of $TosNH_2$ and those of other, unidentified minor products. However, between eight and ten resonances were identified as belonging to the major product of the aziridination reaction. The high number of individual resonances indicates low symmetry in the molecule, thus ruling out the presence of an aziridine. Other indications that the product is not an aziridine are the presence of a broad peak at 4.7 ppm assignable to an amino proton and the presence of four resonances in the olefinic region of the spectrum. Since the substrate initially had four olefinic protons, it would appear that neither alkene functionality has been reduced. Despite good data being available from both the ^1H NMR and mass spectra, this product could not be identified (for details of the spectra see Section 4.8.2 and Appendix 2).

Aziridination Of Other Multiply-Bonded Substrates Many compounds similar in structure to aziridines have been synthesised and it is possible to envisage the formation of each of these derivatives from the reaction of a nitrene with a suitable substrate. Compounds such as 1-azirines and diaziridines have been known since the late 60's and early 70's, but 2-azirines have yet to be synthesised since they would have 4 π-electrons and would therefore be antiaromatic.[118-120] Triaziridines have only been known since the 80's and are synthesised by the reaction of nitrene with azoisopropane followed by photolysis of the resulting azimine.[121] Another interesting aziridine derivative is the 2,4-diazabicyclo[1.1.0]butane system which has two aziridine rings fused along the carbon-carbon bond.[122] These derivatives are all shown in Figure 3.1.1 below.



(a) 1-azirine (b) 2-azirine (c) diaziridine (d) triaziridine
(e) 2,4-diazabicyclo[1.1.0]butane (f) azimine

Figure 3.1.2 Unusual aziridine derivatives

It can be envisaged that reaction between a nitrene and an azo compound could produce a triaziridine, although it is more likely that an azimine would be formed. However, the ^{1}H NMR spectrum of a reaction between PhI=NTos and azobenzene catalysed by $[Cu(Et_2dtc)_2]$ only showed resonances for $TosNH_2$ and unreacted azobenzene. Reaction between a nitrene and an alkyne could possibly result either in the formation of a 2-azirine or, if two equivalents of

nitrene react, a 2,4-diazabicyclo[1.1.0]butane derivative. The formation of the two derivatives shown in Figure 3.1.2 can also be envisaged, although the latter reaction is unlikely since the product would have eight π-electrons and would therefore be antiaromatic.

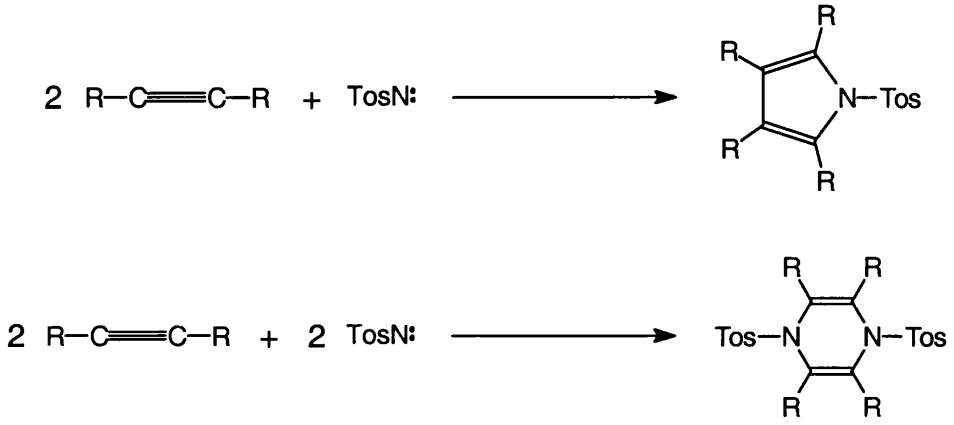


Figure 3.1.3 Hypothetical products from reaction of alkyne with nitrene

Reaction of PhI=NTos with dimethyl acetylene dicarboxylate (DMAD) catalysed by $[Cu(Et_2dtc)_2]$ showed no evidence of any transfer of nitrene in either the ^1H NMR spectrum or the mass spectrum. However, a colour change from dark brown to yellow was observed during reaction of PhI=NTos with di-*n*-propyl acetylene catalysed by $[Cu(Et_2dtc)_2]$. In addition, the ^1H NMR spectrum showed four peaks not attributable to the starting material and the mass spectrum gave some evidence for the reaction of the alkyne with a TosN species. Despite these promising indications that reaction had taken place, no product could be identified or characterised.

In summary, styrene is the substrate that consistently provides the highest yield of aziridine, although some catalyst-substrate combinations also give high yields. The aziridination of dienes was not successful, with low yields of unidentified products being obtained except when using bicyclo-[2.2.1]-1,5-heptadiene. Similarly, the aziridination of more unusual substrates generally gave poor results, although some interaction of nitrene with a non-activated alkyne was observed.

3.1.5 Reactions Using Different Nitrene Sources

Although PhI=NTos is by far the most widely used nitrene source in catalysed aziridination reactions, there exist several other methods of generating nitrenes. Perhaps the most common is the use of azides which, in the presence of a catalyst or when thermally or photolytically excited, decompose to yield N_2 and a nitrene. This was the method utilised by Kwart and Kahn in the first catalytic formation of aziridines from olefins.[43] Evans has assessed the aziridination ability of four nitrene sources, chosen because of their ability to form imido complexes from molybdenum-oxo complexes.[34] These potential nitrene sources are shown in Figure 3.1.4, the yields obtained by Evans being 96% for PhI=NTos and 12% for $TosN_3$, the remaining two being inactive.[46]

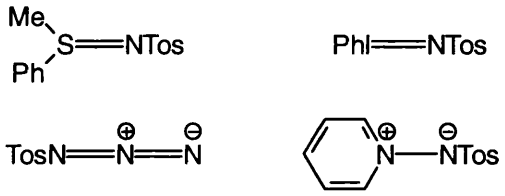


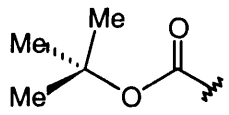
Figure 3.1.4 Nitrene sources investigated by Evans

Since our studies with PhI=NTos had shown differences to the results of Evans, it was decided to assess two other nitrene sources from this group. Me_2S=NTos was readily prepared from Me_2S and TosNClNa and was assessed using $[Cu(Et_2dtc)_2]$ as catalyst.[123] No colour change was observed and no peaks due to aziridine were found in the ^1H NMR spectrum after standard work-up. $TosN_3$ was prepared by reaction of TosCl with NaN_3 and was assessed using $[Tp^*Cu(C_2H_4)]$ / $[Tp^*Cu]_2$ (1:1) as catalyst.[124] The solution became pale yellow during the reaction, and the ^1H NMR spectrum showed a 35% yield of aziridine. These two results appear to correlate well with those of Evans, suggesting that his assertions that N-1-pyridinium sulfonamidate is inactive and that PhI=NTos is the most active nitrene source are correct. However, the future development of new nitrene sources could lead to higher yields, greater selectivity and a wider range of aziridine products.

The molybdenum-imido complexes mentioned above are known to react with phosphines, causing a two-electron reduction along with formation of a phosphorus imine.[125] It is possible to envisage styrene acting as the reductant in an analogous reaction which forms aziridines. These complexes could thus possibly provide an alternative source of nitrene and therefore one example, $[Mo(Et_2dtc)_2(N^tBu)_2]$ was assessed as such using $[Tp^*Cu(C_2H_4)]$ / $[Tp^*Cu]_2$ (1:1) as catalyst. Upon reduction, the imido complex is known to undergo a colour change from orange to purple.[125] However, no such colour change was observed during the aziridination reaction and no aziridine was detected in the ^1H NMR spectrum. The reaction was left to stir for a further three days, but no colour change was observed. A solution of one equivalent of PPh_3 in CH_2Cl_2 was therefore added to the reaction mixture. PPh_3 is known to abstract the imido group from molybdenum bis-imido complexes affording a molybdenum(IV) imido complex and $Ph_3P{=}NR$.[125] The addition of PPh_3 had no effect on the aziridination reaction, with no colour change taking place and no evidence of either aziridine or phosphorus imine being found in the ^1H NMR spectrum.

TosNClNa, utilised in the synthesis of $Me_2S{=}NTos$, is known to transfer the TosN moiety to organic substrates in reactions involving ferrous chloride and therefore has the potential to act as a nitrene source in aziridination reactions.[126] TosNClNa is supplied as a dihydrate and was assessed both in its hydrated and dehydrated forms using $[Cu(Et_2dtc)_2]$ as catalyst. The yields obtained were 44% and 45% respectively, highlighting the fact that the presence of water does not significantly affect aziridination reactions. The yields were slightly higher than half of those obtained with PhI=NTos, suggesting that TosNClNa is a good source of nitrene and is perhaps the second most effective nitrene source known. Indeed, using $[Tp^*Cu(PPh_3)]$ as catalyst, 73% yield was obtained, only 7% lower than that obtained with PhI=NTos. However, a reaction using $[(Ph_3P)CuCl]_4$, the most efficient catalyst with PhI=NTos (see Section 3.1.3), gave no aziridine at all. This suggests that the reaction mechanism functioning when TosNClNa is employed is somewhat different to that operating during aziridination reactions using PhI=NTos.

The fact that TosNClNa has been shown to act as a nitrene source in aziridination reactions allows the possibility of utilising a new generation of nitrene sources not based on the *p*-toluenesulfonyl group. The *p*-toluenesulfonyl group is rarely used as a nitrogen protecting group in organic synthesis due to the difficulty of its eventual removal.[127] Other amide-based protecting groups such as the *t*-butyl carbamate (BOC) group shown in Figure 3.1.4 are much more widely used since they are much more easily removed. These type of carbamate protecting groups can easily be converted to N-sodio, N-chloroamine nitrene sources by a conproportionation reaction between the relevant amine and dichloroamine followed by reaction with NaOH. There is therefore the possibility of the development of a new class of nitrene sources that will allow tailoring of the properties of the protecting group on nitrogen, a development that would be highly attractive to synthetic organic chemists.



t-butyl carbamate (BOC)

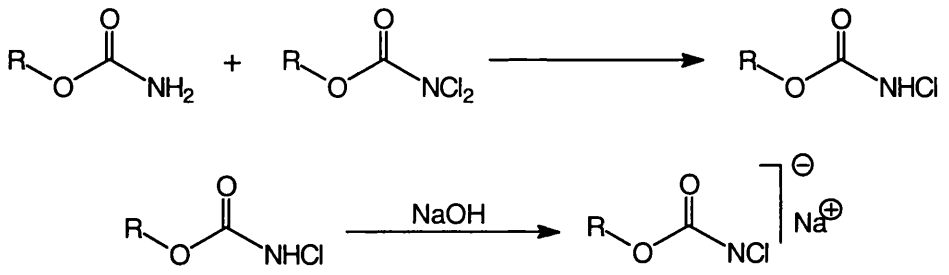


Figure 3.1.4 Synthesis of N-sodio, N-chloroamine nitrene sources

In summary, whilst it appears that PhI=NTos is the most effective nitrene source known, the activity of TosNClNa opens the possibility of a new generation of nitrene sources that are more attractive to the synthetic organic chemist. However, the yields obtained with TosNClNa do not correlate with those obtained with PhI=NTos, suggesting the existence of an alternative mechanism for nitrene formation.

3.1.6 Asymmetric Aziridination Reactions

Many of the research groups studying copper catalysed aziridination have concentrated their efforts on asymmetric aziridination since nucleophilic ring-opening of the products would allow access to a wide range of chiral compounds. Efficient synthesis of chiral compounds is a goal of many organic chemists. Generally, the approach has been to use a simple copper compound such as [Cu(OTf)] as catalyst in the presence of a chiral ligand. Some of the more common chiral ligands employed are shown in Figure 3.1.5, with particular combinations of catalysts, ligands and substrates providing yields as high as 89% and enantioselectivities as high as 98%.[49,53]

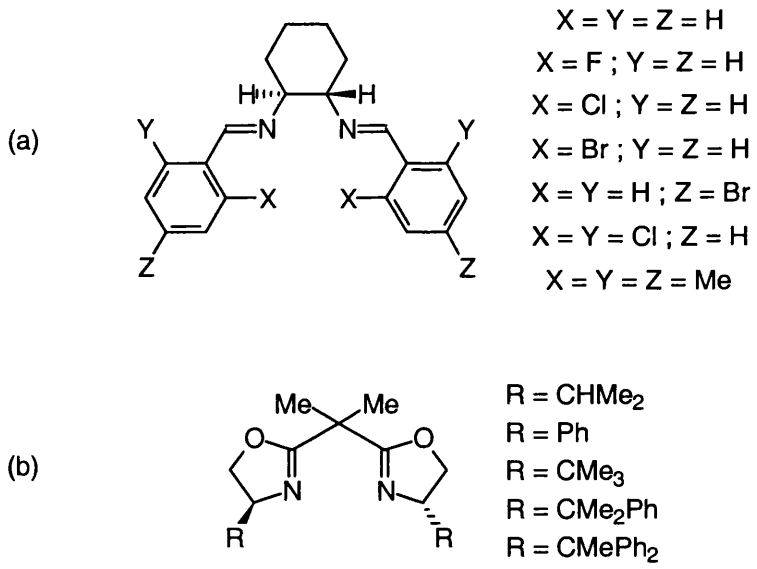


Figure 3.1.5 Chiral ligands utilised by (a) Jacobsen and (b) Evans

Evans employs the bis-oxazoline ligands shown in Figure 3.1.5(b),[53] whereas Jacobsen prefers the benzylidene derivatives of cyclohexane shown in Figure 3.1.5(a).[49] As part of his research, Jacobsen has recently reported the isolation of a complex of copper involving a chiral benzylidene derivative of cyclohexane and styrene which shows substantial interactions between the aromatic groups on the chiral ligand and those on the styrene.[50]

The enantioselective excess obtained in chiral aziridination reactions can be determined in several different ways. Many types of chiral columns for HPLC are

available, although they are expensive and it is not possible to judge beforehand which column would be most suitable for a particular chiral compound. A much more convenient, if less accurate, method is to perform ^{1}H NMR spectroscopy in the presence of a suitable chiral shift reagent. The reagent, which is a single enantiomer, loosely binds the molecule of interest, thereby forming a pair of diastereomers. The paramagnetic centre of the reagent causes a small change in the chemical shift of the product peaks which is different for each enantiomer. The signals for each enantiomer are thus separated and the relative intensities of each signal and therefore the relative concentrations of each enantiomer can be determined by integration. This method was chosen for the reactions reported in this section due to its simplicity, convenience and the ready availability of a suitable chiral shift reagent. The accuracy of this method is determined by the quality of the integration, which is in turn determined by the broadness of the peaks and their separation. However, if the separation is increased by adding more chiral shift reagent, the paramagnetic centre causes broadening of the peaks of interest, thereby negating any advantage. The low accuracy of this method necessitated an approximation of the margin of error. This was determined to be ±1% after several calculations of the enantiomeric excess of racemic aziridine.

Reactions Using A Chiral Catalyst Since $[Tp^{Menth}Cu(PPh_3)]$ could not be isolated as a pure product (see Section 2.1.2.4), aziridinations were performed using a mixture of CuCl and $TlTp^{Menth}$ as catalyst.[78] It was anticipated that this mixture would form a chiral copper complex *in situ*, possibly $[Tp^{Menth}Cu]_2$, and a precipitate of TlCl. The precipitate was removed by filtration before the catalyst solution was added to the reaction mixture. Two reactions were performed using this catalyst, the first at room temperature and the second at -78°C. The reaction at room temperature gave 87% yield of aziridine, significantly higher than the other dimeric pyrazolylborate complexes assessed (see Section 3.1.2). This high yield could be due to the increased steric strain present due to the bulky ligands, causing an increased tendency to dissociate and thus to open coordination sites for catalysis to occur. The enantioselectivity could not be

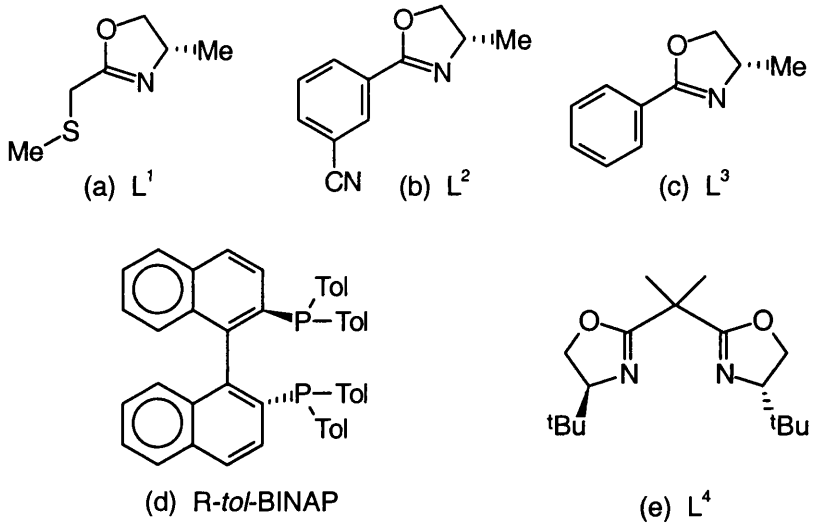
determined quantitatively due to poor separation, but the ^{1}H NMR spectrum with the chiral shift reagent showed a peak for one enantiomer that appeared to be larger than the other, thereby suggesting that a small enantiomeric excess was present. The reaction performed at -78°C gave 47% yield of aziridine but no enantioselective excess was detected.

The other chiral catalyst prepared was [Cu(Pydmdtc)$_2$] which also could not be isolated as a pure product. Two aziridination reactions were performed, one at room temperature and one at 0°C. The first reaction gave 71% yield of aziridine, consistent with other copper(II) dithiocarbamate catalysts, whilst the second gave 56% yield. Both reactions appeared to give a 2% enantioselective excess which is low, but the fact that differentiation is taking place is encouraging since the chiral carbon in this complex is distant from the catalytic centre and therefore would not be expected to exert much influence. In addition, amines with bulkier substituents on their chiral carbon atoms are commercially available (see Figure 3.1.6 below) which may allow the possibility of higher enantioselectivities using chiral dithiocarbamate catalysts derived from these amines.

(a) (*S*)-1-(2-Pyrrolidinylmethyl)pyrrolidine (b) (*S*)-2-Pyrrolidone-5-carboxylic acid

Figure 3.1.6 Commercially available chiral amines

Aziridinations Using A Copper Complex And Chirai Ligands All of the chiral ligands utilised in this section were donated to the group by others, most notably the donation by Dr Peter Heard of the three novel chiral ligands shown in Figure 3.1.7 (a), (b) and (c) below. These are 2-methylthiomethyl-4-(*S*)-methyl-1,3-oxazoline, 2-(2-cyanophenyl)-4-(*S*)-methyl-1,3-oxazoline and 2-phenyl-4-(*S*)-methyl-1,3-oxazoline respectively, henceforth referred to as L^1, L^2 and L^3.[128]



(a) L^1 (b) L^2 (c) L^3

(d) R-*tol*-BINAP (e) L^4

Figure 3.1.7 Chiral ligands

Aziridination reactions were performed using both $[Cu(MeCN)_4]ClO_4$ and $[Cu(OTf)_2]$ as the catalyst, with the reactions using $[Cu(OTf)_2]$ having to be performed in MeCN due to insolubility of the metal-ligand mixture in CH_2Cl_2.

$[Cu(MeCN)_4]ClO_4$ was assessed as a catalyst in the presence of three chiral ligands. Using L^1, 78% yield was obtained at room temperature, with 65% yield being obtained at -78°C. The enantioselectivities obtained were 6% and 10% respectively which is encouraging since the methyl substituent on the chiral carbon is relatively small and larger enantioselectivities may be obtained with larger substituents. L^2 was also assessed, although it was not expected to induce enantioselectivity since it is a monodentate ligand. As such, unless there is substantial π-bonding between the nitrogen and the copper, the ligand will freely rotate about the Cu-N bond, thereby providing no stabilisation or destabilisation of either of the enantiomeric transition states. The aziridination, performed at 0°C, gave 68% yield of aziridine, but no enantioselectivity was detected. The ligand L^4 has already been reported by Evans to provide an 89% isolated yield of aziridine with an enantioselective excess of 63% using styrene as the solvent at 0°C.[53] However, using the general aziridination procedure in CH_2Cl_2 at the same temperature, 68% yield of aziridine was obtained with an enantiomeric excess of 20%.

The fact that good yields of aziridine were obtained using $[Cu(MeCN)_4]ClO_4$ in the presence of chiral ligands suggests that these ligands do coordinate to the copper centre since, in the absence of any ligand, $[Cu(MeCN)_4]ClO_4$ is inactive as a catalyst.

Evans has reported that the electronegativity of the anion appears to have an important effect on the enantioselectivity obtained in aziridination reactions[53] and compares this with similar observations for the copper catalysed cyclopropanation system.[41] It was thus expected that a TfO^- anion would provide higher enantioselectivities than a ClO_4^- anion and therefore aziridinations using $[Cu(OTf)_2]$ were investigated.

The combination of $[Cu(OTf)_2]$ and L^1 gave 41% yield with 9% enantioselective excess, the enantioselectivity being consistent with the two results obtained using $[Cu(MeCN)_4]ClO_4$. The two monodentate ligands L^2 and L^3 did not give an enantioselectivity greater than the possible experimental error, which is not unexpected (*vide supra*). In addition, *R*-Tol-BINAP was assessed in conjunction with $[Cu(OTf)_2]$ and gave a 30% yield with 7% enantioselective excess. The only aziridinations using BINAP-based ligands thus far reported were recently published by Shi and despite having substituents that were bulkier than a tolyl group, the enantioselectivities were similarly low.[113]

3.1.7 Conclusions On Catalyst Efficiency

Many aziridination catalysts have been assessed, with $[(Ph_3P)CuCl]_4$ being perhaps the most active catalyst yet reported. It also has the advantage, along with the two other highly effective catalysts $[Cu(Et_2dtc)_2]$ and $[Tp^*Cu(PPh_3)]$, of being an air-stable complex. Copper(III) dithiocarbamate complexes with an $[FeCl_4]^-$ anion are also active catalysts, with the copper(III) centre probably being reduced during the aziridination reaction by Cl^-. Although PhI=NTos is the most active nitrene source, TosNClNa also gives good yields of aziridine and offers the potential for the generation of a new class of nitrene sources based on the N-sodio, N-haloamine structure. Many different substrates have also been

assessed, with some reactions showing the potential for the synthesis of novel compounds. Attempts to perform aziridination in an enantioselective fashion gave poor results but were still promising, with the most successful novel chiral ligand L^1 giving 10% enantiomeric excess.

3.2 MECHANISM OF AZIRIDINATION

3.2.1 Introduction

Copper catalysed aziridination is a relatively new area of research and as such, only a few studies into the mechanism of catalysis have been published. Evans[45,46,53] and Jacobsen[47,49,50] have provided the most insight, but other groups have also contributed to the discussion.[48,63,113,114] This section intends to briefly cover this information and will then discuss the mechanistic information obtained during the course of this project.

3.2.2 Evidence For Copper(I) As The Active Cataiytic Species

A good starting point for any examination of a catalytic system is the determination of the oxidation state of the active catalytic species. Evans[46,53] and Jacobsen[47] both have conflicting views on this point. Evans has shown that similar enantioselectivities can be obtained when employing either [Cu(OTf)] or [$Cu(OTf)_2$] as aziridination catalysts upon several different substrates, indicating the presence of a common oxidation state.[53] He then reasons that since PhI=NTos, in common with other iodine(III) reagents, is an oxidant, the oxidation state of the active catalyst is more likely to be copper(II) than copper(I). Jacobsen, by contrast, concentrates on the similarities between aziridination and cyclopropanation, which is generally agreed to occur by reaction of a copper(I) species to form a transient copper(III) carbene complex.[10,47] Despite the logic of Evans' argument, our research indicates a leaning towards the proposal of copper(I) as the active catalyst resting state which will be explained in full during the course of this section.

In the first instance, our research has concluded that phosphine complexes are amongst the most active catalysts for aziridination reactions using PhI=NTos and

it is also well known that phosphines are not able to complex with copper(II) except in special circumstances.[108] In an aziridination reaction using [Tp*Cu(PPh_3)], evidence was found at the end of the reaction for the continued coordination of phosphine, although whether this because of the presence of unreacted catalyst or not is not possible to say. However, the phosphine could dissociate on oxidation to copper(II), although the phosphine would also have to be oxidised to prevent the further reduction of copper.

An important result that strongly suggests the presence of copper(I) is that obtained when attempting a competition experiment between cyclopropanation and aziridination. It is generally agreed that cyclopropanation is catalysed by a copper(I) species and that copper(II) complexes are inactive, although they may be reduced *in situ* to the active copper(I) analogue. Equimolar amounts of ethyl diazoacetate and PhI=NTos were reacted with ten equivalents of styrene using [$Cu(Et_2dtc)_2$] as the catalyst in an attempt to gauge whether one type of catalysis was preferred to another, or whether they both operated by a similar process. The ^1H NMR spectrum of the reaction mixture showed that both cyclopropanation and aziridination had taken place, roughly in the ratio 4:6. A substantial amount of dimerisation of free carbene had also taken place. That cyclopropanation had taken place is not significant in itself, since it could have been catalysed by entirely different copper centres to those involved in aziridination. However, a second experiment that attempted to assess the efficiency of [$Cu(Et_2dtc)_2$] as a cyclopropanation catalyst showed that it is inactive. This therefore implies that the active species that catalysed the cyclopropanation in the competition experiment must have been produced during the aziridination cycle, since the only component that differs between the two reactions is PhI=NTos. Furthermore, it was discovered that $[Cu(Et_2dtc)]_4$ and $[Cu(Et_2dtc)_2]^-$ were also inactive as cyclopropanation catalysts, suggesting that neither of these species are formed during aziridinations using [$Cu(Et_2dtc)_2$].

This strong evidence that a copper(I) species is present during aziridination, even when catalysed by a copper(II) complex, suggests that although iodine(III)

reagents are generally regarded as oxidants, reduction is somehow taking place. This evidence is contrary to the logic used by Evans when proposing that a copper(II) complex is the active catalytic species.[53]

Two other instances of reduction taking place in the presence of PhI=NTos have been observed during the course of this investigation. In the first case, $[Co(TosNSC(NEt_2)SNTos)_2]$ was synthesised during an aziridination reaction using a cobalt(III) dithiocarbamate catalyst. This evidence is circumstantial, however, since it cannot be determined whether the reduction took place before the formation of the diamido ligand or whether it occurred because of the formation of the ligand. The second instance occurred when investigating the catalytic properties of copper(III) dithiocarbamate complexes. Although the evidence in this case points towards the reduction from copper(III) to copper(II) being caused by Cl^- released from the $[FeCl_4]^-$ anion (see Section 3.1.2), the release has to be initiated by some means, as $[Cu(Et_2dtc)_2][FeCl_4]$ is in itself relatively stable.

One other piece of evidence that points towards copper(I) being the active catalytic species relies on the ability of 2,9-dimethyl-1,10-phenanthroline (neocuproine) to specifically bind copper(I). This technique was successfully utilised by Williams in the determination of Cu^+ as the active catalytic species in the formation of NO from S-nitrosothiols.[130] However the report only referred to this property of neocuproine in aqueous solution and no evidence in the literature could be found of its use in organic media. Nevertheless, experiments were performed to determine whether neocuproine would inhibit aziridination in the same manner as during the formation of NO from S-nitrosothiols. A general aziridination reaction using $[Cu(Et_2dtc)_2]$ as catalyst was performed in the presence of one equivalent of neocuproine and 39% yield of aziridine was obtained. This corresponded to almost exactly half the yield normally obtained with $[Cu(Et_2dtc)_2]$, clearly indicating some kind of inhibition. Furthermore, a similar reaction using two equivalents of neocuproine resulted in complete inhibition.

However, these results are tempered by the fact that synthesis of a copper(II) as well as a copper(I) complex of neocuproine is possible.[131,132] The copper(II) complex is highly moisture sensitive, but the copper(I) complex, $[Cu(dmp)_2]ClO_4$, was easily synthesised as a dark orange crystalline solid from $[Cu(MeCN)_4]ClO_4$ and two equivalents of neocuproine in CH_2Cl_2. $[Cu(dmp)_2]ClO_4$ was assessed as an aziridination catalyst and gave 68% yield, contrary to expectations that it would be inactive. In fact the final reaction mixture contained large quantities of unreacted catalyst which suggests that the yield may be increased still further on addition of fresh reagents. An explanation for this behaviour is that the presence of neocuproine with $[Cu(Et_2dtc)_2]$ in the aziridination reaction mixture does not result in the formation of a copper(I) complex with neocuproine.

3.2.3 Evidence For A Mononuclear Catalytic Site

Jacobsen has produced evidence that any imido intermediate would be mononuclear in nature. Several aziridination reactions were performed using ligands of varying enantiomeric purity and a linear correlation between ligand ee and product ee was obtained.[47] Although, as Jacobsen notes, these results do not necessarily preclude polynuclear catalytic centres, a mononuclear centre clearly is more likely. Jacobsen has also performed a series of aziridination and cyclopropanation reactions using $[Cu(PF_6)]$ in the presence of chiral ligands and again a linear correlation was obtained.[47] This is a clear indication that the two reactions proceed by a similar mechanism and that similar intermediates may be involved.

3.2.4 Evidence For Aikene Precoordination

Many discussions on the mechanism of copper catalysed aziridination omit any reference to the order of reaction of reagents, possibly due to lack of evidence. The many similarities between aziridination and cyclopropanation have lead to a general acceptance that formation of a transient nitrene complex precedes alkene coordination. However, our research has provided evidence that the alkene is the first of the reagents to coordinate to the copper centre.

It has already been mentioned that alkenes have been shown to be generally only able to coordinate to copper(I), a fact which reinforces both the proposal of copper(I) as the active catalytic species and that of alkene precoordination. Perez has successfully utilised [Tp*Cu(C_2H_4)] as both a cyclopropanation and an aziridination catalyst and Jacobsen has published a crystallographic structure determination on a complex in which styrene is coordinated to a chiral copper diimine complex (see Figure 1.3.18 in Section 1.3.3.2).[50] This paper also includes spectroscopic evidence for the coordination of many other olefins, highlighting the generality of olefin coordination to copper(I).

The ability of selected copper dithiocarbamate and phosphine complexes to coordinate olefins was assessed by ^{1}H NMR spectroscopy, with the signals for coordinated alkene presumed to have a similar chemical shift to the 4.41 ppm given for the ethylene signals in [Tp*Cu(C_2H_4)].[61] The complexes [Cu(Et_2dtc)]$_4$, [Cu(Et_2dtc)$_2$], [Cu(Et_2dtc)$_2$]$^-$, [(Ph_3P)CuCl]$_4$, [(Ph_3P)$_2$CuCl] and [(Ph_3P)$_3$CuCl] were dissolved in $CDCl_3$ and either styrene or ethylene added. Styrene did not appear to coordinate to any of the complexes, but some interesting signals were detected in the spectra of the reactions of [Cu(Et_2dtc)$_2$], [Cu(Et_2dtc)$_2$]$^-$ and [(Ph_3P)$_2$CuCl] with ethylene. Surprisingly, a very small, broad peak at approximately 4.1 ppm was seen in the spectrum of [Cu(Et_2dtc)$_2$] and ethylene, with the experiments with both [Cu(Et_2dtc)$_2$]$^-$ and [(Ph_3P)$_2$CuCl] producing much more noticeable signals (at 4.4 and 4.8 ppm respectively). Despite these promising signals in the ^{1}H NMR spectra of ethylene appearing on addition of catalyst, they could not be unambiguously assigned to coordinated alkene.

If, instead of olefin precoordination, the nitrene species were to react with the copper first, the resulting imido complex would have to be stable enough to exist until an alkene could react with it. This is unlikely to be the case since a copper imido complex would be expected to be highly unstable. It would be thought that for an unstable copper imido species to react with an olefin before decomposition, a large excess of olefin would be required. In fact, research

discussed in Section 3.1.3 has shown that good yields are readily obtainable even in the presence of low concentrations of alkene.

The suggestion that insertion of a nitrene into the Cu-S bond of copper dithiocarbamate complexes is a process unrelated to aziridination (see Section 3.1.2) can also aid the proposal for olefin precoordination. Since insertion takes place in the absence of olefin, it is possible to envisage that it is the result of the decomposition of a copper imido species produced by the action of PhI=NTos on copper dithiocarbamate complexes and is the prime cause of catalyst deactivation. Indeed, an aziridination reaction was performed in which the PhI=NTos was reacted with the dithiocarbamate catalyst prior to addition of styrene. No aziridine was formed in this reaction, a result which could have been due to deactivation of the catalyst by reaction with excess nitrene. Equally, the inactivity could have been caused by catalytic decomposition of PhI=NTos prior to reaction with olefin and it was not possible to distinguish between the two processes spectroscopically.

3.2.5 Nitrene Transfer To Alkene

Evans has published evidence that the transfer of the nitrene to the alkene takes place via a concerted mechanism.[46] The possibility of a step-wise radical ring formation step was investigated by aziridination of *trans*-2-phenyl-1-vinylcyclopropane. If a radical mechanism does exist, it was expected that this substrate would undergo a cyclopropylcarbinyl rearrangement according to the sequence shown in Figure 3.2.1.

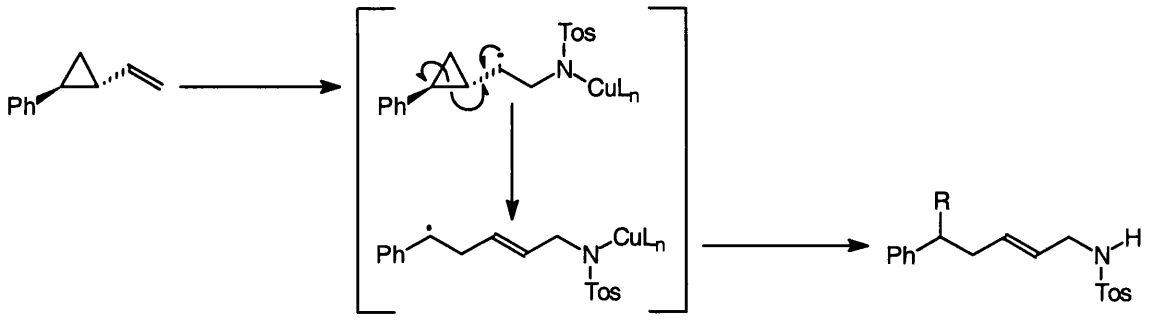


Figure 3.2.1 Cyclopropylcarbinyl rearrangement of *trans*-2-phenyl-1-vinylcyclopropane

The aziridination of *trans*-2-phenyl-1-vinylcyclopropane using PhI=NTos and [$Cu(ClO_4)$] as the catalyst gave 43% yield of aziridine and none of the rearrangement product, a result which clearly suggests a concerted mechanism for nitrene transfer.

3.2.6 Proposed Catalytic Cycle

The mechanism of copper catalysed aziridination of olefins by PhI=NTos is yet to be proven, but the investigations directed towards this aim have provided several indications as to the likely mechanism involved. The preceding sections have discussed individual aspects of the mechanism which can now be brought together to form a viable catalytic cycle. This cycle is shown pictorially in Figure 3.2.2.

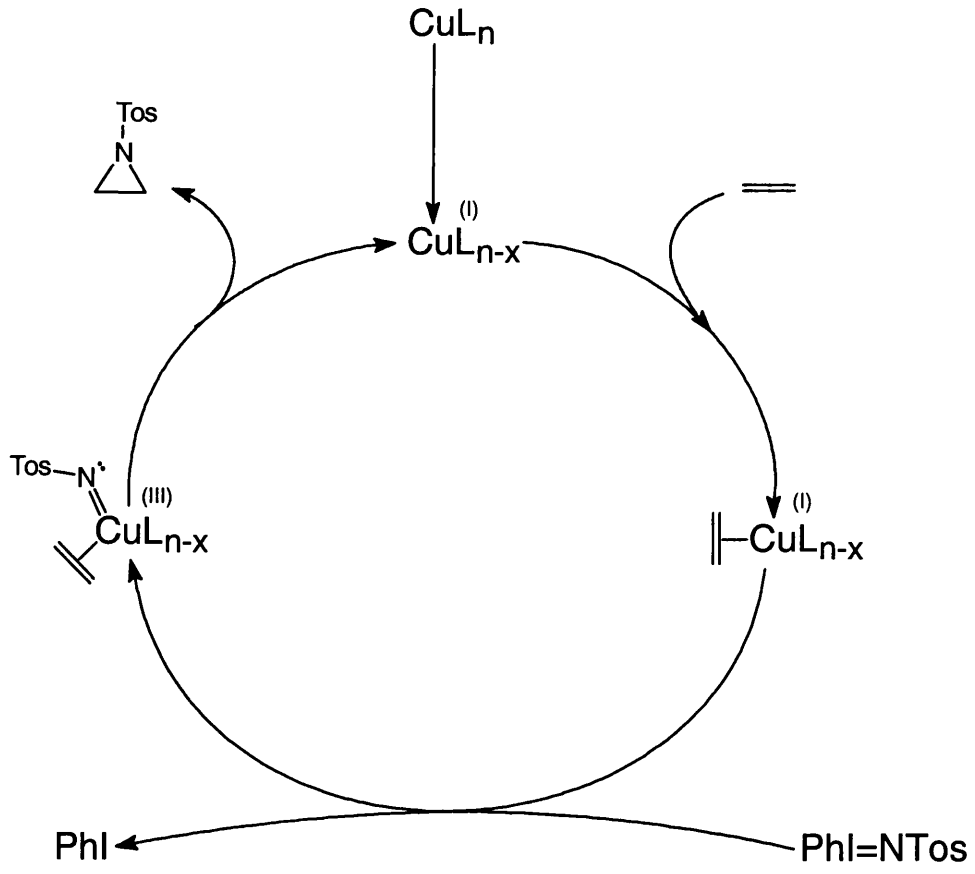


Figure 3.2.2 Proposed catalytic cycle for copper catalysed aziridination

Initial reduction of the copper pre-catalyst, if it is not already in the +1 oxidation state, to a copper(I) species takes place along with loss of a ligand, if necessary, to allow access by the other reagents to multiple open coordination sites. Once the copper(I) species has been formed, coordination of the alkene substrate takes place. This then reacts with a molecule of PhI=NTos, forming a copper(III) imido complex along with reduction of iodine to form PhI. The nitrene moiety then transfers to the alkene along with dissociation of the aziridine product reforming the initial copper(I) species to close the cycle.

3.3 CONCLUSIONS

After an initial general discussion on copper, catalysis and aziridines, this thesis has described the synthesis of many different copper complexes belonging to several different structural types. Copper complexes of all three major oxidation states were synthesised. The copper complexes were then used as catalysts in aziridination reactions and the yields of these reactions were related to the structural and solution properties of the catalysts. It was found that examples of all three major oxidation states were active catalysts, with the activity of the copper(III) complexes being thought to be due to reduction by Cl^-. Phosphine complexes were found to be the most proficient catalysts, although other complexes such as $[Cu(Et_2dtc)_2]$ also gave excellent yields. Aziridinations of many different types of substrate yielded little information, although some promising results were obtained. Although PhI=NTos was by far the best source of nitrene used, other sources were investigated and the use of TosNClNa gave good yields in some cases. This opens up the possibility of a new class of nitrene source based on N-sodio, N-haloamine compounds. Asymmetric aziridinations with novel chiral ligands also gave promising results.

Aziridination reactions with copper dithiocarbamate complexes led to the isolation and characterisation of a novel class of ligand formed by the insertion of NTos groups into Cu-S bonds. It appears that insertion results from interaction of a nitrene with the copper dithiocarbamate moiety in the absence of any substrate with which to form aziridine. This insertion reaction also appears to be

generally applicable to transition metal dithiocarbamate complexes and the crystal structures of four of these novel amido and diamido complexes were discussed.

The mechanism of aziridination was investigated and evidence was obtained for each of the individual aspects of the catalytic process: the catalyst oxidation state and its formation, the nuclearity of the catalytic site, the order of reaction of nitrene and substrate and the transfer of nitrene to substrate. A mechanism based on the evidence obtained was then proposed.

4.0 EXPERIMENTAL DETAILS

4.1 GENERAL EXPERIMENTAL

4.1.1 General Procedures

All reactions involving Cu(I) species and all aziridinations were performed under an atmosphere of nitrogen using standard Schlenk techniques unless specified otherwise. All air-sensitive complexes were stored in a Vacuum Atmospheres HE-493 glove box under an atmosphere of nitrogen. Column chromatography was performed using a 10 cm long, 2 cm diameter column of deactivated alumina with CH_2Cl_2 as eluent unless otherwise specified

4.1.2 Reagents

Nitrogen (BOC, 99.998%) was used as received. Solvents were predried over Na wire, or 3Å molecular sieves in the case of dichloromethane, before distilling from the appropriate drying agent. Na/K alloy (1:3 ratio) was used for drying diethyl ether and 40/60 petrol, K metal was used for tetrahydrofuran, Na metal was used for toluene and CaH_2 was used for dichloromethane and acetonitrile. Methanol, ethanol (95%) and acetone were used as received. CuCl was purified by washing thoroughly with dilute acetic acid followed by ethanol and diethyl ether. Excess solvent was removed under vacuum and the purified product was stored in a dry box. Chloramine-T (TosNClNa) was supplied as a dihydrate and was dehydrated carefully, due to risk of explosion, by heating to 60°C under vacuum in a thermostatically controlled water bath and was left overnight behind a blast screen. All other chemical were used as received.

$TlTp^{Menth}$ and KBp* were prepared by Ms Geeta Madar and Mr Cheuk Au respectively, both under the supervision of Dr Andrea Sella.[78] A small quantity of NaTp was obtained from Dr Derek Tocher. $[Cu(Me,^{n}Hexdtc)_2]$, $[In(Me,Etdsc)_3]$, $[Zn(Me,C_{18}H_{37}dtc)_2]$ and $[Cd(Me,^{n}Prdtc)_2]$ were given by Prof. Paul O'Brien of Imperial College. Small quantities of L^1, L^2 and L^3 were donated by Dr Peter Heard of Birkbeck College and a small amount of L^4 was obtained from Prof. William Motherwell.

4.1.3 Instrumentation

Infra-red spectra were run as KBr discs on a Nicolet 205 FT-IR spectrometer. NMR spectra were run on Varian XL200, Bruker AC300, and Varian VXR400 spectrometers. Air sensitive samples were prepared in a glove box, and were sealed in an NMR tube fitted with a Young's tap. ^{1}H NMR spectra were referenced to the residual solvent peak. FAB and EI mass spectra were both run on a VG-ZAB-SE unit which can accommodate EI and FAB probes. $APCI^+$ mass spectra were sent to the University of London central mass spectrometry service at the School of Pharmacy.

4.2 PREPARATION OF COPPER COMPLEXES

4.2.1 Copper Pyrazolylborate Complexes

Preparation of NaTp* and KTp* [75]

In a round-bottomed flask equipped with a condenser was placed KBH_4 or $NaBH_4$ (94 mmol) and 3,5-dimethylpyrazole (60 g, 625 mmol), and the whole system was placed under an atmosphere of nitrogen. The mixture was heated to 120°C until evolution of hydrogen began to slow, then the temperature was raised to 240°C until evolution of hydrogen had ceased. The molten reaction mixture was then poured into stirred 40/60 petrol (150 ml) and the solvent removed under vacuum to give a white solid which was a mixture of excess 3,5-dimethylpyrazole and product. The two components were separated by sublimation under dynamic vacuum at 100°C to give NaTp* (20.1 g, 67% yield) or KTp* (26.8 g, 85% yield), with the excess 3,5-dimethylpyrazole being recovered.

*Characterising data for NaTp**

^{1}H NMR (d_6-acetone): δ 5.54 (3H, s, C-H); 2.29 (9H, s, 3-Me); 2.00 (9H, s, 5-Me).

*Characterising data for KTp**

^{1}H NMR (d_6-acetone): δ 5.53 (3H, s, C-H); 2.16 (9H, s, 3-Me); 2.04 (9H, s, 5-Me).

Preparation of [TpCu(PPh$_3$)] and [Tp*Cu(PPh$_3$)] [62]

To NaTp or KTp* (1.27 mmol) and [CuCl] (0.126 g, 1.27 mmol) in CH_2Cl_2 (15 ml) was added with stirring a solution of PPh_3 (0.33 g, 1.27 mmol) in CH_2Cl_2 (15 ml). After 5 hours, the solution was filtered and the solvent removed under vacuum to get [TpCu(PPh$_3$)] (0.135 g, 20 % yield) which was recrystallised by allowing a warm CH_2Cl_2 solution to cool to -20°C overnight. [Tp*Cu(PPh$_3$)] (0.57 g, 72% yield) was recrystallised from CH_2Cl_2 and 40/60 petrol.

Characterising data for [TpCu(PPh$_3$)]

Mass Spectrum (FAB): (M^+) 538 (88); (M^+-pz) 471 (60); (M^+-PPh_3) 279 (50); ($CuHB(pz)_2^+$) 209 (100).

*Characterising data for [Tp*Cu(PPh$_3$)]*

Analysis (%) calculated for $C_{33}H_{37}N_6BPCu$: C, 63.61; H, 5.94; N, 13.49. Found: C, 63.46; H, 5.87; N, 13.21.

^{1}H NMR ($CDCl_3$): δ 7.32-7.67 (15H, m, aromatic); 5.61 (3H, s, CH); 2.37 (9H, s, 3- or 5-Me); 1.66 (9H, s, 5- or 3-Me).

Mass Spectrum (FAB): (M^+) 622 (30); (M^+-dmpz) 527 (48); (M^+-PPh_3) 360 (13); ($CuHB(dmpz)_2^+$) 265 (100).

Preparation of [TpCu]$_2$ and [Tp*Cu]$_2$ [58]

A mixture of [CuCl] (0.31 g, 3.125 mmol) and NaTp* (1 g, 3.125 mmol) in THF (50 ml) was stirred for 2 hours. The solvent was then removed under vacuum and the product extracted into benzene (2 x 30 ml). Recrystallisation by slow cooling to -20°C of a warm CH_2Cl_2 solution afforded colourless crystals of [Tp*Cu]$_2$ (1.95 g, 87 % yield). Preparation of [TpCu]$_2$ was identical but on a 1.27 mmol scale and yield was not determined.

Characterising data for [TpCu]$_2$

Analysis (%) calculated for $C_{18}H_{20}N_{12}B_2Cu_2$: C, 39.06; H, 3.62; N, 30.38. Found: C, 38.66; H, 3.61; N, 29.79.

IR (cm^{-1}): 2438 (m, B-H); 2403 (m, B-H); 1509 (m); 1387 (s); 1296 (s); 1126 (s).

^{1}H NMR ($CDCl_3$): δ 7.67 (6H, d, *J* = 2.1 Hz, 3-CH); 7.16 (6H, d, *J* = 1.4 Hz, 4-CH); 6.19 (6H, dd, *J* = 2.1 Hz & 1.4 Hz, 5-CH).

Mass Spectrum (FAB): (M^+-1) 552 (100); (M^+-pz) 485 (8); ($CuTp^+$) 276 (8); ($CuHB(pz)_2^+$) 209 (71).

*Characterising data for [Tp*Cu]$_2$*

Analysis (%) calculated for $C_{30}H_{44}N_{12}B_2Cu_2$: C, 49.93; H, 6.10; N, 23.30. Found: C, 49.80; H, 6.03; N, 23.58.

IR (cm^{-1}): 2529 (w, B-H); 1542 (s); 1176 (s); 1080 (m); 1036 (m); 984 (w).

^{1}H NMR ($CDCl_3$): δ 5.70 (3H, s, CH); 2.41 (9H, s, 3- or 5-Me); 1.67 (9H, s, 5- or 3-Me).

Mass Spectrum (FAB): (M^+-1) 720 (100); (M^+- $(dmpz)_2$) 518 (72); ($CuTp^{*+}$) 423 (11); ($CuHB(dmpz)_2^+$) 265 (31).

Preparation of [Tp*Cu(CO)] [18]

Carbon monoxide was bubbled through a stirred solution of [CuCl] (1.44 g, 15 mmol) and KTp* (4.54 g, 15 mmol) in THF (120 ml) of for 3 hours. The solution was filtered and the solvent removed to give an air-sensitive white solid (2.34 g, 40 % yield) which was recrystallised from CH_2Cl_2 and 40/60 petrol.

*Characterising data for [Tp*Cu(CO)]*

Analysis (%) calculated for $C_{16}H_{22}N_6BOCu$: C, 49.42; H, 5.66; N, 21.62. Found: C, 49.55; H, 5.66; N, 21.38.

IR (cm^{-1}): 2500 (m, B-H); 2061 (s, C=O); 1544 (s); 1262 (m); 1197 (s); 1178 (s); 693 (m); 642 (s).

^{1}H NMR ($CDCl_3$): δ 5.68 (3H, s, CH); 2.30 (9H, s, 3- or 5-Me); 2.25 (9H, s, 5- or 3-Me).

Mass Spectrum (FAB): (M^+) 389 (3.5); (M^+-CO) 360 (40); ($CuBH(dmpz)_2^+$) 265 (100).

Preparation of [CuTp*$_2$]

A mixture of $[CuCl_2]\cdot 2H_2O$ (0.25 g, 1.5 mmol) and NaTp* (1g, 3 mmol) in CH_2Cl_2 (50 ml) was stirred overnight (17 hours), during which time the solution became

blue. After filtration and removal of solvent under vacuum, the product was isolated as large blue crystals by overnight cooling of a hot CH_2Cl_2 solution to room temperature.

*Characterising data for [Tp*Cu]$_2$*

Analysis (%) calculated for $C_{30}H_{44}N_{12}B_2Cu$: C, 54.75; H, 6.69; N, 25.55. Found: C, 54.62; H, 6.75; N, 25.64.

IR (cm^{-1}): 2507 (m, B-H); 1548 (s); 1540 (s); 1445 (s); 845 (m); 808 (s); 768 (s); 470 (m).

Mass Spectrum (EI): (M^+) 657 (6); (M^+-dmpz) 562 (77); (M^+-2dmpz) 467 (100); ($CuTp^{*+}$-1) 359 (5); ($CuHB(dmpz)_2^+$) 265 (42); ($dmpz^+$) 96 (9).

Attempted preparation of [Tp^{Menth}Cu(PPh$_3$)]

A CH_2Cl_2 solution of [CuCl] (0.057 g, 0.576 mmol), PPh_3 (0.15 g, 0.576 mmol) and [TlTp^{Menth}] (0.43 g, 0.576 mmol) of was stirred overnight, a bright white precipitate of TlCl being formed in the process. The reaction mixture was filtered and the solvent removed from the filtrate under vacuum.

Spectroscopic data for [Tp^{Menth}Cu(PPh$_3$)]

IR (cm^{-1}): 3054 (w); 2955 (s); 2927 (s); 2866 (s); 2423 (w, B-H); 1633 (w); 1556 (w); 1478 (m); 1457 (m); 1436 (m); 1370 (m); 1310 (m); 1262 (w); 1144 (m); 1096 (m); 1024 (w); 998 (w); 802 (w); 745 (m); 696 (s); 526 (m); 506 (m).

^1H NMR ($CDCl_3$): δ 7.2-7.8 (15H, m, aromatic); 0.3-3.0 (90H, m, aliphatic).

Mass Spectrum (FAB): 1802 (2); 1366 (7); 1277 (15); 933 (8); (M^+) 858 (3); 845 (9); 691 (23); 669 (19); ($CuHB(Menthpz)_2$) 429 (100); 325 (22); 183 (12).

Preparation of [CuBp$_2$] and [CuBp*$_2$] [134]

An aqueous solution of KBp or KBp* (3 mmol) was added with stirring to an aqueous solution of [$CuCl_2$] (0.2 g, 1.5 mmol), respectively forming either a lilac or salmon pink precipitate. The mixture was stirred for a further 5 minutes and was then filtered and washed thoroughly with water. After air drying, [$CuBp_2$] (0.45 g, 83% yield) was obtained, the yield of [$CuBp^*_2$] not being determined. [$CuBp_2$] was recrystallised to give large purple crystals suitable for diffraction by

slow evaporation of a CH_2Cl_2 solution. [$CuBp^*_2$] was recrystallised by slow cooling of a hot toluene solution.

Characterising data for [$CuBp_2$]

Analysis (%) calculated for $C_{12}H_{16}N_8B_2Cu$: C, 40.28; H, 4.48; N, 31.33. Found: C, 40.24; H, 4.23; N, 31.70.

IR (cm^{-1}): 2440 (s, B-H); 2396 (m, B-H); 2345 (w, B-H); 2280 (w, B-H); 1503 (m); 1407 (s); 1307 (s); 1211 (m); 1185 (m); 1154 (m); 1064 (s); 886 (m); 764 (s); 721 (w); 634 (w).

Mass Spectrum (FAB): (M^+-2) 355 (25); (M^+-Bp) 209 (100).

Crystallographic data are summarised in Appendix 1.1

Characterising data for [$CuBp^*_2$]

Analysis (%) calculated for $C_{20}H_{32}N_8B_2Cu$: C, 51.12; H, 6.82; N, 23.86. Found: C, 51.61; H, 6.86; N, 24.35.

IR (cm^{-1}): 2459 (s, B-H); 2365 (w, B-H); 2330 (w, B-H); 2296 (m, B-H); 2253 (m, B-H); 2211 (m, B-H); 1535 (s); 1454 (m); 1423 (m); 1384 (m); 1183 (s); 1168 (s); 1113 (s); 1061 (m); 895 (m); 786 (m); 620 (m); 464 (w).

Mass Spectrum (FAB): (M^+-2) 467 (25); (M^+-dmpz) 373 (13); (M^+-Bp*) 265 (100).

Reaction of copper pyrazolylborate complexes with PhI=NTos

All of the reactions were performed using 0.15 mmol of copper complex. [Tp*Cu(CO)] and [Tp*Cu(PPh_3)] were reacted with PhI=NTos (2 equivalents) of while [Tp*Cu(C_2H_4)] / [Tp*Cu]$_2$ (1:1) was reacted with PhI=NTos (½, 1 and 10 equivalents). A CH_2Cl_2 solution (20 ml) of the copper pyrazolylborate complex was added to a stirred slurry of the PhI=NTos in CH_2Cl_2 (20 ml). In each case the reaction mixture rapidly became green in colour. The solution was stirred overnight, then the solvent was removed under vacuum. The reaction mixture was opened to air then dissolved in the minimum amount of CH_2Cl_2 which was allowed to evaporate slowly. In each case the main products were an intractable brown solid, an unidentified green solid and [$CuTp^*_2$].

4.2.2 Copper Dithiocarbamate Complexes

Attempted preparation of [Cu(Me_2dtc)] and preparation of [Cu(Et_2dtc)]$_4$ [84]

This preparation involves the use of CS_2, and therefore was performed entirely (including crystallisation) in a fumehood. Fresh, finely divided copper powder was prepared by the reaction of zinc dust with $CuSO_4$ in water. Any excess zinc was reacted with dilute HCl before the copper powder was washed with water and then acetone before being dried under vacuum.

A solution of [Cu(Me_2dtc)$_2$] or [Cu(Et_2dtc)$_2$] (0.83 mmol) in CS_2 (100 ml) was added to a round-bottomed flask containing fresh, finely divided copper powder prepared as above (0.053 g, 0.83 mmol). The mixture was stirred overnight (17 hours). In the case of [Cu(Me_2dtc)], a weak brown solution and a brown insoluble solid were obtained. After filtration, the insoluble product was washed with CH_2Cl_2 and any excess solvent was removed under vacuum. In the case of [Cu(Et_2dtc)]$_4$, a yellow solution which contained a small amount of solid was obtained. The mixture was filtered before being concentrated and then layered with Et_2O to give a yellow crystalline product (0.21g, 60% yield).

Spectroscopic data for [Cu(Me_2dtc)]

Mass Spectrum (FAB): 1215 (10); 1187 (7); 460 (54); 421 (21); 391 (24); 329 (33); 308 (93); 289 (100); 242 (21).

Characterising data for [Cu(Et_2dtc)]$_4$

Analysis (%) calculated for $C_5H_{10}NS_2Cu$: C, 28.37; H, 4.73; N, 6.62. Found: C, 28.38; H, 4.77; N, 6.85.

^{1}H NMR ($CDCl_3$): δ 4.00 (2H, q, J = 7.1 Hz, CH_2); 1.30 (3H, t, J = 7.1 Hz, CH_3).

Mass Spectrum (APCI$^+$): (Cu(Et_2dtc)$_2^+$) 356 (50); (Cu$_3$(Et_2dtc)$_3^+$) 635 (4); (Cu$_4$(Et_2dtc)$_3^+$) 698 (13); (M^+) 846 (2); (Cu$_5$(Et_2dtc)$_4^+$) 910 (11); (Cu$_5$(Et_2dtc)$_5^+$) 1059 (6); (Cu$_6$(Et_2dtc)$_5^+$) 1122 (100); (Cu$_7$(Et_2dtc)$_6^+$) 1333 (57).

Attempted preparation of [Cu(Et_2dtc)$_2$]$^-$

To a stirred solution of [Cu(Et_2dtc)]$_4$ (0.2 g, 0.95 mmol) in CH_2Cl_2 (30 ml) was added NaEt_2dtc (0.162 g, 0.95 mmol) which slowly dissolved over 20 minutes,

the solution turning a slightly darker yellow. Reaction was allowed to continue for 3 weeks, during which time small aliquots were removed and ^{1}H NMR spectra taken to assess the extent of reaction. After 17 days, reaction appeared to be complete with approximately 25 % of the reaction mixture being converted to product. $[Cu(Et_2dtc)_2]^-$ could not be isolated, the only identified products of attempted isolation under N_2 and in air being $[Cu(Et_2dtc)]_4$ and $[Cu(Et_2dtc)_2]$ respectively.

Spectroscopic data for $[Cu(Et_2dtc)_2]^-$

^{1}H NMR ($CDCl_3$): δ 3.70 (8H, q, J = 8 Hz, CH_2); 1.27 (12H, t, J = 8 Hz, CH_3).

Preparation of $[Cu(Me_2dtc)_2]$ and $[Cu(Et_2dtc)_2]$

An aqueous solution of $NaMe_2dtc{\cdot}2H_2O$ or $NaEt_2dtc{\cdot}3H_2O$ (7.45 mmol) was added with stirring to a dilute aqueous solution of $[CuCl_2]$ (0.5 g, 3.7 mmol), causing a thick, chocolate brown precipitate to appear. The reaction mixture was stirred for 4 hours, then filtered under vacuum, washed thoroughly with water (5 x 20 ml), and air dried to get pure $[Cu(Et_2dtc)_2]$ (87% yield). Crystallisation can be effected by slow evaporation of a CH_2Cl_2 solution. $[Cu(Me_2dtc)_2]$ was obtained pure in 44% yield by extraction into CH_2Cl_2, washing with water, drying over $MgSO_4$ and removal of solvent under vacuum.

Characterising data for $[Cu(Me_2dtc)_2]$

Analysis (%) calculated for $C_6H_{12}N_2S_4Cu$: C, 23.72; H, 3.95; N, 9.23. Found: C, 23.98; H, 3.98; N, 9.15.

IR (cm^{-1}): 1523 (s, C=N); 1450 (w); 1387 (s); 1248 (m); 1146 (m); 1021 (w); 978 (w).

Characterising data for $[Cu(Et_2dtc)_2]$

Analysis (%) calculated for $C_{10}H_{20}N_2S_4Cu$: C, 33.38; H, 5.56; N, 7.79; S, 35.61. Found: C, 33.33; H, 5.58; N, 7.74; S, 35.56.

IR (cm^{-1}): 1505 (s, C=N); 1432 (s); 1272 (s); 1205 (m); 1145 (m); 1070 (m); 994 (m); 910 (m); 884 (m); 569 (w).

Mass Spectrum (EI): (M^+) 359 (14); (Et_2dtc^+) 149 (17); (Et_2NCS^+) 116 (100); ($EtNCS^+$) 88 (59).

Preparation of [Cu(Pyddtc)$_2$] and attempted preparation of [Cu(Pydmdtc)$_2$]

To a solution of NaOH (1.32 g, 33 mmol) and pyrrolidine or *S*-2-pyrrolidinemethanol (33 mmol) in MeOH (40 ml) at 0°C was added dropwise CS_2 (2.51 g, 33 mmol). The reaction mixture was poured immediately into a solution of [$CuCl_2$] (2.22 g, 16.5 mmol) in water (500 ml). The dark brown precipitate thus produced was filtered, washed several times with water, and air dried to give crude product (5.28 g, 90% yield). Crystalline [Cu(Pyddtc)$_2$] was obtained by repeated dissolution in CH_2Cl_2, separation from an insoluble yellow solid by filtration and slow evaporation of solvent. For [Cu(Pydmdtc)$_2$], the brown solid was dissolved in CH_2Cl_2, washed with several portions of water, dried over $MgSO_4$ and the solvent removed under vacuum. In an effort to recrystallise the product, many combinations of MeOH, Et_2O, $PhCH_3$, CH_2Cl_2 and 40/60 petrol were used with layering and vapour diffusion techniques. In addition, a CH_2Cl_2 solution was allowed to evaporate slowly and another was cooled slowly to -20°C. None of these methods produced pure product.

Characterising data for [Cu(Pyddtc)$_2$]

Analysis (%) calculated for $C_{10}H_{16}N_2S_4Cu$: C, 33.76; H, 4.50; N, 7.88. Found: C, 33.70; H, 4.47; N, 7.46.

Mass Spectrum ($APCI^+$): (M^+) 355 (100); ($Cu_2(Pyddtc)_3^+$) 566 (19); ($Cu_3(Pyddtc)_4^+$) 921 (2).

Spectroscopic data for the brown solid

Analysis (%) found for brown solid: C, 31.82; H, 4.44; N, 5.04.

IR (cm^{-1}): 2962 (w); 2923 (w); 2873 (w); 1633 (m); 1427 (s, C=N); 1331 (m); 1221 (w); 1145 (m); 1039 (s); 961 (m); 917 (w); 802 (m).

Mass Spectrum (FAB): ($Cu_4(Pydmdtc)_3$) 782 (6); (M^+) 415 (12).

Preparation of $[Cu(R_2dtc)_2][FeCl_4]$ $R_2 = Me_2, Et_2, Pyd$ [87]

A solution of $[FeCl_3]\cdot 6H_2O$ (0.2 g, 1.23 mmol) in the minimum amount of acetone was added dropwise with stirring to a solution of $[Cu(R_2dtc)_2]$ (0.61 mmol) in benzene (50 ml). After 30 minutes, the solution was filtered and air dried to give a green solid (55 % yield). Green needle crystals were obtained by layering a CH_2Cl_2 solution with toluene or benzene. The crystals of $[Cu(Et_2dtc)_2][FeCl_4]$ were suitable for diffraction and included half a molecule of benzene per molecule of product in the crystal lattice.

Characterising data for $[Cu(Me_2dtc)_2][FeCl_4]$

Analysis (%) calculated for $C_6H_{12}N_2S_4Cl_4CuFe$: C, 14.36; H, 2.39; N, 5.58. Found: C, 14.56; H, 2.31; N, 5.43.

Characterising data for $[Cu(Et_2dtc)_2][FeCl_4]$

Analysis (%) calculated for $C_{13}H_{23}N_2S_4Cl_4CuFe$: C, 26.15; H, 3.86; N, 4.69; S, 21.46; Cl, 23.81. Found: C, 26.10; H, 3.89; N, 4.66; S, 21.46; Cl, 23.94.

IR (cm^{-1}): 1560 (s, C=N); 1458 (m); 1439 (m); 1382 (w); 1350 (m); 1281 (m); 1194 (w); 1153 (w); 1097 (w); 1073 (w); 846 (w); 682 (w).

Mass Spectrum ($APCI^+$): (M^+) 359 (100).

Crystallographic data are summarised in Appendix 1.2

Characterising data for $[Cu(Pyddtc)_2][FeCl_4]$

Analysis (%) calculated for $C_{10}H_{16}N_2S_4CuFeCl_4$: C, 21.68; H, 2.89; N, 5.06. Found: C, 21.81; H, 2.84; N; 4.58.

Preparation of $[Cu(R_2dtc)_2]ClO_4$ R = Me, Et [87]

CAUTION: The $[Cu(R_2dtc)_2]ClO_4$ complexes prepared both detonated violently on heating above 100°C and when scraped with a spatula.

An acetone solution of $[Cu(ClO_4)_2]\cdot 6H_2O$ (0.1 g, 0.278 mmol) was added dropwise to a stirred solution of $[Cu(R_2dtc)_2]$ (0.278 mmol) in $CHCl_3$ (100 ml) over 1 hour. After stirring for a further two hours, the reaction mixture was left overnight (19 hours). The $[Cu(Et_2dtc)_2]ClO_4$ remained in solution, but after

filtration and concentration of the green filtrate, needle-like crystals were obtained by layering the dark green solution with benzene. $[Cu(Me_2dtc)_2]ClO_4$ precipitated from the reaction mixture and was filtered. The resultant green solid was purified by dissolution in CH_2Cl_2, filtration, and removal of solvent under vacuum. Crystals suitable for diffraction were obtained by slow evaporation and cooling of a CH_2Cl_2 solution.

Characterising data for $[Cu(Me_2dtc)_2]ClO_4$

Analysis (%) calculated for $C_6H_{12}N_2S_4ClO_4Cu$: C, 17.87; H, 2.98; N, 6.95. Found: C, 18.10; H, 2.88; N, 6.96.

Mass Spectrum ($APCI^+$): (M^+) 303 (15).

Crystallographic data are summarised in Appendix 1.3

Characterising data for $[Cu(Et_2dtc)_2]ClO_4$

Analysis (%) calculated for $C_{11.5}H_{23}N_2O_{4.5}S_4ClCu$: C, 28.28; H, 4.71; N, 5.74. Found: C, 27.65; H, 4.50; N, 5.97.

^1H NMR (d_6-acetone): δ 4.0 (8H, q (v. broad), CH_2); 1.37 (12H, t, $J = 8$ Hz, CH_3); 1.52 (3H, s, acetone).

Mass Spectrum ($APCI^+$): (M^+) 359 (100); (Et_2NCS^+) 116 (6).

Reaction of $[Cu(Et_2dtc)_2]ClO_4$ with NEt_4Cl

$[Cu(Et_2dtc)_2]ClO_4$ (0.1 g, 0.22 mmol) was dissolved in CH_2Cl_2 under an atmosphere of N_2. Et_4NCl (0.036 g, 0.22 mmol) was then added against a counterflow of N_2 and the reaction mixture stirred for 1 hour, during which time the initial green colour of the solution changed to a dark red/brown. The solvent was removed under vacuum and the resultant solid was washed with MeOH. The insoluble black solid remaining was shown by IR and mass spectrometry to be $[Cu(Et_2dtc)_2]$.

4.2.3 Copper insertion products

This section describes only those insertion reactions from which insertion products were isolated in sufficient yield for complete characterisation. For

reactions producing lower yields and non-productive reactions, see Section 4.2.4. For the synthesis of PhI=NTos, see Section 4.4.1.

Preparation of [Cu(TosNSC(NEt$_2$)S)$_2$] and [Cu(TosNSC(NEt$_2$)SNTos)$_2$]

Under an atmosphere of N_2, a solution of [Cu(Et$_2$dtc)$_2$] (0.2 g, 0.556 mmol) in CH_2Cl_2 (approximately 30 ml) was added to a stirred suspension of PhI=NTos (0.83 g, 2.22 mmol) in CH_2Cl_2 (approximately 20 ml). On addition of the copper complex, the solution immediately changed from dark brown to dark green. After leaving to stir overnight, the solvent was removed from the clear green solution under vacuum and the resultant solid opened to air. This procedure will henceforth be referred to as the general insertion reaction. The resultant green solid was dissolved in the minimum amount of CH_2Cl_2 before being layered with toluene. This crystallisation method produced dark green crystals of [Cu(TosNSC(NEt$_2$)SNTos)$_2$] (62.1 mg, 11% of maximum yield) and dark brown crystals of [Cu(TosNSC(NEt$_2$)S)$_2$] (97.2 mg, 25% of maximum yield). These two products were separated from each other manually. The crystals of [Cu(TosNSC(NEt$_2$)S)$_2$], despite desolvating over the course of several days, were suitable for diffraction.

Characterising data for [Cu(TosNSC(NEt$_2$)S)$_2$]

Analysis (%) calculated for $C_{24}H_{34}N_4S_6O_4Cu$: C, 41.29; H, 4.87; N, 8.03. Found: C, 41.12; H, 4.71; N, 7.95.

IR (cm^{-1}): 1518 (s, C=N); 1458 (w); 1440 (m); 1383 (w); 1354 (w); 1301 (m); 1283 (m); 1200 (w); 1147 (s); 1085 (m); 1020 (w); 978 (w); 882 (m); 813 (m); 791 (w); 662 (m); 582 (m); 551 (m); 469 (w).

Crystallographic data are summarised in Appendix 1.5

Characterising data for [Cu(TosNSC(NEt$_2$)SNTos)$_2$]

Analysis (%) calculated for $C_{46}H_{58}N_6S_8O_8Cl_2Cu$: C, 45.53; H, 4.78; N, 6.93. Found: C, 45.22; H, 4.60; N, 6.75.

IR (cm^{-1}): 1638 (w); 1618 (w); 1597 (w); 1532 (m, C=N); 1495 (w); 1455 (m); 1443 (m); 1386 (w); 1353 (w); 1301 (s); 1283 (s); 1193 (w); 1148 (s); 1085 (m);

891 (s); 819 (s); 789 (m); 742 (w); 727 (w); 706 (w); 655 (m); 577 (s); 548 (m); 467 (w).

Mass Spectrum (FAB): (M^+) 1036 (9); (M^+-TosNSC(NEt_2)SNTos) 549 (7); (TosNSC(NEt_2)SNTos$^+$) 488 (15).

Preparation of [Cu(TosNSC(NMe_2)SNTos)$_2$]

The general insertion reaction was performed using [Cu(Me_2dtc)$_2$] and PhI=NTos (1:4 ratio) on a 0.329 mmol scale. Green crystals suitable for diffraction were grown by slow evaporation of a CH_2Cl_2 solution of the product. The crystals were then cleaned by repeated washing in CH_2Cl_2 in which they were only sparingly soluble.

Characterising data for [Cu(TosNSC(NMe_2)SNTos)$_2$]

Analysis (%) calculated for $C_{36}H_{44}N_6S_8O_8Cl_4Cu$: C, 37.58; H, 3.83; N, 7.31. Found: C, 37.05; H, 3.76; 7.05.

IR (cm^{-1}): 1629 (w); 1599 (w); 1551 (w, C=N); 1493 (w); 1446 (w); 1404 (w); 1301 (m); 1147 (s); 1086 (m); 1021 (w); 889 (m); 814 (s); 656 (m); 576 (s); 548 (s).

Mass Spectrum (FAB): (M^+) 980 (100); (M^+-TosNSC(NMe_2)SNTos) 521 (23); (TosNSC(NMe_2)SNTos$^+$) 460 (21).

Crystallographic data are summarised in Appendix 1.4

4.2.4 Other copper insertion reactions

This section will describe all insertion reactions attempted on copper complexes, successful or not, with the exception of those detailed in Section 4.2.3. In all cases the general insertion reaction was performed using the given ratio of complex to insertion reagent on the given scale. For the synthesis of PhI=NTos, see Section 4.4.1. Mass spectrometry was performed on the reaction mixtures to look for evidence of insertion before isolation by layering of two concentrated CH_2Cl_2 solutions with toluene and 40/60 petrol was attempted.

4.2.4.1 Insertion using Phi=NTos

Yields of identified insertion products depended greatly on the scale of reaction performed. The larger the scale the higher the yield, presumably due to a quantity of the product remaining in the crystallisation mother liquor. Ratios of reagents given are for dithiocarbamate complex : PhI=NTos.

Insertion into $[Cu(Et_2dtc)]_4$

1:4 ratio on a 0.056 mmol scale. The solution turned from pale yellow to dark brown then quickly to dark green. $[Cu(TosNSC(NEt_2)SNTos)_2]$ was isolated in 6% yield

Insertion into $[Cu(Et_2dtc)_2]$

1:2 ratio on a 0.278 mmol scale and 1:4 ratio on a 0.139 mmol scale. Both reaction mixtures turned from dark brown to dark green, but neither reaction produced any evidence of insertion by mass spectrometry.

insertion into $[Cu(Pyddtc)_2]$

1:5 ratio on a 0.281 mmol scale. The solution turned from dark brown to dark green and. The mass spectrum showed evidence for the existence of $[Cu(TosNSC(CH_2)_4SNTos)_2]$, however, none could be isolated.

Insertion into $[Cu(Pydmdtc)_2]$

1:5 ratio on a 0.048 mmol scale. The reaction mixture was clear after approximately 10 minutes and after removal of solvent under vacuum the resultant solid was a dull orange colour. The mass spectrum showed no evidence of insertion.

Insertion into $[Cu(TosNSC(NEt_2)S)_2]$

1:4 ratio on a 0.0186 mmol scale. The solution turned slowly from pale brown to a dark green colour and $[Cu(TosNSC(NEt_2)SNTos)_2]$ was isolated in 7% yield.

Insertion into $[Cu(Me_2dtc)_2][FeCl_4]$

A reaction of a 1:4 ratio on a 0.2 mmol gave an immediate colour change from dark green to dark red. On exposure to air, however, the solution became green. Slow evaporation of this solution gave only $TosNH_2$ (by ^1H NMR) and the starting material $[Cu(Me_2dtc)_2][FeCl_4]$ (by mass spectrometry and elemental analysis). A reaction of a 1:10 ratio on a 0.2 mmol scale gave a slow colour change to a greeny brown colour. The mass spectrum showed evidence for the existence of $[Cu(TosNSC(NMe_2)SNTos)_2]$ but none was able to be isolated.

4.2.4.2 insertion using TosNClNa

Ratios of reagents given are for dithiocarbamate complex : TosNClNa

insertion into $[Cu(Me_2dtc)_2]$

1:4 ratio on a 0.165 mmol scale. The dark brown solution changed overnight to a cloudy green. $[Cu(TosNSC(NEt_2)SNTos)_2]$ was isolated and identified by IR spectroscopy.

Insertion into $[Cu(Et_2dtc)_2]$

1:10 ratio on a 0.278 mmol scale. The dark brown solution changed overnight to a cloudy green, which was filtered, reduced in volume and left overnight. The solution and the white solid thus produced were separated by filtration, the solvent then being allowed to evaporate to give 0.2g product (69% yield).

4.2.4.3 Insertion using PhI=O

Ratios of reagents given are for dithiocarbamate complex : PhI=O

insertion into $[Cu(Et_2dtc)_2]$

1:6 ratio on a 0.139 mmol scale. The dark brown solution changed to a cloudy green over 3 hours. After 2 hours exposure to air, the green product became brown and the mass spectrum only showed evidence for the existence of the starting material.

An identical reaction was performed under the strict exclusion of air. The product remained green, but no evidence of insertion was found in the mass spectrum.

4.2.4.4 Insertion using ethyl diazoacetate

Ratios of reagents given are for dithiocarbamate complex : ethyl diazoacetate

Insertion into $[Cu(Et_2dtc)_2]$

1:19 ratio on a 0.14 mmol scale. No colour change was noted and only the starting material $[Cu(Et_2dtc)_2]$ could be identified and isolated.

Insertion into $[Cu(Et_2dtc)]_4$

1:22 ratio on a 0.236 mmol scale. The initially pale yellow colour of the solution darkened slightly overnight. No insertion products were identified, but a clear, high-boiling liquid was noticed in the solvent trap. This was tentatively identified as $EtO_2CCH{=}CHCO_2Et$ on the basis of its ^1H NMR and mass spectra.

Characterising data for $EtO_2CCH{=}CHCO_2Et$

^1H NMR ($CDCl_3$): δ 6.87 (1H, s, CH); 6.25 (1H, s, CH); 4.27 (4H, q, J = 7 Hz, CH_2); 1.33 (6H, t, J = 7 Hz, CH_3).

Mass Spectrum (FAB): (M^+) 173 (100).

4.2.5 Copper Phosphine Complexes

Preparation of $[(Ph_3P)_nCuCl]$ n = 1, 2, 3 [17]

A mixture of [CuCl] (0.25 g, 2.5 mmol) and PPh_3 (0.655 g, 2.5 mmol or 1.31 g, 5 mmol or 1.97 g, 7.5 mmol) in THF (approximately 50 ml) was refluxed under N_2 for 5 hours. If the reaction mixture became cloudy, more THF was added and the solution returned to reflux until the reaction mixture became clear. The solution was filtered under N_2 while still hot, then placed in a freezer at -20°C overnight. Pure crystalline $[(Ph_3P)_2CuCl]$ (76% yield) and $[(Ph_3P)_3CuCl]$ (74% yield) were thus obtained. Crude $[(Ph_3P)CuCl]_4$ (35% yield) was recrystallised by slow cooling to 5°C of a hot CH_2Cl_2 solution.

Characterising data for $[(Ph_3P)CuCl]_4$

Analysis (%) calculated for $C_{72.5}H_{61}P_4Cu_4Cl_5$: C, 58.53; H, 4.10; N, 0.00. Found: C, 58.52; H, 3.90; N, 0.00.

IR (cm^{-1}): 1478 (m); 1433 (s); 1095 (m); 1025 (s); 745 (s); 693 (s); 523 (s); 500 (s).

^1H NMR ($CDCl_3$): δ 7.6-7.1 (45H, m, aromatic); 3.73 (2H, m, CH_2O (THF)); 1.84 (2H, m, CH_2 (THF)).

^{31}P NMR (CH_2Cl_2): δ 4.69 (4P, s (broad), PPh_3).

Mass Spectrum (FAB): (M^+-Cl) 686 (3); ($Cu(PPh_3)_2^+$) 587 (29); ($CuPPh_3^+$) 325 (49); (PPh_3^+) 262 (42).

Characterising data for $[(Ph_3P)_2CuCl]$

Analysis (%) calculated for $C_{40}H_{38}OP_2CuCl$: C, 69.06; H, 5.47; N, 0.00. Found: C, 68.76; H, 5.46; N, 0.00.

IR (cm^{-1}): 3050 (w); 2967 (w); 2862 (w); 1480 (m); 1433 (s); 1184 (w); 1093 (m); 1066 (m); 1027 (w); 998 (w); 909 (w); 744 (s); 695 (s); 512 (s).

^1H NMR ($CDCl_3$): δ 7.45-7.15 (30H, m, aromatic); 3.71 (4H, m, CH_2O (THF)); 1.82 (4H, m, CH_2 (THF)).

^{31}P NMR (CH_2Cl_2): δ 2.28 (2P, s, PPh_3).

Mass Spectrum (FAB): (M^++Cu) 687 (28); (M^+) 623 (2); (M^+-Cl) 587 (100); ($CuPPh_3^+$) 325 (94); (PPh_3^+) 262 (98).

Characterising data for $[(Ph_3P)_3CuCl]$

Analysis (%) calculated for $C_{56}H_{49}OP_3CuCl$: C, 72.96; H, 5.32; N, 0.00. Found: C, 72.48; H, 5.34; N, 0.00.

IR (cm^{-1}): 3052 (w); 1480 (m); 1434 (s); 1093 (m); 1068 (w); 1027 (w); 774 (s); 696 (s); 515 (s); 480 (m).

^1H NMR ($CDCl_3$): δ 7.4-7.1 (45H, m, aromatic); 3.78 (2H, m, CH_2O (THF)); 1.84 (2H, m, CH_2 (THF)).

^{31}P NMR (CH_2Cl_2): δ 1.88 (3P, s, PPh_3).

Mass Spectrum (FAB): ($Cu(PPh_3)_2^+$) 587 (81); ($CuPPh_3^+$) 325 (78); (PPh_3^+) 262 (100).

Preparation of $[Cu(dppe)_2]ClO_4$

A solution of $[Cu(MeCN)_4]ClO_4$ (0.2 g, 0.61 mmol) in MeCN (30 ml) was added to a stirred slurry of dppe (0.487 g, 1.22 mmol) in MeCN (30 ml) and left to stir overnight. After removal of solvent under vacuum, the crude product was purified by precipitation of impurities. This was effected by layering a CH_2Cl_2 solution of the crude product with MeOH, filtering and removing the solvent under vacuum. Pure product (0.25 g, 42% yield) was thus obtained.

Characterising data for $[Cu(dppe)_2]ClO_4$

Analysis (%) calculated for $C_{52}H_{48}N_0O_4P_4ClCu$: C, 65.07; H, 5.01; N, 0.00. Found: C, 64.48; H, 4.91; N, 0.00.

^1H NMR ($CDCl_3$): δ 7.4-7.0 (20H, m, aromatic); 2.46 (4H, m, CH_2).

Mass Spectrum (FAB): (M^+) 859 (69); (M^+-dppe) 461 (100); ($CuPPh_2^+$) 248 (46).

4.2.6 Preparation of other copper complexes

Preparation of $[Cu(MeCN)_4]ClO_4$

Initially, $[Cu(MeCN)_4](ClO_4)_2$ was obtained by recrystallising $[Cu(H_2O)_6](ClO_4)_2$ from anhydrous MeCN. A mixture of $[Cu(MeCN)_4](ClO_4)_2$ (2.3 g, 5.4 mmol) and freshly prepared Cu powder (0.34 g, 5.4 mmol) in MeCN (50ml) was refluxed under N_2 until the solution became colourless. While still hot, the solution was filtered under N_2 into a warmed schlenk tube using a heated filter cannula. The solution was then cooled slowly to 5°C and the supernatant solvent was decanted to give the crystalline product (1.36 g, 39% yield).

Characterising data for $[Cu(MeCN)_4]ClO_4$

Analysis (%) calculated for $C_8H_{12}N_4O_4ClCu$: C, 29.36; H, 3.67; N, 17.13. Found: C, 29.43; H, 3.62; N, 17.04.

IR (cm^{-1}): Reacts readily with moisture to give a spectrum identical to that of $[Cu(H_2O)_6](ClO_4)_2$.

^1H NMR ($CDCl_3$): δ 2.17 (12H, s, Me).

Preparation of $[Cu(OTf)_2]$

To a stirred 10% aqueous solution of TfOH (12.6 mmol, 19 ml) was added in small portions $[CuCO_3]\cdot[Cu(OH)_2]\cdot H_2O$ (0.775 g, 3.24 mmol) and the reaction was stirred overnight. After filtration of the excess starting copper compound, the water was removed under vacuum to give a blue solid. This product was dehydrated by heating under vacuum using a water bath containing freshly boiled water (at higher temperatures, the product decomposed) to give a white solid. $[Cu(OTf)_2]$ is extremely hygroscopic and as such, all attempts at characterisation resulted in partial hydration of the product.

4.3 PREPARATION OF OTHER METAL COMPLEXES

4.3.1 Dithiocarbamate complexes

Preparation of $[Ni(Et_2dtc)_2]$ and $[Co(Et_2dtc)_3]$

An aqueous solution of $NaEt_2dtc\cdot 3H_2O$ (0.63 g, 2.8 mmol) was added to a stirred dilute aqueous solution of $[NiCl_2]\cdot 6H_2O$ or $[CoCl_2]\cdot 6H_2O$ (0.34 g, 1.4 mmol), a green precipitate being instantly obtained. The reaction mixture was stirred for 30 minutes, then filtered under vacuum and air dried. The crude product was recrystallised by layering a CH_2Cl_2 solution with 40/60 petrol to get pure crystalline $[Ni(Et_2dtc)_2]$ (0.44 g, 88% yield) or pure crystalline $[Co(Et_2dtc)_3]$ (0.21 g, 63% yield).

Characterising data for $[Ni(Et_2dtc)_2]$

Analysis (%) calculated for $C_{10}H_{20}N_2S_4Ni$: C, 33.80; H, 5.63; N, 7.89. Found: C, 33.80; H, 5.70; N, 7.90.

^1H NMR ($CDCl_3$): δ 3.62 (8H, q, J = 7 Hz, CH_2); 1.25 (12H, t, J = 7 Hz, CH_3).

Mass Spectrum (FAB): (M^+) 354 (81).

Characterising data for $[Co(Et_2dtc)_3]$

Analysis (%) calculated for $C_{15}H_{30}N_3S_6Co$: C, 35.79; H, 5.96; N, 8.35. Found: C, 35.66; H, 5.97; N, 8.26.

IR (cm^{-1}): 2975 (w); 2929 (w); 2868 (w); 1489 (s, C=N); 1457 (s); 1435 (s); 1376 (w); 1355 (w); 1268 (s); 1214 (m); 1135 (m); 1077 (w).

^{1}H NMR ($CDCl_3$): δ 3.84 (6H, sx, J = 6 Hz, CH_2); 3.62 (6H, sx, J = 6 Hz, CH_2); 1.28 (18H, t, J = 6 Hz, CH_3).

Mass Spectrum (FAB): (M^+) 503 (7); (M^+-Et_2dtc) 355 (100); (M^+-2Et_2dtc) 207 (9); (Et_2NCS^+) 116 (26).

4.3.2 Insertion products

This section describes only those insertion reactions from which insertion products were isolated in sufficient yield for complete characterisation. For reactions producing lower yields and non-productive reactions, see Section 4.3.3. For the synthesis of PhI=NTos, see Section 4.4.1.

Preparation of [Ni(TosNSC(NEt$_2$)S)$_2$]

The general insertion reaction was performed using [Ni(Et_2dtc)$_2$] and PhI=NTos (1:6 ratio) on a 0.28 mmol scale. The initial dull green colour gradually changed to a dark blue/green colour. The reaction mixture was left to stir overnight and then allowed to settle, affording a pale blue precipitate and a green solution. After filtration, the blue solid was dissolved in CH_2Cl_2 and the solvent was allowed to evaporate slowly, dark blue crystals suitable for diffraction being produced.

Characterising data for [Ni(TosNSC(NEt$_2$)S)$_2$]

Analysis (%) calculated for $C_{24}H_{34}N_4S_6O_4Ni$: C, 41.56; H, 4.91; 8.08. Found: C, 41.88; H, 4.43; N, 7.48.

IR (cm^{-1}): 1630 (m); 1598 (w); 1520 (s, C=N); 1459 (w); 1440 (m); 1383 (w); 1354 (w); 1314 (m); 1281 (m); 1201 (w); 1149 (s); 1085 (m); 1020 (w); 869 (w); 814 (m); 665 (m); 583 (m); 550 (m).

^{1}H NMR ($CDCl_3$): δ 8.69 (4H, d, J = 5 Hz, 2-aromatic); 7.37 (4H, d, J = 5 Hz, 3-aromatic); 3.62 (4H, q, J = 4.6 Hz, CH_2); 3.36 (4H, q, J = 4.6 Hz, CH_2); 2.42 (6H, s, Tos-CH_3); 1.17 (4H, q, J = 4.6 Hz, Et-CH_3); 0.99 (4H, q, J = 4.6 Hz, Et-CH_3).

Mass Spectrum (FAB): (M^+) 693 (50); (M^+-Tos) 538 (8); (Ni(TosNSC(NEt$_2$)S)$^+$) 376 (12).

Crystallographic data are summarised in Appendix 1.6

Preparation of [Co(TosNSC(NEt$_2$)SNTos)$_2$]

This complex could only be isolated from aziridination reaction mixtures using [Co(Et$_2$dtc)$_3$] as the catalyst. For attempts to prepare the complex directly, see Section 4.3.3 below. The general aziridination procedure was used, the reaction mixture stirred overnight and the solvent then removed under vacuum to give a green solid. On addition of CH_2Cl_2, the green product dissolved leaving a sparingly soluble blue solid. This was dissolved completely in CH_2Cl_2 and slow evaporation of the solvent produced crystals suitable for diffraction.

Characterising data for [Co(TosNSC(NEt$_2$)SNTos)$_2$]

Analysis (%) calculated for $C_{38}H_{48}N_6S_8O_8Co$: C, 44.23; H, 4.66; N, 8.15. Found: C, 43.76; H, 4.78; N, 7.98.

IR (cm^{-1}): 1634 (w); 1599 (w); 1527 (m, C=N); 1494 (w); 1445 (w); 1314 (s); 1150 (s); 1087 (m); 873 (s); 819 (m); 793 (w); 663 (m); 581 (m); 551 (m).

Mass Spectrum (FAB): (M^+) 1032 (4); (Co(TosNSC(NEt$_2$)SNTos)$^+$) 546 (5); (Tos^+) 155 (100).

Crystallographic data are summarised in Appendix 1.7

4.3.3 Other insertion reactions

This section will describe all insertion reactions attempted on metal complexes other than copper, successful or not, with the exception of those detailed in Section 4.3.2. In all cases the general insertion reaction was performed using the given ratio of complex to PhI=NTos on the given scale. For the synthesis of PhI=NTos, see Section 4.4.1. Mass spectrometry was performed on the reaction mixtures to look for evidence of insertion before attempting isolation by layering of two concentrated CH_2Cl_2 solutions with toluene and 40/60 petrol.

Insertion into [Zn(Me,C$_{18}$H$_{37}$dtc)$_2$]

1:10 ratio on a 0.128 mmol scale. The solution changed overnight from clear to orange, but no product could be isolated.

Insertion into [$Ni(Et_2dtc)_2$]

1:10 ratio on a 0.14 mmol scale. Solution changed slowly from dull green to brown, eventually lightening to a pale orange colour. The mass spectrum showed no evidence of insertion.

Insertion into [$Co(Et_2dtc)_3$]

A reaction of a 1:6 ratio on a 0.0569 mmol scale gave a greeny brown solution. The mass spectrum showed no evidence of insertion, but had a large peak for starting material. The starting material [$Co(Et_2dtc)_3$] was isolated on crystallisation of the reaction mixture. A reaction of a 1:14 ratio on a 0.197 mmol scale gave a clear orange brown solution after 4 hours, but the mass spectrum showed no sign of insertion.

4.3.4 Miscellaneous Complexes

Preparation of $NEt_4[FeCl_4]$

To EtOH (50 ml) cooled in an ice bath was added in small portions $[FeCl_3]\cdot 6H_2O$ (0.5 g, 1.85 mmol) until all had dissolved. This solution was then added dropwise to a stirred solution of NEt_4Cl (0.306 g, 1.85 mmol) in EtOH (100 ml), a bright yellow precipitate being instantly formed. The reaction mixture was filtered and the yellow product washed thoroughly with EtOH before recrystallisation by slow cooling of a hot MeOH solution.

Characterising data for $NEt_4[FeCl_4]$

Analysis (%) calculated for $C_8H_{20}NCl_4Fe$: C, 29.27; H, 6.10; N, 4.27. Found: C, 29.29; H, 6.20; N, 4.04.

4.4 PREPARATION OF MISCELLANEOUS COMPOUNDS

4.4.1 Nitrene Sources

Preparation of PhI=NTos

KOH (1.09 g, 19.4 mmol) was dissolved in MeOH (30 ml) and the mixture cooled in an ice bath. $TosNH_2$ (1.33 g, 7.75 mmol) was added and the mixture was stirred. Once the $TosNH_2$ had all dissolved, $PhI(OAc)_2$ (2.5 g, 7.75 mmol) was

added in one portion and the reaction mixture was left to stir for 3 hours. The clear yellow solution was then poured into water (250 ml) and cooled to 5°C overnight. The pale yellow precipitate thereby produced was filtered and air dried before any residual water was removed under vacuum. The product was purified by adding dried MeCN (100 ml) under N_2 using Schlenk techniques. The product was insoluble but residual $TosNH_2$ dissolved. The pure product was isolated by filtration, washing with more dried MeCN and air drying. A yield of approximately 70% was possible, with yields greatly determined by the reaction time, the time taken to precipitate from the water/MeOH mixture and the dryness of the MeCN.

Characterising data for PhI=NTos

Analysis (%) calculated for $C_{13}H_{12}NSO_2I$: C, 41.82; H, 3.22; N, 3.75. Found: C, 41.93; H, 3.23; N, 3.72.

^1H NMR (d_6-DMSO): δ 7.70-7.00 (9H, m, aromatic); 2.25 (3H, s, CH_3).

Mass Spectrum (CI): (M^+) 377 (7); (Tos^+) 157 (100).

Preparation of Ph_3P=NTos

This reaction was performed entirely under an atmosphere of N_2. A solution of PPh_3 (0.176 g, 0.67 mmol) in CH_2Cl_2 (30 ml) was added to a stirred slurry of PhI=NTos (0.25 g, 0.67 mmol) in CH_2Cl_2 (30 ml) and the reaction mixture was stirred for 3 hours. The slightly cloudy reaction mixture was filtered, reduced in volume, the product then being precipitated by addition of 40/60 petrol. After filtration, any excess solvent was removed under vacuum before the product was stored in a dry box.

Characterising data for Ph_3P=NTos

^1H NMR ($CDCl_3$): δ 7.75-7.35 (5H, m, Ph); 7.54 (2H, d, J = 8 Hz, 2-aromatic); 6.98 (2H, d, J = 8 Hz, 3-aromatic); 2.28 (3H, s, Tos-CH_3).

^{31}P NMR (CH_2Cl_2): δ 20.92.

Preparation of Me_2S=NTos

This reaction was performed entirely in a fumehood. A solution of TosNClNa·$2H_2O$ (2.9 g, 11 mmol) in MeOH (20 ml) was added very slowly to a stirred solution of Me_2S (1.5 g, 24.2 mmol) in MeOH (20 ml). The reaction mixture was allowed to stand in a water bath at approximately 60°C for 5 hours. After the removal of solvent under vacuum, the resultant solid was crushed with a pestle and mortar, washed thoroughly with water (to remove NaCl), filtered and air dried to get crude product (1.15 g, 50% yield). This product was shown by ^{1}H NMR to contain 7% $TosNH_2$ which was removed by recrystallisation from a hot CH_2Cl_2 solution.

Characterising data for Me_2S=NTos

^{1}H NMR ($CDCl_3$): δ 7.79 (2H, d, J = 8.3 Hz, 2-aromatic); 7.26 (2H, d, J = 8.3 Hz, 3-aromatic); 2.71 (6H, s, SMe_2); 2.41 (3H, s, Tos-CH_3).

Mass Spectrum (FAB): (M^+) 232 (100).

Preparation of $TosN_3$

A solution of NaN_3 (3.5 g, 53.8 mmol) in water (10 ml) was added to a stirred solution of TosCl (8.5 g, 44.6 mmol) in EtOH (50 ml). If any NaN_3 precipitated from solution, small quantities of water were added until the NaN_3 redissolved. The reaction mixture was stirred overnight, then the product was extracted into CH_2Cl_2 before drying over $MgSO_4$, filtration and removal of solvent under vacuum gave a colourless oily liquid. Column chromatography was then used to isolate the pure product.

Characterising data for $TosN_3$

Analysis (%) calculated for $C_5H_7N_3SO_2$: C, 42.64; H, 3.55; N, 21.32; S, 16.24. Found: C, 42.84; H, 3.45; N, 21.54; S, 16.45.

^{1}H NMR ($CDCl_3$): δ 7.85 (2H, d, J = 8.5 Hz, 2-aromatic); 7.41 (2H, d, J = 8.5 Hz, 3-aromatic); 2.49 (3H, s, Tos-CH_3).

Mass Spectrum (EI): (M^+) 197 (9); (Tos^+) 155 (94); (Tos^+-SO_2) 91 (98); (N_2^+) 28 (100).

Preparation of EtO_2CNHCl

EtO_2CNCl_2 (8.17 g, 51.7 mmol) was mixed with EtO_2CNH_2 (4.56 g, 51.2 mmol) in a round-bottomed flask. The flask was stoppered, covered in tin foil and stirred for 24 hours. A small aliquot was removed for ^1H NMR, which showed the product to be 83% pure. The remainder was stored in the dark at 5°C.

Spectroscopic data for EtO_2CNHCl

^1H NMR ($CDCl_3$): δ 6.53 (1H, s (broad), NH); 4.24 (2H, q, J = 7.1 Hz, CH_2); 1.30 (3H, t, J = 7.1 Hz, CH_3).

4.4.2 Preparation of other compounds

Preparation of PhI=O

$PhI(OAc)_2$ (0.5 g, 1.55 mmol) was crushed in a pestle and mortar before being transferred to a round-bottomed flask. A small amount of water was added to loosen the solid before stirring and dropwise addition over 45 minutes of a 1M aqueous solution of NaOH (30 ml, 30 mmol). The reaction mixture was stirred for 2 hours and was then filtered, washed well with water and air dried. The resultant solid was crushed in a pestle and mortar and was triturated thoroughly with $CHCl_3$ before washing with $CHCl_3$, filtering and air drying. Pure product (0.78 g, 57% yield) was thus obtained.

Characterising data for PhI=O

Analysis (%) Calculated for C_6H_5IO: C, 32.73; H, 2.27; N, 0.00; I, 57.73. Found: C, 32.70; H, 2.00; N, 0.00; I, 57.58.

4.5 GENERAL AZIRIDINATION REACTIONS

Catalyst (0.048 mmol) in CH_2Cl_2 (25 ml) was added to a stirred slurry of PhI=NTos (0.18 g, 0.48 mmol) and styrene (0.5 g, 4.8 mmol) in CH_2Cl_2 (25 ml). The reaction mixture was stirred overnight and the solvent removed under vacuum. A sample of the reaction mixture was taken for ^1H NMR. If the $CDCl_3$ solution was cloudy, it was filtered through a small plug of Fuller's earth. The yield of the reaction was calculated by comparing the integrals of the aziridine with those of $TosNH_2$ (the product of hydrolysis of unreacted PhI=NTos).

Aziridinations were repeated until two closely corresponding yields (±6%) were obtained. This normally involved performing two or three aziridinations. Percentage yields of aziridine are summarised in Tables 4.1-4.5 shown below, being the mean of the two most closely corresponding yields. The aziridine was isolated from some reaction mixtures by performing column chromatography. Isolated yields were between 5% and 25% lower than those calculated from ^1H NMR spectra.

Catalyst	Yield (%)
$[TpCu(PPh_3)]$	29
$[TpCu]_2$	77
$[Tp^*Cu(PPh_3)]$	80
$[Tp^*Cu]_2$	63
$[Tp^*Cu(CO)]$	100
$[CuTp^*_2]$	5
$[CuBp_2]$	40
$[CuBp^*_2]$	42

Table 4.1 Yields of aziridinations using copper pyrazolylborate catalysts

Catalyst	Yield (%)
$[Cu(Et_2dtc)_2]$ *	69
$[Cu(Et_2dtc)]_4$	78
$[Cu(Me_2dtc)_2]$	70
$[Cu(Et_2dtc)_2]$	80
$[Cu(Pyddtc)_2]$	82
$[Cu(S\text{-}Pydmdtc)_2]$	71
$[Cu(Me,{}^nHexdtc)_2]$	83
$[Cu(Me_2dtc)_2][FeCl_4]$	55
$[Cu(Et_2dtc)_2][FeCl_4]$	76
$[Cu(Pyddtc)_2][FeCl_4]$	51
$[Cu(Me_2dtc)_2]ClO_4$	0
$[Cu(Et_2dtc)_2]ClO_4$	5

* Mixture of 25% $[Cu(Et_2dtc)_2]$ and 75% $[Cu(Et_2dtc)]_4$

Table 4.2 Yields of aziridinations using copper dithiocarbamate catalysts

Catalyst	Yield (%)
$[(Ph_3P)CuCl]_4$	90
$[(Ph_3P)_2CuCl]$	91
$[(Ph_3P)_3CuCl]$	85
$[Cu(dppe)_2]ClO_4$	86

Table 4.3 Yields of aziridinations using copper phosphine catalysts

Catalyst	Yield (%)
$[CuCl]$	0
$[CuCl_2]$	0
$[Cu(OTf)_2]$	0
$[Cu(MeCN)_4]ClO_4$	0
$[Cu_2(MeCO_2)_4]\cdot 2H_2O$	80
$[Cu(TosNSC(NEt_2)S)_2]$	0
$[Cu(TosNSC(NEt_2)SNTos)_2]$	25
$[Cu(dmp)_2]ClO_4$	68

Table 4.4 Yields of aziridinations using miscellaneous copper catalysts

Catalyst	Yield (%)
$[FeCl_4]NEt_4$	5
$[Ni(Et_2dtc)_2]$	3
$[Co(Et_2dtc)_3]$	13
$[Zn(Me,C_{18}H_{37}dtc)_2]$	2
$[In(Me,Etdsc)_3]$	2
$[Cd(Me,^nPrdtc)_2]$	10

Table 4.5 Yields of aziridinations using miscellaneous metal catalysts

Aziridination using $[Cu(Et_2dtc)_2]ClO_4$ in the presence of $NEt_4[FeCl_4]$

The general aziridination procedure was performed using an equimolar mixture of $[Cu(Et_2dtc)_2]ClO_4$ and $NEt_4[FeCl_4]$ as the catalyst. A 43 % yield of aziridine was obtained.

Aziridination using $[Cu(Et_2dtc)_2]ClO_4$ in the presence of NEt_4Cl

The general aziridination procedure was performed using an equimolar mixture of $[Cu(Et_2dtc)_2]ClO_4$ and NEt_4Cl as catalyst. On addition of CH_2Cl_2 to the catalyst, a brown solution was obtained, which turned green during the reaction. A 72 % yield of aziridine was obtained.

Aziridinations in MeCN

Three general aziridination reactions were performed in MeCN instead of CH_2Cl_2, all using $[Cu(MeCN)_4]ClO_4$ as catalyst. The first reaction was worked up as soon as the reaction mixture had become clear. No aziridine was obtained from this reaction. The second reaction was allowed to run overnight (i.e. the same reaction time as under the general reaction conditions) and gave 25% yield of aziridine. The third reaction was allowed to run for 7 days and also gave 25% yield.

Aziridinations using $[Cu(MeCN)_4]ClO_4$ in the presence of dppe

The general aziridination reaction was performed twice in MeCN using a mixture of $[Cu(MeCN)_4]ClO_4$ with 1 and 2 equivalents of dppe as the catalyst. The clear reaction mixture became green and then yellow during the reaction, ^1H NMR spectroscopy showing 10 % and 5 % yield of aziridine respectively.

Characterising data for N-Tosyl-2-Phenylaziridine

Analysis (%) calculated for $C_{15}H_5NSO_2$: C, 65.93; H, 5.49; N, 5.13. Found: C, 65.65; H, 5.51; N, 5.01.

^1H NMR: δ 7.90 (2H, d, J = 8.5 Hz, 2-aromatic); 7.36 (2H, d, J = 8.5 Hz, 3-aromatic); 3.80 (1H, dd, J = 7.0 Hz & 4.5 Hz, 2-ring CH); 3.01 (1H, d, J = 7.0 Hz, 3-ring CH); 2.46 (3H, s, Tos-CH_3); 2.41 (1H, d, J = 4.5 Hz, 3-ring CH).

4.6 REVERSE AZIRIDINATION REACTIONS

The procedure for reverse aziridinations is identical to the general procedure, except that the substrate is placed with the catalyst instead of with the PhI=NTos before the start of the reaction. Yields are identical to within ±5% of those obtained using the general procedure.

4.7 AZIRIDINATIONS USING DIFFERENT STOICHIOMETRIES

The procedure is identical to the general procedure, except that the relevant ratios of reagents were altered to those shown. Percentage yields of the reactions of [Tp*Cu(PPh_3)], [Cu(Et_2dtc)$_2$], and [(Ph_3P)CuCl]$_4$ using different ratios of reagents are summarised in Table 4.6, 4.7 and 4.8 respectively. Ratios are expressed as substrate : PhI=NTos : catalyst.

Ratio of Reagents			Yield (%)
Substrate	PhI=NTos	Catalyst	
10	*1*	*0.1*	80
10	*1*	*0.05*	66
10	*1*	*0.01*	66
5	*1*	*0.1*	86
1	*1*	*0.1*	60

Table 4.6 Yields of aziridinations using [Tp*Cu(PPh_3)] as catalyst

Ratio of Reagents			Yield (%)
Substrate	PhI=NTos	Catalyst	
10	*1*	*0.1*	90
10	*1*	*0.05*	93
5	*1*	*0.1*	96
1	*1*	*0.1*	90
1	*1*	*0.05*	88
1	*1*	*0.01*	67

Table 4.7 Yields of aziridinations using [(Ph_3P)CuCl]$_4$ as catalyst

Ratio of Reagents			Yield (%)
Substrate	PhI=NTos	Catalyst	
10	*1*	*0.1*	80
10	*1*	*0.05*	83
10	*1*	*0.01*	86
5	*1*	*0.1*	89
1	*1*	*0.1*	64

Table 4.8 Yields of aziridinations using $[Cu(Et_2dtc)_2]$ as catalyst

Evans' aziridination procedure [46]

The general aziridination procedure was used with 5 equivalents of styrene and 5 mol % of $[Cu(MeCN)_4]ClO_4$ as catalyst. The reaction was performed in MeCN at 0°C and 31 % yield of aziridine was obtained.

4.8 AZIRIDINATIONS OF DIFFERENT SUBSTRATES

The procedure used is identical to the general procedure, except that a variety of substrates other than styrene were utilised.

4.8.1 Aziridination of alkenes

Percentage yields of the aziridinations of acrylonitrile, cyclohexene and methyl methacrylate using different catalysts are summarised in Table 4.9 below.

Catalyst	Styrene	Acrylonitrile	Cyclohexene	Methyl Methacrylate
$[Tp^*Cu(PPh_3)]$	80	24	14	15
$[Tp^*Cu(CO)]$	100	31	3	26
$[CuTp^*_2]$	5			3
$[Cu(Et_2dtc)]_4$	78	39		
$[Cu(Et_2dtc)_2]$	80		14	19
$[Cu(Et_2dtc)_2][FeCl_4]$	76	24		
$[Cu(Et_2dtc)_2]ClO_4$	5	4		
$[(Ph_3P)CuCl]_4$	90	60	29	

Table 4.9 Yields of aziridinations of alkenes

Characterising data for N-tosyl-2-cyanoaziridine

^{1}H NMR: δ 7.87 (2H, d, *J* = 8.0 Hz, 2-aromatic); 7.43 (2H, d, *J* = 8.0 Hz, 3-aromatic); 3.25 (1H, dd, *J* = 7.0 Hz & 4.0 Hz, 2-ring CH); 2.90 (1H, d, *J* = 7.0 Hz, 3-ring CH); 2.67 (1H, d, *J* = 4.0 Hz, 3-ring CH); 2.50 (3H, s, Tos-CH_3).

Characterising data for N-tosyl-2,3-tetramethyleneaziridine

^{1}H NMR ($CDCl_3$): δ 7.84 (2H, d, *J* = 10.3 Hz, 2-aromatic); 7.34 (2H, d, *J* = 10.3 Hz, 3-aromatic); 2.99 (2H, m, ring CH); 2.46 (3H, s, Tos CH_3); 1.81 (4H, m, 2-ring CH_2); 1.52-1.15 (4H, m, 3-ring CH_2).

Characterising data for N-tosyl-2-methyl-2-methoxycarbonylaziridine

^{1}H NMR ($CDCl_3$): δ 7.84 (2H, d, *J* = 8.3 Hz, 2-aromatic); 7.33 (2H, d, *J* = 8.3 Hz, 3-aromatic); 3.75 (3H, s, OMe); 2.79 (1H, s, 3-ring CH); 2.71 (1H, s, 3-ring CH); 2.44 (3H, s, Tos-CH_3); 1.89 (3H, s, Me).

4.8.2 Aziridination of dienes and trienes

Aziridination of 1,5-cyclooctadiene

On addition of 1,5-cyclooctadiene to PhI=NTos, a vigorously exothermic reaction took place resulting in a dark orange slurry. The reaction mixture was dissolved in CH_2Cl_2, stirred for 2 hours and then the solvent was removed under vacuum to give a pale yellow solid, identified as $TosNH_2$ by ^{1}H NMR spectroscopy.

A reverse aziridination reaction was performed using [Tp*Cu(C_2H_4)] / $[Tp^*Cu]_2$ (1:1) as the catalyst. The solution became slightly green on addition of diene and became darker green on addition of PhI=NTos.

Spectroscopic data

^{1}H NMR ($CDCl_3$): δ 7.70 (d, *J* = 10.0 Hz, 2-aromatic); 7.3 (d, *J* = 10 Hz, 3-aromatic); 4.06 (td, *J* = 5.0 & 9.0 Hz); 3.40 (d, *J* = 8.0 Hz).

Aziridination of 1,3-cyclooctadiene

The general aziridination procedure was performed using [Tp*Cu(C_2H_4)] / [Tp*Cu]$_2$ (1:1) as the catalyst. The initially colourless solution became green and darkened as the reaction proceeded.

Spectroscopic data

^{1}H NMR ($CDCl_3$): δ 5.90-5.30 (m); 3.38 (d, *J* = 7.5 Hz); 2.99 (m); 2.35-1.30 (m).

Aziridination of bicyclo-[2.2.1]-1,5-heptadiene

The general aziridination procedure was performed using [Tp*Cu(C_2H_4)] / [Tp*Cu]$_2$ (1:1) as the catalyst. The solution turned green slowly during the course of the reaction. ^{1}H NMR of the reaction mixture showed a high yield of an unidentified product which was isolated by column chromatography.

Spectroscopic data

^{1}H NMR ($CDCl_3$): δ 7.67 (2H, d, *J* = 8.0 Hz, 2-aromatic); 7.28 (2H, d, *J* = 8.0 Hz, 3-aromatic); 6.27 (1H, dd, *J* = 7.9 Hz & 1.0 Hz, olefinic); 6.11 (1H, dd, *J* = 5.5 Hz & 2.7 Hz, olefinic); 5.23 (1H, dd, *J* = 7.9 Hz & 1.0 Hz, olefinic); 5.19 (1H, dd, *J* = 5.7 Hz & 2.7 Hz, olefinic); 4.71 (1H, s (broad), NH); 2.63 (1H, m, alkyl); 2.40 (3H, s, Tos-CH_3); 1.70 (2H, dtd, *J* = 10.2 Hz, 4.1 Hz & 0.9 Hz, alkyl); 1.28 (1H, d, *J* = 10.4 Hz, alkyl).

Mass Spectrum (FAB): 106 (100); 155 (28); (mono-aziridine) 262 (89); 361 (5); 467 (5); 562 (6); 785 (9).

The spectra themselves are shown in Appendix 2

Aziridination of cycloheptatriene

The general aziridination procedure was performed using [Tp*Cu(C_2H_4)] / [Tp*Cu]$_2$ (1:1) as the catalyst. After reaction overnight the reaction mixture was a dark yellow colour. Neither ^{1}H NMR or FAB mass spectrometry gave any evidence for the presence of aziridine.

Aziridination of 2,5-dimethyihexa-1,5-diene

The general aziridination procedure was performed using [Tp*Cu(C_2H_4)] / [Tp*Cu]$_2$ as the catalyst.

Spectroscopic Data

^{1}H NMR ($CDCl_3$): δ 7.85-7.2 (m, Tos-aromatic); 5.90-4.90 (m, olefinic); 3.33 (d, J = 6.7 Hz); 2.95 (m); 2.38 (s, Tos-CH_3); 2.3-1.2 (m, alkyl).

4.8.3 Aziridinations of other substrates

Addition of nitrene to PhN=NPh

[Cu(Et_2dtc)$_2$] was used as the catalyst. ^{1}H NMR indicated the presence of PhN=NPh and TosNH_2 only.

Addition of nitrene to DMAD

[Cu(Et_2dtc)$_2$] was used as catalyst, the solution changing from dark brown to green during the reaction. Neither ^{1}H NMR nor FAB mass spectrometry showed any evidence of an organic product.

Addition of nitrene to ^{n}PrC≡C^{n}Pr

[Cu(Et_2dtc)$_2$] was used as the catalyst and the colour of the solution changed from dark brown to green to yellow during the reaction. The ^{1}H NMR spectrum obtained showed four ill-defined peaks at δ 4.35, 3.45, 2.20 and 1.35 not attributable to the starting alkyne. The FAB mass spectrum contained a small (2%) peak for the 2-azirine with a series of peaks at lower m/e values separated by 14 mass units. The spectrum also contained a peak corresponding to Tos (34%) and a peak corresponding to ^{n}PrC(N)C^{n}Pr (10%).

4.9 AZIRIDINATIONS USING DIFFERENT NITRENE SOURCES

In all cases the general aziridination procedure was followed using the appropriate nitrene source. In each case the catalyst used is specified.

Aziridination using $TosNH_2$

$[Tp^*Cu]_2$ was used as the catalyst and no colour change was observed during the reaction. ^1H NMR showed no evidence of aziridination.

Aziridination using $Me_2S{=}NTos$

$[Cu(Et_2dtc)_2]$ was used as the catalyst and no colour change was observed during the reaction. The solution was opened to air and transferred to a round-bottomed flask and stirred for a further day before the reaction was worked up in the normal way. The ^1H NMR spectrum showed no sign of any aziridine but $Me_2S{=}NTos$ and $TosNH_2$ were identified. Crystals of $[Cu(Et_2dtc)_2]$ were isolated and identified by IR spectroscopy.

Aziridination using $[Mo(Et_2dtc)_2(N^tBu)_2]$

A mixture of $[Tp^*Cu(C_2H_4)]$ / $[Tp^*Cu]_2$ (1:1) was used as the catalyst and the reaction was performed on 1/3 normal scale (using 0.16 mmol $[Mo(Et_2dtc)_2(N^tBu)_2]$). The reaction was run over 4 days during which time no colour change was observed. A CH_2Cl_2 solution of PPh_3 (0.16 mmol) was added and the reaction continued a further 2 days. ^1H NMR showed no evidence of aziridine.

Aziridination using $TosNClNa{\cdot}2H_2O$

The reaction was performed using $[Cu(Et_2dtc)_2]$, $[(Ph_3P)CuCl]_4$ and $[Tp^*Cu(PPh_3)]$ as the catalyst. The yields of aziridine were 44%, 0% and 73% respectively.

Aziridination using TosNClNa

$[Cu(Et_2dtc)_2]$ was used as catalyst and 45% yield of aziridine was obtained.

4.10 ASYMMETRIC AZIRIDINATIONS

The enantiomeric excess of the product was determined in each case by ^1H NMR using a chiral shift reagent. The chiral shift reagent employed was tris[3-(heptafluoropropyl-hydroxymethylene)-(+)-camphorato] praseodymium(III), 40 mg being added to a $CDCl_3$ solution of aziridine (10 mg). The experimental

error in this process was estimated to be ±1% after performing several enantiomeric excess determinations on racemic aziridine.

4.10.1 Aziridinations using $[Cu(Pydmdtc)_2]$

The general aziridination procedure was performed twice, at room temperature and at 0°C. The first reaction gave 71% yield of aziridine with 2% ee and the second gave 56 % yield with 2% ee.

4.10.2 Aziridinations using $[Cu(MeCN)_4]ClO_4$ and chiral ligands

Aziridination using L^1

The general reaction procedure was performed twice, once at room temperature and once at -78°C. The first reaction gave 78% yield in 6% ee and the second gave 65% yield in 10% ee.

Aziridination using L^2

The general reaction procedure was performed, giving 56% yield of aziridine but no enantioselectivity could be detected.

Aziridination using L^4

The general aziridination procedure was performed at 0°C. A 68% yield of aziridine was obtained in 20%ee.

4.10.3 Aziridinations using $[Cu(OTf)_2]$ and chirai iigands

In each case the general aziridination reaction was performed in MeCN due to the insolubility of the $[Cu(OTf)_2]$-ligand combination in CH_2Cl_2. 1.2 equivalents of the chiral ligand were used with $[Cu(OTf)_2]$ as the catalyst and the reaction was performed at 0°C. Yields and enantiomeric excesses are given in Table 4.10.

Chiral Ligand	Yield (%)	ee (%)
L^1	90	9
L^2	91	1
L^3	85	1
BINAP	86	1

Table 4.10 Yields and enantioselectivities of chiral aziridinations

4.10.4 Aziridinations using [CuCl] and $TlTp^{Menth}$

The general aziridination procedure was performed twice using 1.2 equivalents of $TlTp^{Menth}$, once at room temperature and once at -78°C. In both cases a bright white precipitate (believed to be TlCl) formed instantly and was removed from the reaction mixture by filtration prior to removal of solvent under vacuum. The first reaction gave 87% yield of aziridine but the ee could not be determined due to paramagnetic impurities. The second reaction gave 47% yield of aziridine, but no enantiomeric excess was detected.

4.11 MISCELLANEOUS REACTIONS

4.11.1 Aziridination in the presence of water

The general aziridination reaction was performed using $[Cu(Et_2dtc)_2]$ as catalyst and a mixture of CH_2Cl_2 (30 ml) and water (10 ml) as the solvent. A 57% yield of aziridine was obtained.

4.11.2 Aziridination using catalysts pre-reacted with nitrene

A CH_2Cl_2 solution (20 ml) of $[Tp^*Cu(C_2H_4)]$ / $[Tp^*Cu]_2$ (1:1) was added to a stirred slurry of PhI=NTos in CH_2Cl_2 (20 ml). The reaction mixture was stirred overnight before being added to a stirred CH_2Cl_2 solution (20 ml) of styrene. After a further day of reaction the solvent was removed under vacuum, the ^1H NMR spectrum of the reaction mixture showing no sign of aziridine.

4.11.3 Aziridinations in the presence of ethyl diazoacetate

The general aziridination procedure was performed using $[Cu(Et_2dtc)_2]$ as the catalyst and using equal amounts of PhI=NTos and N_2CHCO_2Et. The ^1H NMR

spectrum showed resonances for aziridine, cyclopropane and $EtO_2CCH=CHCO_2Et$ (formed by dimerisation of the carbene moiety) roughly in the ratio 6:4:2 as estimated by the ratio of CH_2 resonances in the cyclopropane and dimer signals (δ 4.20 and 4.27 respectively) to those of the aziridine.

4.11.4 Cyclopropanation reactions

The following procedure was performed using $[Cu(Et_2dtc)]_4$, $[Cu(Et_2dtc)_2]^-$, $[Cu(Et_2dtc)_2]$ and $[(Ph_3P)CuCl]_4$ as catalyst. To a stirred CH_2Cl_2 solution (20 ml) of catalyst (0.096 mmol) and styrene (1 g, 9.6 mmol) was added dropwise over 3 hours a CH_2Cl_2 solution (70 ml) of N_2CHCO_2Et (0.11 g, 0.96 mmol). The reaction mixture was stirred overnight, filtered if cloudy, then the solvent was removed under vacuum. The first three reactions showed no evidence of cyclopropanation. The reaction with $[(Ph_3P)CuCl]_4$, however, resulted in a ^1H NMR and a mass spectrum with strong evidence for the formation of a cyclopropane.

Characterising data for 1-(ethylacetato)-2-phenyl cyclopropane

^1H NMR ($CDCl_3$): δ 4.20 (3H, t, J = 7.0, CH_3); 3.90 (2H, q, J = 7.0, ethyl CH_2); 2.54 (1H, m); 2.10 (1H, m); 1.93 (1H, m); 1.62 (1H, m).

Mass Spectrum (FAB): (M^+) 190 (27); (M^+-Et) 162 (5); (M^+-OEt) 145 (20); (M^+-O_2Et) 127 (6); (M^+-CO_2Et) 117 (100).

The general aziridination procedure was performed twice, replacing PhI=NTos with N_2CHCO_2Et and using $[Cu(Et_2dtc)]_4$ and $[Cu(Et_2dtc)_2]$ as catalysts. No evidence of cyclopropanation was found.

4.11.5 Epoxidation reactions

The general aziridination reaction was performed using $[Cu(Et_2dtc)_2]$ as the catalyst and replacing PhI=NTos with PhI=O. No evidence of epoxidation was found by ^1H NMR spectroscopy.

4.11.6 Neocuproine experiments

Preparation of $[Cu(dmp)_2]ClO_4$

To a stirred CH_2Cl_2 solution (30 ml) of $[Cu(MeCN)_4]ClO_4$ (0.1 g, 0.306 mmol) was added a solution of 0.159 g (0.765 mmol) of 2,9-dimethyl-1,10-phenanthroline in CH_2Cl_2 (20 ml). The solution immediately turned a red colour and after 1 hour of reaction, the solvent was removed under vacuum. The resultant crude product was recrystallised by slow evaporation of a CH_2Cl_2 solution.

Characterising data for $[Cu(dmp)_2]ClO_4$

Analysis (%) Calculated For $C_{29.5}H_{25}N_4Cl_2O_4Cu$: C, 55.07; H, 4.02; N, 9.01. Found: C, 55.69; H, 3.78; N, 9.00.

^1H NMR ($CDCl_3$): δ 8.53 (2H, d, J = 4.0 Hz, aromatic); 8.16 (2H, s, aromatic); 7.82 (2H, d, J = 4.0 Hz, aromatic); 2.48 (6H, s, Me).

Mass Spectrum (FAB): (M^+) 479 (100); (M^+-dmp) 271 (56).

Aziridination in the presence of neocuproine

The general aziridination reaction was performed using $[Cu(Et_2dtc)_2]$ with 1 and 2 equivalents of neocuproine as catalyst. In both cases the brown catalyst solution turned red during the reaction. The first reaction gave 39% yield of aziridine and the second showed no sign of aziridine. The mass spectrum of the second reaction mixture also showed a large peak corresponding to a $Cu(dmp)^+$ fragment.

4.11.7 Aziridinations without catalyst

Reaction of styrene and TosNClNa

Styrene (0.5 g, 4.8 mmol) and TosNClNa (0.11 g, 0.48 mmol) were stirred overnight in CH_2Cl_2 (30 ml). The solution was then filtered and the solvent removed under vacuum. The ^1H NMR spectrum gave no evidence of aziridine.

Reaction of styrene with $[Cu(TosNSC(NEt_2)SNTos)_2]$ and $[Cu(TosNSC(NEt_2)S)_2]$

Styrene (0.5 g, 4.8 mmol) and $[Cu(TosNSC(NEt_2)SNTos)_2]$ (0.039 g, 0.0379 mmol) were dissolved in CH_2Cl_2 (40 ml) under an atmosphere of N_2 and stirred for 1 week. The reaction mixture was then opened to air and stirred for a further week. A small aliquot was removed, the ^1H NMR and mass spectra of which showed no evidence of aziridine. Water (10 ml) was added to the reaction mixture which was stirred for a further 2 days before the CH_2Cl_2 was allowed to evaporate. The crystals of $[Cu(TosNSC(NEt_2)SNTos)_2]$ thus formed were removed manually before the water was removed under vacuum. The ^1H NMR and mass spectra both showed evidence of aziridine formation.

An identical procedure was performed with $[Cu(TosNSC(NEt_2)S)_2]$. However, no evidence of aziridine was found in the ^1H NMR or the mass spectra of either sample.

4.11.8 Olefin coordination experiments

Coordination of styrene

In each experiment, two drops of styrene were added to a $CDCl_3$ solution of the relevant complex. The coordination experiment was performed using $[Cu(Et_2dtc)]_4$, $[Cu(Et_2dtc)_2]^-$, $[Cu(Et_2dtc)_2]$, $[Co(Et_2dtc)_3]$, $[(Ph_3P)CuCl]_4$, $[(Ph_3P)_2CuCl]$ and $[(Ph_3P)_3CuCl]$. In the case of $[Cu(Et_2dtc)_2]^-$, the sample was prepared in a glove box. The resultant ^1H NMR spectrum was compared to that of styrene. None of the experiments showed any evidence of coordination.

Coordination of ethylene

In each experiment a $CDCl_3$ NMR solution of the desired complex was prepared. Ethylene was then bubbled through the solution for approximately 5 seconds. The coordination experiment was performed using $[Cu(Et_2dtc)]_4$, $[Cu(Et_2dtc)_2]^-$, $[Cu(Et_2dtc)_2]$, $[Co(Et_2dtc)_3]$, $[(Ph_3P)CuCl]_4$, $[(Ph_3P)_2CuCl]$ and $[(Ph_3P)_3CuCl]$. In the case of $[Cu(Et_2dtc)_2]^-$, the NMR sample was prepared in a glove box and the ethylene was added via a narrow needle through a subaseal. All the ^1H NMR spectra were compared to that of ethylene. The $[Cu(Et_2dtc)]_4$, $[Co(Et_2dtc)_3]$,

$[(Ph_3P)CuCl]_4$ and $[(Ph_3P)_3CuCl]$ experiments showed no evidence of coordination. The $[Cu(Et_2dtc)_2]^-$ experiment showed a small peak at δ 4.4, the $[Cu(Et_2dtc)_2]$ experiment showed a very small, broad peak at δ 4.1 and the $[(Ph_3P)_2CuCl]$ experiment showed a noticeable, sharp peak at δ 4.8.

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APPENDICES

Appendix 1.1 - Crystallographic data for [$CuBp_2$]

Empirical Formula	$C_6 H_8 B Cu_{0.5} N_4$
Crystal System	Orthorhombic
Space Group	P bca
a, Å	14.390(3)
b, Å	6.1770(10)
c, Å	17.810(4)
α, deg	90
β, deg	90
γ, deg	90
Volume, $Å^3$	1583.1(5)
Z	8
Calculated Density Mg/m^3	1.500
F(000)	732
Crystal Size, mm	0.78 x 0.62 x 0.22
Wavelength, Å	0.71073
Theta Range, deg	2.69 to 25.06
Index Ranges	0<=h<=17; -7<=k<=0; -21<=l<=21
Data Measured	2739
Unique Data	1396
No. of Parameters	106
R	0.0311
R_w	0.0844
Largest Peak/Hole, $e/Å^{-3}$	0.276 and -0.821

Atomic coordinates ($x10^4$) for [$CuBp_2$].

	x	y	z
Cu	0	0	0
N(1)	588(1)	-307(3)	1004(1)
N(2)	96(1)	-1029(3)	1602(1)
N(3)	-861(1)	-2411(3)	220(1)
N(4)	-1188(1)	-2776(3)	920(1)
C(1)	688(2)	-1585(4)	2147(1)
C(2)	1580(2)	-1224(4)	1907(1)
C(3)	1484(2)	-434(4)	1190(1)
C(4)	-1112(2)	-4109(4)	-197(1)
C(5)	-1609(2)	-5558(4)	239(2)
C(6)	-1635(1)	-4652(3)	935(1)
B(1)	-972(2)	-1128(4)	1555(1)

Bond Lengths [Å] for [$CuBp_2$]

Cu(1)-N(3)#1	1.976(2)	N(3) -C(4)	1.335(3)
Cu(1)-N(3)	1.976(2)	N(3) -N(4)	1.351(2)
Cu(1)-N(1)	1.987(2)	N(4) -C(6)	1.326(3)
Cu(1)-N(1)#1	1.987(2)	N(4) -B(1)	1.552(3)
N(1) -C(3)	1.334(3)	C(1) -C(2)	1.371(3)
N(1) -N(2)	1.355(2)	C(2) -C(3)	1.375(3)
N(2) -C(1)	1.336(3)	C(4) -C(5)	1.384(4)
N(2) -B(1)	1.541(3)	C(5) -C(6)	1.359(3)

Bond Angles [deg] for [$CuBp_2$]

N(3)#1-Cu(1)-N(3)	180.0	C(4)	-N(3)	-Cu(1)	130.6(2)
N(3)#1-Cu(1)-N(1)	89.07(6)	N(4)	-N(3)	-Cu(1)	121.81(12)
N(3) -Cu(1)-N(1)	90.93(6)	C(6)	-N(4)	-N(3)	109.4(2)
N(3)#1-Cu(1)-N(1)#1	90.93(6)	C(6)	-N(4)	-B(1)	131.0(2)
N(3) -Cu(1)-N(1)#1	89.07(6)	N(3)	-N(4)	-B(1)	119.5(2)
N(1) -Cu(1)-N(1)#1	180.0	N(2)	-C(1)	-C(2)	109.3(2)
C(3) -N(1) -N(2)	106.9(2)	C(1)	-C(2)	-C(3)	104.6(2)
C(3) -N(1) -Cu(1)	129.8(2)	N(1)	-C(3)	-C(2)	110.4(2)
N(2) -N(1) -Cu(1)	121.14(13)	N(3)	-C(4)	-C(5)	109.7(2)
C(1) -N(2) -N(1)	108.8(2)	C(6)	-C(5)	-C(4)	105.0(2)
C(1) -N(2) -B(1)	131.7(2)	N(4)	-C(6)	-C(5)	109.2(2)
N(1) -N(2) -B(1)	119.4(2)	N(2)	-B(1)	-N(4)	105.4(2)
C(4) -N(3) -N(4)	106.7(2)				

Symmetry transformations used to generate equivalent atoms : #1 = -x, -y, -z

Appendix 1.2 - Crystallographic data for $[Cu(Et_2dtc)_2][FeCl_4]\cdot\frac{1}{2}C_6H_6$

Formula	$C_{13}H_{23}Cl_4CuFeN_2S_4$
Crystal System	Triclinic
Space Group	P 1 bar
a, Å	7.970(2)
b, Å	12.207(3)
c, Å	13.2324(12)
α, deg	103.816(13)
β, deg	99.030(13)
γ, deg	92.19(2)
Volume, $Å^3$	1230.8(4)
Z	2
Calculated Density Mg/m^3	1.610
F(000)	604
Crystal Size, mm	0.30 x 0.24 x 0.10
Wavelength, Å	0.71073
Theta Range, deg	2.60 to 25.05
Index Ranges	0<=h<=9; -14<=k<=14; -15<=l<=15
Data Measured	4573
Unique Data	4245
No. of Parameters	229
R	0.0526
R_w	0.1182
Largest Peak/Hole, $e/Å^{-3}$	0.495 and -0.596

Atomic coordinates (x10^4) for $[Cu(Et_2dtc)_2][FeCl_4]\cdot\frac{1}{2}C_6H_6$.

	x	y	z
Fe(1)	2497(1)	808(1)	2679(1)
Cl(1)	1853(3)	-874(2)	1619(2)
Cl(2)	4900(3)	835(2)	3726(2)
Cl(3)	2666(3)	2075(2)	1764(2)
Cl(4)	489(3)	1197(2)	3652(2)
Cu(1)	-5000	5000	0
Cu(2)	0	5000	0
S(1)	-4703(2)	4750(1)	1614(1)
S(2)	-3573(2)	3467(1)	-172(1)
S(3)	1396(2)	3478(1)	-465(1)
S(4)	-727(2)	4583(1)	-1732(1)
N(1)	-2893(6)	2949(4)	1707(4)
N(2)	790(6)	2727(4)	-2595(4)
C(1)	-3601(7)	3606(5)	1157(4)
C(2)	-2954(8)	3152(5)	2848(5)
C(3)	-1430(10)	3906(7)	3524(5)
C(4)	-1973(9)	1984(5)	1234(5)
C(5)	-3031(12)	891(7)	982(8)
C(6)	525(7)	3459(5)	-1754(4)
C(7)	1928(9)	1813(6)	-2524(6)
C(8)	3549(11)	2012(7)	-2910(8)
C(9)	-79(9)	2771(6)	-3657(4)
C(10)	-1662(11)	1970(7)	-4025(6)
C(21)	-4587(17)	-5665(11)	-4349(8)
C(22)	-3713(12)	-4690(13)	-4191(7)
C(23)	-5870(16)	-6004(8)	-5162(10)

Bond Lengths [Å] for $[Cu(Et_2dtc)_2][FeCl_4]\cdot\frac{1}{2}C_6H_6$

Fe(1)-Cl(2)	2.175(2)	S(4) -C(6)	1.724(6)
Fe(1)-Cl(1)	2.183(2)	N(1) -C(1)	1.296(7)
Fe(1)-Cl(3)	2.192(2)	N(1) -C(2)	1.479(7)
Fe(1)-Cl(4)	2.204(2)	N(1) -C(4)	1.474(7)
Cu(1)-S(1)#1	2.2067(14)	N(2) -C(6)	1.302(7)
Cu(1)-S(1)	2.2067(14)	N(2) -C(7)	1.476(8)
Cu(1)-S(2)	2.210(2)	N(2) -C(9)	1.479(8)
Cu(1)-S(2)#1	2.210(2)	C(2) -C(3)	1.518(9)
Cu(2)-S(4)#2	2.2027(14)	C(4) -C(5)	1.489(10)
Cu(2)-S(4)	2.2027(14)	C(7) -C(8)	1.494(11)
Cu(2)-S(3)#2	2.213(2)	C(9) -C(10)	1.507(10)
Cu(2)-S(3)	2.213(2)	C(21)-C(22)	1.31(2)
S(1) -C(1)	1.715(6)	C(21)-C(23)	1.34(2)
S(2) -C(1)	1.729(6)	C(22)-C(23)#3	1.36(2)
S(3) -C(6)	1.732(6)	C(23)-C(22)#3	1.36(2)

Bond Angles [deg] for $[Cu(Et_2dtc)_2][FeCl_4]\cdot\frac{1}{2}C_6H_6$

Cl(2) -Fe(1)-Cl(1)	109.96(11)	C(6) -S(4) -Cu(2)	86.6(2)
Cl(2) -Fe(1)-Cl(3)	110.25(9)	C(1) -N(1) -C(2)	120.9(5)
Cl(1) -Fe(1)-Cl(3)	110.14(10)	C(1) -N(1) -C(4)	121.8(5)
Cl(2) -Fe(1)-Cl(4)	108.29(10)	C(2) -N(1) -C(4)	117.3(5)
Cl(1) -Fe(1)-Cl(4)	108.61(9)	C(6) -N(2) -C(7)	121.4(5)
Cl(3) -Fe(1)-Cl(4)	109.54(9)	C(6) -N(2) -C(9)	120.8(5)
S(1)#1-Cu(1)-S(1)	180.0	C(7) -N(2) -C(9)	117.8(5)
S(1)#1-Cu(1)-S(2)	101.23(5)	N(1) -C(1) -S(1)	126.2(4)
S(1) -Cu(1)-S(2)	78.77(5)	N(1) -C(1) -S(2)	124.9(4)
S(1)#1-Cu(1)-S(2)#1	78.77(5)	S(1) -C(1) -S(2)	108.9(3)
S(1) -Cu(1)-S(2)#1	101.23(5)	N(1) -C(2) -C(3)	112.1(5)
S(2) -Cu(1)-S(2)#1	180.0	N(1) -C(4) -C(5)	112.0(6)
S(4)#2-Cu(2)-S(4)	180.0	N(2) -C(6) -S(4)	125.9(4)
S(4)#2-Cu(2)-S(3)#2	78.83(6)	N(2) -C(6) -S(3)	125.6(5)
S(4) -Cu(2)-S(3)#2	101.17(6)	S(4) -C(6) -S(3)	108.4(3)
S(4)#2-Cu(2)-S(3)	101.17(6)	N(2) -C(7) -C(8)	111.6(6)
S(4) -Cu(2)-S(3)	78.83(6)	N(2) -C(9) -C(10)	111.9(6)
S(3)#2-Cu(2)-S(3)	180.0	C(22) -C(21)-C(23)	120.8(10)
C(1) -S(1) -Cu(1)	86.4(2)	C(21) -C(22)-C(23)#3	120.3(10)
C(1) -S(2) -Cu(1)	85.9(2)	C(22)#3-C(23)-C(21)	118.9(9)
C(6) -S(3) -Cu(2)	86.1(2)		

Symmetry transformations used to generate equivalent atoms : #1 = -x-1, -y+1, -z; #2 = -x, -y+1, -z; #3 = -x-1, -y-1, -z-1

Appendix 1.3 - Crystallographic data for $[Cu(Me_2dtc)_2]ClO_4$

Empirical Formula	$C_6 H_{12} Cl Cu N_2 O_4 S_4$
Crystal System	Triclinic
Space Group	P 1 bar
a, Å	7.457(3)
b, Å	9.349(6)
c, Å	11.487(7)
α, deg	100.51(5)
β, deg	102.69(4)
γ, deg	97.94(4)
Volume, $Å^3$	754.8(8)
Z	2
Calculated Density Mg/m^3	1.775
F(000)	408
Crystal Size, mm	0.82 x 0.46 x 0.18
Wavelength, Å	0.71073
Theta Range, deg	2.59 to 25.05
Index Ranges	0<=h<=8; -11<=k<=11; -13<=l<=13
Data Measured	2849
Unique Data	2620
No. of Parameters	163
R	0.0489
R_w	0.1224
Largest Peak/Hole, $e/Å^{-3}$	0.466 and -1.143

Atomic coordinates ($x10^4$) for $[Cu(Me_2dtc)_2]ClO_4$.

	x	y	z
Cu	4034(1)	9286(1)	6524(1)
S(1)	4861(1)	10713(1)	8407(1)
S(2)	1535(1)	10349(1)	6532(1)
S(3)	3299(1)	7939(1)	4606(1)
S(4)	6592(1)	8288(1)	6517(1)
Cl	11348(1)	6766(1)	8264(1)
C(1)	2644(5)	11147(4)	8064(3)
C(2)	2943(6)	12613(6)	10114(4)
C(3)	-18(6)	12238(5)	8459(4)
C(4)	5447(5)	7400(4)	5015(3)
C(5)	5028(6)	5745(4)	3027(4)
C(6)	8002(6)	6119(5)	4712(4)
N(1)	1905(4)	11959(4)	8832(3)
N(2)	6126(4)	6457(3)	4293(3)
O(1)	9597(5)	799(4)	7661(4)
O(2)	11015(6)	8184(4)	8845(3)
O(3)	12359(5)	6114(5)	9179(4)
O(4)	12422(6)	7006(4)	7387(4)

Bond Lengths [Å] for $[Cu(Me_2dtc)_2]ClO_4$

Cu(1)-S(1)	2.231(2)	Cl(1)-O(3)	1.435(4)
Cu(1)-S(2)	2.2308(14)	Cl(1)-O(4)	1.447(3)
Cu(1)-S(4)	2.2372(14)	Cl(1)-O(2)	1.451(4)
Cu(1)-S(3)	2.237(2)	C(1) -N(1)	1.320(5)
S(1) -C(1)	1.735(4)	C(2) -N(1)	1.477(5)
S(2) -C(1)	1.746(4)	C(3) -N(1)	1.477(5)
S(3) -C(4)	1.737(4)	C(4) -N(2)	1.327(5)
S(4) -C(4)	1.741(4)	C(5) -N(2)	1.483(5)
Cl(1)-O(1)	1.432(3)	C(6) -N(2)	1.473(5)

Bond Angles [deg] for $[Cu(Me_2dtc)_2]ClO_4$

S(1)-Cu(1)-S(2)	79.03(6)	O(3)-Cl(1)-O(2)	109.2(3)
S(1)-Cu(1)-S(4)	100.30(6)	O(4)-Cl(1)-O(2)	108.5(2)
S(2)-Cu(1)-S(4)	178.24(4)	N(1)-C(1) -S(1)	125.7(3)
S(1)-Cu(1)-S(3)	177.13(4)	N(1)-C(1) -S(2)	125.0(3)
S(2)-Cu(1)-S(3)	101.57(6)	S(1)-C(1) -S(2)	109.3(2)
S(4)-Cu(1)-S(3)	79.01(6)	N(2)-C(4) -S(3)	125.4(3)
C(1)-S(1) -Cu(1)	85.75(13)	N(2)-C(4) -S(4)	124.8(3)
C(1)-S(2) -Cu(1)	85.51(13)	S(3)-C(4) -S(4)	109.8(2)
C(4)-S(3) -Cu(1)	85.60(13)	C(1)-N(1) -C(3)	121.7(3)
C(4)-S(4) -Cu(1)	85.50(13)	C(1)-N(1) -C(2)	121.9(3)
O(1)-Cl(1)-O(3)	108.9(2)	C(3)-N(1) -C(2)	116.4(3)
O(1)-Cl(1)-O(4)	110.2(3)	C(4)-N(2) -C(6)	121.1(3)
O(3)-Cl(1)-O(4)	110.3(3)	C(4)-N(2) -C(5)	120.6(3)
O(1)-Cl(1)-O(2)	109.6(3)	C(6)-N(2) -C(5)	118.2(3)

Appendix 1.4-Crystallographic data for $[Cu(TosNSC(NMe_2)SNTos)_2]\cdot 2CH_2Cl_2$

Formula	$C_{36}H_{44}Cl_4CuN_6O_8S_8$
Crystal System	Monoclinic
Space Group	C 2/c
a, Å	12.457(2)
b, Å	22.648(5)
c, Å	19.224(4)
α, deg	90
β, deg	106.59(3)
γ, deg	90
Volume, $Å^3$	5198(2)
Z	4
Calculated Density Mg/m^3	1.470
F(000)	2364
Crystal Size, mm	0.36 x 0.26 x 0.24
Wavelength, Å	0.71073
Theta Range, deg	2.54 to 25.00
Index Ranges	0<=h<=14; 0<=k<=26; -22<=l<=21
Data Measured	4469
Unique Data	4274
No. of Parameters	285
R	0.0624
R_w	0.1462
Largest Peak/Hole, $e/Å^{-3}$	0.471 and -0.740

Atomic coordinates (x10^4) for [Cu(TosNSC(NMe$_2$)SNTos)$_2$]·2CH$_2$Cl$_2$.

	x	y	z
Cu	0	412(1)	2500
S(1)	-469(1)	1227(1)	1113(1)
S(2)	2163(1)	-390(1)	3156(1)
S(3)	649(1)	169(1)	994(1)
S(4)	2526(1)	560(1)	2317(1)
N(1)	4(3)	588(2)	1479(2)
N(2)	1640(3)	215(2)	2710(2)
N(3)	2824(4)	239(2)	1032(2)
C(30)	2080(4)	308(2)	1402(3)
C(31)	4038(5)	264(4)	1373(3)
C(32)	2461(6)	133(4)	227(3)
O(1)	-1058(3)	1157(2)	348(2)
O(2)	-1082(3)	1471(2)	1594(2)
O(3)	1290(3)	-613(2)	3458(2)
O(4)	3263(3)	-280(2)	3657(2)
C(1)	732(5)	1683(2)	1172(3)
C(2)	1265(6)	1665(3)	621(3)
C(3)	2235(6)	1994(3)	699(4)
C(4)	2674(6)	2359(3)	1309(4)
C(5)	2115(6)	2371(3)	1839(4)
C(6)	1153(6)	2033(3)	1794(4)
C(7)	3712(7)	2742(4)	1384(5)
C(11)	2342(4)	-906(2)	2492(3)
C(12)	3414(5)	-1050(3)	2451(3)
C(13)	3539(5)	-1437(3)	1913(3)
C(14)	2614(5)	-1691(2)	1417(3)
C(15)	1546(5)	-1539(2)	1461(3)
C(16)	1402(4)	-1152(2)	1998(3)
C(17)	2766(6)	-2130(3)	842(3)
Cl(1)	5853(2)	-1639(1)	6294(2)
Cl(2)	5154(2)	-1032(2)	4883(1)
C(100)	6229(7)	-1182(4)	5676(5)

Bond Lengths [Å] for [Cu(TosNSC(NMe$_2$)SNTos)$_2$]·2CH$_2$Cl$_2$

Cu(1)-N(1)#	2.005(4)	N(3) -C(32)	1.502(7)
Cu(1)-N(1)	2.005(4)	C(1) -C(6)	1.405(8)
Cu(1)-N(2)#	2.016(4)	C(1) -C(2)	1.402(8)
Cu(1)-N(2)	2.016(4)	C(2) -C(3)	1.392(9)
S(1) -O(1)	1.451(4)	C(3) -C(4)	1.411(10)
S(1) -O(2)	1.465(4)	C(4) -C(5)	1.389(9)
S(1) -N(1)	1.642(4)	C(4) -C(7)	1.529(9)
S(1) -C(1)	1.796(6)	C(5) -C(6)	1.403(9)
S(2) -O(4)	1.453(4)	C(11)-C(12)	1.399(7)
S(2) -O(3)	1.461(4)	C(11)-C(16)	1.395(7)
S(2) -N(2)	1.649(4)	C(12)-C(13)	1.400(8)
S(2) -C(11)	1.793(5)	C(13)-C(14)	1.392(8)
S(3) -N(1)	1.687(4)	C(14)-C(15)	1.400(8)
S(3) -C(30)	1.759(5)	C(14)-C(17)	1.539(7)
S(4) -N(2)	1.694(4)	C(15)-C(16)	1.405(7)
S(4) -C(30)	1.781(5)	Cl(1)-C(100)	1.738(9)
N(3) -C(30)	1.330(6)	Cl(2)-C(100)	1.750(8)
N(3) -C(31)	1.467(7)		

Bond Angles for $[Cu(TosNSC(NMe_2)SNTos)_2]\cdot 2CH_2Cl_2$

N(1)#1-Cu(1)-N(1)	157.0(2)	C(30) -N(3) -C(32)	121.2(5)
N(1)#1-Cu(1)-N(2)#1	87.4(2)	C(31) -N(3) -C(32)	115.8(5)
N(1) -Cu(1)-N(2)#1	97.7(2)	N(3) -C(30)-S(3)	120.9(4)
N(1)#1-Cu(1)-N(2)	97.7(2)	N(3) -C(30)-S(4)	119.8(4)
N(1) -Cu(1)-N(2)	87.4(2)	S(3) -C(30)-S(4)	119.3(3)
N(2)#1-Cu(1)-N(2)	154.5(2)	C(6) -C(1) -C(2)	121.2(6)
O(1) -S(1) -O(2)	118.5(3)	C(6) -C(1) -S(1)	118.7(5)
O(1) -S(1) -N(1)	110.7(2)	C(2) -C(1) -S(1)	120.0(4)
O(2) -S(1) -N(1)	104.5(2)	C(3) -C(2) -C(1)	119.1(6)
O(1) -S(1) -C(1)	107.3(3)	C(2) -C(3) -C(4)	121.5(6)
O(2) -S(1) -C(1)	108.5(3)	C(5) -C(4) -C(3)	117.7(6)
N(1) -S(1) -C(1)	106.8(2)	C(5) -C(4) -C(7)	120.5(7)
O(4) -S(2) -O(3)	117.7(2)	C(3) -C(4) -C(7)	121.8(7)
O(4) -S(2) -N(2)	111.2(2)	C(4) -C(5) -C(6)	122.9(6)
O(3) -S(2) -N(2)	105.4(2)	C(1) -C(6) -C(5)	117.6(6)
O(4) -S(2) -C(11)	107.3(2)	C(12) -C(11)-C(16)	119.9(5)
O(3) -S(2) -C(11)	108.4(2)	C(12) -C(11)-S(2)	120.4(4)
N(2) -S(2) -C(11)	106.4(2)	C(16) -C(11)-S(2)	119.6(4)
N(1) -S(3) -C(30)	103.5(2)	C(13) -C(12)-C(11)	119.8(5)
N(2) -S(4) -C(30)	103.5(2)	C(12) -C(13)-C(14)	121.3(5)
S(1) -N(1) -S(3)	115.4(2)	C(15) -C(14)-C(13)	118.2(5)
S(1) -N(1) -Cu(1)	119.6(2)	C(15) -C(14)-C(17)	121.1(5)
S(3) -N(1) -Cu(1)	124.3(2)	C(13) -C(14)-C(17)	120.7(6)
S(2) -N(2) -S(4)	113.9(2)	C(14) -C(15)-C(16)	121.4(5)
S(2) -N(2) -Cu(1)	120.9(2)	C(11) -C(16)-C(15)	119.4(5)
S(4) -N(2) -Cu(1)	124.1(2)	Cl(1) -C(100)-Cl(2)	115.0(5)
C(30) -N(3) -C(31)	122.9(5)		

Symmetry transformations used to generate equivalent atoms : #1 = -x, y, -z+½

Appendix 1.5 - Crystallographic data for $[Cu(TosNSC(NEt_2)S)_2]\cdot CH_2Cl_2$

Formula	$C_{25}H_{36}Cl_2CuN_4O_4S_6$
Crystal System	Monoclinic
Space Group	P21/c
a, Å	12.7830(4)
b, Å	14.5350(4)
c, Å	19.6760(4)
α, deg	90
β, deg	102.5320(10)
γ, deg	90
Volume, $Å^3$	3568.72(17)
Z	4
Calculated Density Mg/m^3	1.458
F(000)	1620
Crystal Size, mm	0.5 x 0.2 x 0.2
Wavelength, Å	0.71070
Theta Range, deg	3.49 to 25.00
Index Ranges	0<=h<=15; 0<=k<=17; -23<=l<=22
Data Measured	43653
Unique Data	6115
No. of Parameters	379
R	0.0490
R_w	0.1303
Largest Peak/Hole, $e/Å^{-3}$	0.750 and -0.998

Atomic coordinates ($x10^4$) for $[Cu(TosNSC(NEt_2)S)_2]\cdot CH_2Cl_2$.

	x	y	z
Cu(1)	2229(1)	8565(1)	2128(1)
Cl(1)	3129(2)	8117(2)	4577(1)
Cl(2)	3263(3)	10076(2)	4426(1)
S(1)	-59(1)	8051(1)	1402(1)
S(2)	510(1)	7688(1)	2814(1)
S(3)	2673(1)	7142(1)	2611(1)
S(4)	3799(1)	8711(1)	1137(1)
S(5)	4432(1)	9506(1)	2442(1)
S(6)	2164(1)	10140(1)	2302(1)
O(1)	265(3)	8656(2)	907(2)
O(2)	-1152(2)	8073(3)	1472(2)
O(3)	4881(3)	8457(2)	1125(2)
O(4)	2942(3)	8137(2)	785(2)
N(1)	737(2)	8319(2)	2145(2)
N(2)	1552(3)	6189(2)	3349(2)
N(3)	3657(3)	8734(2)	1940(2)
N(4)	3884(3)	11187(2)	2736(2)
C(1)	221(3)	6906(3)	1201(2)
C(2)	1012(4)	6728(3)	842(2)
C(3)	1260(4)	5824(4)	724(3)
C(4)	738(4)	5092(3)	961(3)
C(5)	-42(4)	5291(4)	1315(3)
C(6)	-315(4)	6184(3)	1435(3)
C(7)	1041(5)	4110(4)	829(4)
C(8)	1597(3)	6907(3)	2952(2)
C(9)	564(4)	5919(4)	3582(3)
C(10)	517(6)	6355(6)	4261(3)
C(11)	2489(4)	5582(3)	3579(3)
C(12)	2552(5)	4843(4)	3059(4)
C(13)	3610(3)	9833(3)	788(2)
C(14)	4482(4)	10354(3)	733(3)
C(15)	4328(5)	11237(4)	464(3)
C(16)	3323(4)	11598(3)	236(2)
C(17)	2462(4)	11062(4)	288(2)
C(18)	2583(4)	10181(3)	568(2)
C(19)	3179(6)	12561(4)	-57(4)
C(20)	3498(3)	10385(3)	2501(2)
C(21)	5042(3)	11392(3)	2881(3)
C(22)	5597(4)	11124(5)	3601(3)
C(23)	3185(4)	11952(3)	2861(3)
C(24)	2823(6)	12527(4)	2222(4)
C(1S)	3354(15)	8950(8)	4100(5)

Bond lengths [Å] for $[Cu(TosNSC(NEt_2)S)_2]\cdot CH_2Cl_2$.

Cu(1)	-N(1)	1.949	(3)	N(2)	-C(9)	1.486	(5)
Cu(1)	-N(3)	1.954	(3)	N(4)	-C(20)	1.310	(5)
Cu(1)	-S(3)	2.2969	(11)	N(4)	-C(21)	1.476	(5)
Cu(1)	-S(6)	2.3188	(10)	N(4)	-C(23)	1.481	(5)
Cl(1)	-C(1S)	1.595	(10)	C(1)	-C(2)	1.377	(6)
Cl(2)	-C(1S)	1.771	(12)	C(1)	-C(6)	1.386	(6)
S(1)	-O(2)	1.434	(3)	C(2)	-C(3)	1.383	(7)
S(1)	-O(1)	1.438	(3)	C(3)	-C(4)	1.389	(7)
S(1)	-N(1)	1.637	(3)	C(4)	-C(5)	1.365	(7)
S(1)	-C(1)	1.764	(4)	C(4)	-C(7)	1.515	(7)
S(2)	-N(1)	1.680	(3)	C(5)	-C(6)	1.377	(7)
S(2)	-C(8)	1.768	(4)	C(9)	-C(10)	1.492	(9)
S(3)	-C(8)	1.691	(4)	C(11)	-C(12)	1.498	(8)
S(4)	-O(4)	1.431	(3)	C(13)	-C(14)	1.372	(6)
S(4)	-O(3)	1.436	(3)	C(13)	-C(18)	1.386	(6)
S(4)	-N(3)	1.631	(3)	C(14)	-C(15)	1.385	(7)
S(4)	-C(13)	1.764	(4)	C(15)	-C(16)	1.370	(7)
S(5)	-N(3)	1.670	(3)	C(16)	-C(17)	1.370	(7)
S(5)	-C(20)	1.770	(4)	C(16)	-C(19)	1.510	(7)
S(6)	-C(20)	1.702	(4)	C(17)	-C(18)	1.390	(7)
N(2)	-C(8)	1.313	(5)	C(21)	-C(22)	1.492	(7)
N(2)	-C(11)	1.477	(6)	C(23)	-C(24)	1.497	(8)

Bond angles [deg] for $[Cu(TosNSC(NEt_2)S)_2]\cdot CH_2Cl_2$.

N(1)	-Cu(1)	-N(3)	169.85(13)	C(21)	-N(4)	-C(23)	115.6 (3)
N(1)	-Cu(1)	-S(3)	88.97 (9)	C(2)	-C(1)	-C(6)	119.9 (4)
N(3)	-Cu(1)	-S(3)	91.97(10)	C(2)	-C(1)	-S(1)	120.0 (3)
N(1)	-Cu(1)	-S(6)	96.44(10)	C(6)	-C(1)	-S(1)	120.0 (3)
N(3)	-Cu(1)	-S(6)	88.21 (9)	C(1)	-C(2)	-C(3)	119.0 (4)
S(3)	-Cu(1)	-S(6)	147.34 (5)	C(2)	-C(3)	-C(4)	121.8 (4)
O(2)	-S(1)	-O(1)	118.8 (2)	C(5)	-C(4)	-C(3)	117.7 (4)
O(2)	-S(1)	-N(1)	109.76(19)	C(5)	-C(4)	-C(7)	122.0 (5)
O(1)	-S(1)	-N(1)	104.16(18)	C(3)	-C(4)	-C(7)	120.3 (5)
O(2)	-S(1)	-C(1)	107.0 (2)	C(4)	-C(5)	-C(6)	121.9 (5)
O(1)	-S(1)	-C(1)	108.9 (2)	C(5)	-C(6)	-C(1)	119.6 (4)
N(1)	-S(1)	-C(1)	107.91(17)	N(2)	-C(8)	-S(3)	122.7 (3)
N(1)	-S(2)	-C(8)	101.93(17)	N(2)	-C(8)	-S(2)	117.8 (3)
C(8)	-S(3)	-Cu(1)	101.31(14)	S(3)	-C(8)	-S(2)	119.3 (2)
O(4)	-S(4)	-O(3)	118.7 (2)	N(2)	-C(9)	-C(10)	111.5 (5)
O(4)	-S(4)	-N(3)	104.24(18)	N(2)	-C(11)	-C(12)	112.2 (5)
O(3)	-S(4)	-N(3)	109.35(19)	C(14)	-C(13)	-C(18)	120.3 (4)
O(4)	-S(4)	-C(13)	109.0 (2)	C(14)	-C(13)	-S(4)	119.8 (3)
O(3)	-S(4)	-C(13)	106.44(19)	C(18)	-C(13)	-S(4)	120.0 (3)
N(3)	-S(4)	-C(13)	108.84(17)	C(13)	-C(14)	-C(15)	119.4 (5)
N(3)	-S(5)	-C(20)	101.57(17)	C(16)	-C(15)	-C(14)	121.7 (5)
C(20)	-S(6)	-Cu(1)	100.01(13)	C(17)	-C(16)	-C(15)	118.0 (4)
S(1)	-N(1)	-S(2)	113.01(18)	C(17)	-C(16)	-C(19)	121.5 (5)
S(1)	-N(1)	-Cu(1)	116.68(17)	C(15)	-C(16)	-C(19)	120.5 (5)
S(2)	-N(1)	-Cu(1)	116.72(17)	C(16)	-C(17)	-C(18)	122.1 (5)
C(8)	-N(2)	-C(11)	121.3 (3)	C(13)	-C(18)	-C(17)	118.5 (4)
C(8)	-N(2)	-C(9)	122.9 (4)	N(4)	-C(20)	-S(6)	123.3 (3)
C(11)	-N(2)	-C(9)	115.8 (4)	N(4)	-C(20)	-S(5)	117.2 (3)
S(4)	-N(3)	-S(5)	114.19(18)	S(6)	-C(20)	-S(5)	119.4 (2)
S(4)	-N(3)	-Cu(1)	119.06(19)	N(4)	-C(21)	-C(22)	112.4 (4)
S(5)	-N(3)	-Cu(1)	115.60(17)	N(4)	-C(23)	-C(24)	111.6 (4)
C(20)	-N(4)	-C(21)	122.2 (3)	Cl(1)	-C(1S)	-Cl(2)	117.1 (6)
C(20)	-N(4)	-C(23)	122.2 (3)				

Appendix 1.6 - Crystallographic data for $[Ni(TosNSC(NEt_2)S)_2]\cdot CHCl_3$

Empirical Formula	$C_{25}\ H_{35}\ Cl_3\ N_4\ Ni\ O_4\ S_6$
Crystal System	Monoclinic
Space Group	P21/c
a, Å	12.8318(4)
b, Å	14.6975(4)
c, Å	19.5611(5)
α, deg	90
β, deg	99.5790(10)
γ, deg	90
Volume, $Å^3$	3637.70(18)
Z	4
Calculated Density Mg/m^3	1.484
F(000)	1680
Crystal Size, mm	0.4 x 0.2 x 0.1
Wavelength, Å	0.71070
Theta Range, deg	3.46 to 24.99
Index Ranges	0<=h<=15; 0<=k<=17; -23<=l<=22
Data Measured	22274
Unique Data	6216
No. of Parameters	389
R	0.0667
R_w	0.1820
Largest Peak/Hole, $e/Å^{-3}$	1.323 and -0.599

Atomic coordinates (x10^4) for [Ni(TosNSC(NEt$_2$)S)$_2$]·CHCl$_3$.

	x	y	z
Ni(1)	2295.9(5)	1197.7(4)	2180.5(3)
S(1)	3900.1(12)	1107.5(10)	1191.1(8)
S(2)	4393.4(11)	206.3(10)	2446.9(8)
S(3)	2117.1(11)	-302.2(9)	2211.2(8)
S(4)	46.8(11)	1652.4(10)	1546.4(5)
S(5)	656.9(12)	2085.8(10)	2933.3(8)
S(6)	2691.9(11)	2601.4(9)	2514.2(8)
O(1)	3165(4)	1790(3)	872(2)
O(2)	5008(4)	1247(3)	1208(3)
O(3)	341(4)	1044(3)	1035(2)
O(4)	-1016(3)	1626(3)	1681(3)
N(1)	3689(3)	1039(3)	1995(2)
N(2)	3713(4)	-1458(3)	2625(3)
N(3)	861(4)	1416(3)	2267(2)
N(4)	1659(4)	3637(3)	3292(3)
C(1)	3576(5)	70(4)	766(3)
C(2)	4353(6)	-549(5)	678(4)
C(3)	4089(6)	-1369(5)	346(4)
C(4)	3042(6)	-1587(5)	97(3)
C(5)	2278(6)	-961(5)	180(3)
C(6)	2514(5)	-137(5)	519(3)
C(7)	2755(9)	-2490(6)	-258(5)
C(8)	3403(4)	-629(4)	2431(3)
C(9)	2948(6)	-2198(4)	2677(4)
C(10)	2679(9)	-2704(6)	2010(6)
C(11)	4851(5)	-1688(5)	2810(4)
C(12)	5289(7)	-1454(6)	3554(4)
C(13)	289(4)	2787(4)	1303(3)
C(14)	1061(5)	2964(4)	902(3)
C(15)	1256(6)	3842(5)	750(4)
C(16)	723(6)	4571(5)	985(4)
C(17)	-28(6)	4374(5)	1383(4)
C(18)	-268(5)	3499(5)	1541(4)
C(19)	985(9)	5548(6)	813(5)
C(20)	1686(4)	2887(4)	2940(3)
C(21)	2601(6)	4248(5)	3426(5)
C(22)	2594(7)	4932(5)	2854(6)
C(23)	720(6)	3932(5)	3586(4)
C(24)	705(8)	3558(8)	4290(5)
Cl(1S)	6768(2)	7043.2(17)	410.2(14)
Cl(2S)	5000(2)	6045(2)	717(2)
Cl(3S)	6971(3)	5134(2)	757.7(18)
C(1S)	6354(8)	6163(6)	905(4)

Bond Lengths [Å] for [Ni(TosNSC(NEt$_2$)S)$_2$]·CHCl$_3$

Ni(1)-N(1)	1.897(4)	S(2) -C(8)	1.764(6)
Ni(1)-N(3)	1.904(4)	S(3) -C(8)	1.703(5)
Ni(1)-S(6)	2.1977(15)	S(4) -O(4)	1.432(5)
Ni(1)-S(3)	2.2183(15)	S(4) -O(3)	1.437(5)
S(1) -O(2)	1.431(5)	S(4) -N(3)	1.647(5)
S(1) -O(1)	1.446(4)	S(4) -C(13)	1.776(6)
S(1) -N(1)	1.643(5)	S(5) -N(3)	1.688(5)
S(1) -C(1)	1.754(6)	S(5) -C(20)	1.767(6)
S(2) -N(1)	1.683(5)	S(6) -C(20)	1.701(5)

N(2) -C(8)	1.318(7)	C(11)-C(12)	1.509(1)
N(2) -C(9)	1.481(8)	C(13)-C(14)	1.387(9)
N(2) -C(11)	1.483(8)	C(13)-C(18)	1.390(9)
N(4) -C(20)	1.303(7)	C(14)-C(15)	1.357(10)
N(4) -C(23)	1.485(8)	C(15)-C(16)	1.391(10)
N(4) -C(21)	1.494(8)	C(16)-C(17)	1.366(11)
C(1) -C(2)	1.381(8)	C(16)-C(19)	1.525(10)
C(1) -C(6)	1.401(9)	C(17)-C(18)	1.369(10)
C(2) -C(3)	1.385(10)	C(21)-C(22)	1.502(13)
C(3) -C(4)	1.388(10)	C(23)-C(24)	1.486(13)
C(4) -C(5)	1.374(10)	Cl(1S)-C(1S)	1.750(8)
C(4) -C(7)	1.515(10)	Cl(2S)-C(1S)	1.724(10)
C(5) -C(6)	1.390(10)	Cl(3S)-C(1S)	1.752(10)
C(9) -C(10)	1.492(13)		

Bond Angles [deg] for $[Ni(TosNSC(NEt_2)S)_2]\cdot CHCl_3$

N(1) -Ni(1)-N(3)	173.6(2)	C(2) -C(1) -C(6)	119.7(6)
N(1) -Ni(1)-S(6)	89.62(14)	C(2) -C(1) -S(1)	120.8(5)
N(3) -Ni(1)-S(6)	89.68(14)	C(6) -C(1) -S(1)	119.5(4)
N(1) -Ni(1)-S(3)	89.33(14)	C(1) -C(2) -C(3)	120.4(7)
N(3) -Ni(1)-S(3)	93.39(14)	C(2) -C(3) -C(4)	120.8(6)
S(6) -Ni(1)-S(3)	160.86(7)	C(5) -C(4) -C(3)	118.2(7)
O(2) -S(1) -O(1)	119.1(3)	C(5) -C(4) -C(7)	121.1(7)
O(2) -S(1) -N(1)	107.9(3)	C(3) -C(4) -C(7)	120.7(7)
O(1) -S(1) -N(1)	104.8(2)	C(4) -C(5) -C(6)	122.4(7)
O(2) -S(1) -C(1)	107.0(3)	C(5) -C(6) -C(1)	118.4(6)
O(1) -S(1) -C(1)	108.2(3)	N(2) -C(8) -S(3)	124.5(4)
N(1) -S(1) -C(1)	109.7(3)	N(2) -C(8) -S(2)	117.1(4)
N(1) -S(2) -C(8)	100.1(2)	S(3) -C(8) -S(2)	118.2(3)
C(8) -S(3) -Ni(1)	100.77(19)	N(2) -C(9) -C(10)	111.4(7)
O(4) -S(4) -O(3)	118.6(3)	N(2) -C(11)-C(12)	112.1(6)
O(4) -S(4) -N(3)	109.0(3)	C(14)-C(13)-C(18)	120.2(6)
O(3) -S(4) -N(3)	105.2(3)	C(14)-C(13)-S(4)	120.0(4)
O(4) -S(4) -C(13)	106.8(3)	C(18)-C(13)-S(4)	119.7(5)
O(3) -S(4) -C(13)	108.6(3)	C(15)-C(14)-C(13)	118.5(6)
N(3) -S(4) -C(13)	108.2(3)	C(14)-C(15)-C(16)	122.8(7)
N(3) -S(5) -C(20)	100.5(2)	C(17)-C(16)-C(15)	117.2(7)
C(20)-S(6) -Ni(1)	102.7(2)	C(17)-C(16)-C(19)	121.9(7)
S(1) -N(1) -S(2)	112.8(3)	C(15)-C(16)-C(19)	120.9(8)
S(1) -N(1) -Ni(1)	119.1(3)	C(16)-C(17)-C(18)	122.3(7)
S(2) -N(1) -Ni(1)	115.4(3)	C(17)-C(18)-C(13)	119.0(7)
C(8) -N(2) -C(9)	121.8(5)	N(4) -C(20)-S(6)	123.8(4)
C(8) -N(2) -C(11)	121.3(5)	N(4) -C(20)-S(5)	118.9(4)
C(9) -N(2) -C(11)	116.9(5)	S(6) -C(20)-S(5)	117.3(3)
S(4) -N(3) -S(5)	112.3(3)	N(4) -C(21)-C(22)	111.5(7)
S(4) -N(3) -Ni(1)	116.4(3)	N(4) -C(23)-C(24)	112.9(7)
S(5) -N(3) -Ni(1)	116.4(3)	Cl(2S)-C(1S)-Cl(1S)	110.1(5)
C(20)-N(4) -C(23)	123.1(6)	Cl(2S)-C(1S)-Cl(3S)	110.2(5)
C(20)-N(4) -C(21)	120.7(5)	Cl(1S)-C(1S)-Cl(3S)	111.2(5)
C(23)-N(4) -C(21)	116.2(5)		

Appendix 1.7 - Crystallographic data for [Co(TosNSC(NEt$_2$)SNTos)$_2$]

Formula	$C_{38}H_{48}CoN_6O_{8.25}S_8$
Crystal System	Monoclinic
Space Group	P21/c
a, Å	15.4966(13)
b, Å	12.7398(7)
c, Å	24.914(2)
α, deg	90
β, deg	91.214(1)
γ, deg	90
Volume, Å^3	4917.5(6)
Z	4
Calculated Density Mg/m^3	1.400
F(000)	2156
Crystal Size, mm	0.3 x 0.2 x 0.1
Wavelength, Å	0.71070
Theta Range, deg	3.30 to 25.00
Index Ranges	0<=h<=18; 0<=k<=15; -29<=l<=29
Data Measured	35247
Unique Data	8400
No. of Parameters	555
R	0.0640
R_w	0.1289
Extinction Coefficient	0.0032(4)
Largest Peak/Hole, e/Å^{-3}	0.603 and -0.270

Atomic coordinates ($x10^4$) for $[Co(TosNSC(NEt_2)SNTos)_2]$.

	x	y	z
Co(1)	2583(1)	7675(1)	1532(1)
S(1)	2668(1)	9789(1)	2233(1)
S(2)	957(1)	6262(1)	1136(1)
S(3)	1184(1)	9520(1)	1606(1)
S(4)	781(1)	7393(1)	2073(1)
S(5)	3309(1)	6073(1)	2458(1)
S(6)	3403(1)	8231(1)	391(1)
S(7)	4504(1)	7229(1)	1898(1)
S(8)	3871(1)	6320(1)	839(1)
O(1)	3569(2)	9542(3)	2186(2)
O(2)	2404(3)	10869(3)	2202(2)
O(3)	1645(3)	5912(3)	800(2)
O(4)	453(3)	5493(3)	1407(2)
O(5)	2396(2)	6089(3)	2557(2)
O(6)	3902(3)	6192(3)	2906(1)
O(7)	2771(2)	9031(3)	479(2)
O(8)	3408(2)	7705(3)	-122(1)
N(1)	2179(2)	9095(3)	1764(2)
N(2)	1405(3)	7066(3)	1558(2)
N(3)	-268(3)	9032(4)	2092(2)
N(4)	3457(2)	6990(3)	2013(2)
N(5)	3259(2)	7403(3)	882(2)
N(6)	5484(3)	6190(4)	1226(2)
C(1)	2324(3)	9298(4)	2850(2)
C(2)	1575(4)	9664(5)	3083(3)
C(3)	1295(4)	9223(6)	3553(3)
C(4)	1750(4)	8434(6)	3813(3)
C(5)	2503(4)	8088(5)	3588(2)
C(6)	2778(4)	8503(4)	3109(2)
C(7)	1437(5)	7954(8)	4327(3)
C(8)	234(4)	7017(6)	732(3)
C(9)	520(5)	7875(5)	471(3)
C(10)	-33(6)	8425(6)	129(3)
C(11)	-855(6)	8176(9)	66(4)
C(12)	-1142(6)	7367(12)	342(6)
C(13)	-612(6)	6769(10)	690(5)
C(14)	-1456(6)	8735(11)	-350(5)
C(15)	485(3)	8679(4)	1943(2)
C(16)	-485(4)	10150(5)	2099(3)
C(17)	-873(5)	10513(7)	1578(4)
C(18)	-957(4)	8303(6)	2286(4)
C(22)	3134(5)	3503(5)	1539(3)
C(23)	3905(5)	3004(5)	1617(3)
C(24)	4510(4)	3461(5)	1959(3)
C(25)	4343(4)	4390(5)	2229(2)
C(26)	4120(6)	1975(5)	1339(3)
C(27)	4452(3)	8742(4)	502(2)
C(28)	5097(4)	8528(4)	149(2)
C(29)	5924(4)	8897(5)	266(3)
C(30)	6110(4)	9470(4)	730(2)
C(31)	5440(4)	9682(4)	1067(2)
C(32)	4614(4)	9324(4)	960(2)
C(33)	7017(4)	9854(6)	853(3)
C(34)	4706(3)	6545(4)	1312(2)
C(35)	6173(4)	6196(5)	1651(3)
C(36)	6682(4)	7195(6)	1657(3)

C(37)	5727(4)	5728(6)	707(3)
C(38)	5543(6)	4554(6)	687(3)
O(1S)	2511(13)	9952(16)	4914(8)

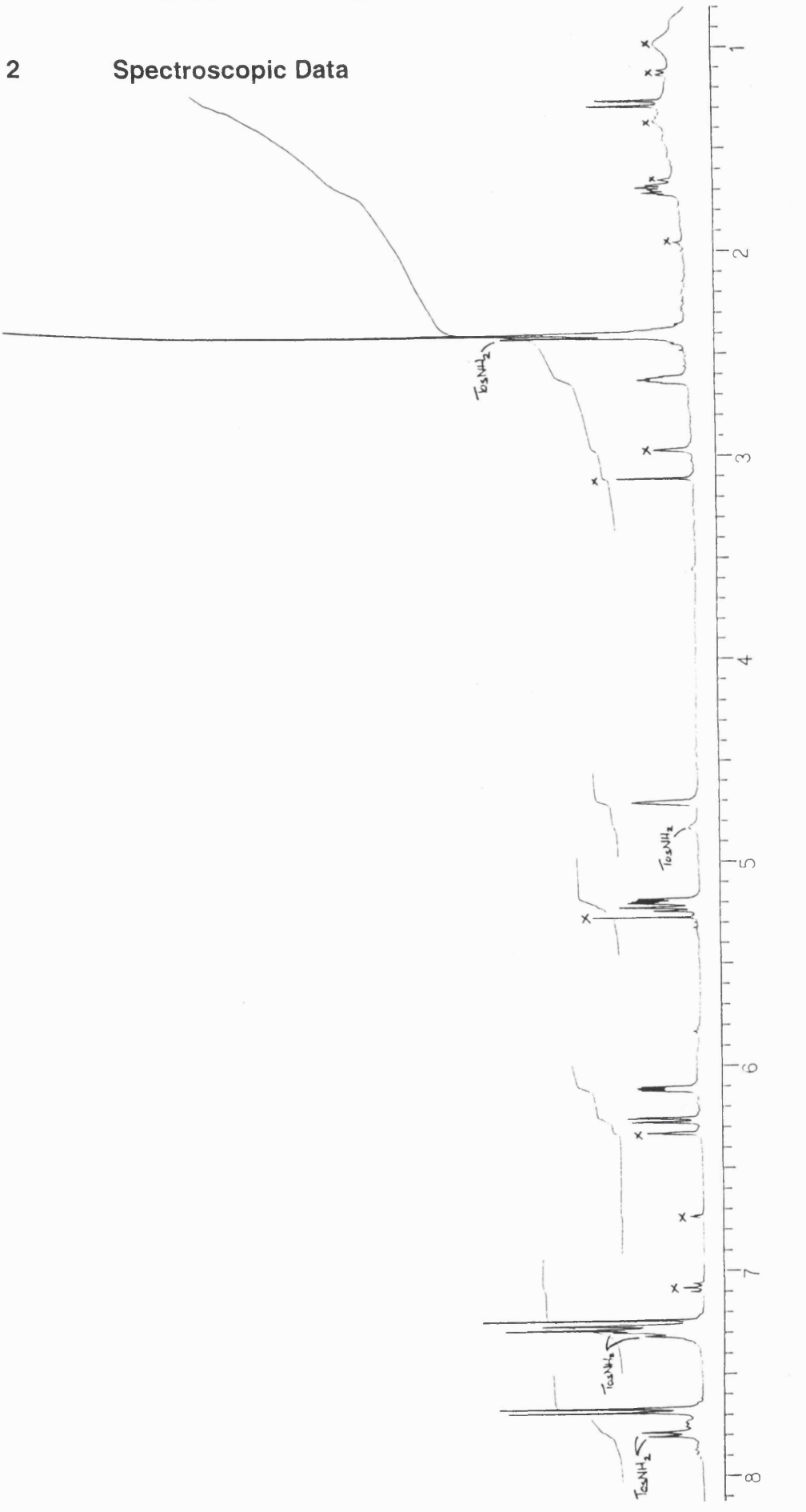
Bond Lengths [Å] for [Co(TosNSC(NEt$_2$)SNTos)$_2$]

Co(1)-N(5)	1.979(4)	C(1) -C(6)	1.387(7)
Co(1)-N(2)	1.985(4)	C(1) -C(2)	1.389(7)
Co(1)-N(4)	1.992(4)	C(2) -C(3)	1.379(9)
Co(1)-N(1)	2.003(4)	C(3) -C(4)	1.381(9)
S(1) -O(2)	1.437(4)	C(4) -C(5)	1.376(8)
S(1) -O(1)	1.440(4)	C(4) -C(7)	1.510(9)
S(1) -N(1)	1.637(4)	C(5) -C(6)	1.381(8)
S(1) -C(1)	1.753(6)	C(8) -C(13)	1.350(10)
S(2) -O(4)	1.431(4)	C(8) -C(9)	1.352(9)
S(2) -O(3)	1.441(4)	C(9) -C(10)	1.386(10)
S(2) -N(2)	1.615(4)	C(10)-C(11)	1.319(11)
S(2) -C(8)	1.773(7)	C(11)-C(12)	1.322(13)
S(3) -N(1)	1.673(4)	C(11)-C(14)	1.553(11)
S(3) -C(15)	1.751(6)	C(12)-C(13)	1.406(12)
S(4) -N(2)	1.674(4)	C(16)-C(17)	1.492(9)
S(4) -C(15)	1.730(5)	C(18)-C(19)	1.508(11)
S(5) -O(6)	1.439(4)	C(20)-C(21)	1.372(8)
S(5) -O(5)	1.442(4)	C(20)-C(25)	1.390(7)
S(5) -N(4)	1.630(4)	C(21)-C(22)	1.389(8)
S(5) -C(20)	1.756(5)	C(22)-C(23)	1.365(9)
S(6) -O(7)	1.434(4)	C(23)-C(24)	1.381(9)
S(6) -O(8)	1.442(4)	C(23)-C(26)	1.522(8)
S(6) -N(5)	1.633(4)	C(24)-C(25)	1.388(8)
S(6) -C(27)	1.767(5)	C(27)-C(28)	1.373(7)
S(7) -N(4)	1.681(4)	C(27)-C(32)	1.379(7)
S(7) -C(34)	1.735(5)	C(28)-C(29)	1.390(8)
S(8) -N(5)	1.678(4)	C(29)-C(30)	1.392(8)
S(8) -C(34)	1.755(5)	C(30)-C(31)	1.377(8)
N(3) -C(15)	1.311(6)	C(30)-C(33)	1.514(8)
N(3) -C(16)	1.463(7)	C(31)-C(32)	1.379(8)
N(3) -C(18)	1.503(8)	C(35)-C(36)	1.498(9)
N(6) -C(34)	1.310(6)	C(37)-C(38)	1.524(10)
N(6) -C(37)	1.476(7)		
N(6) -C(35)	1.490(7)		

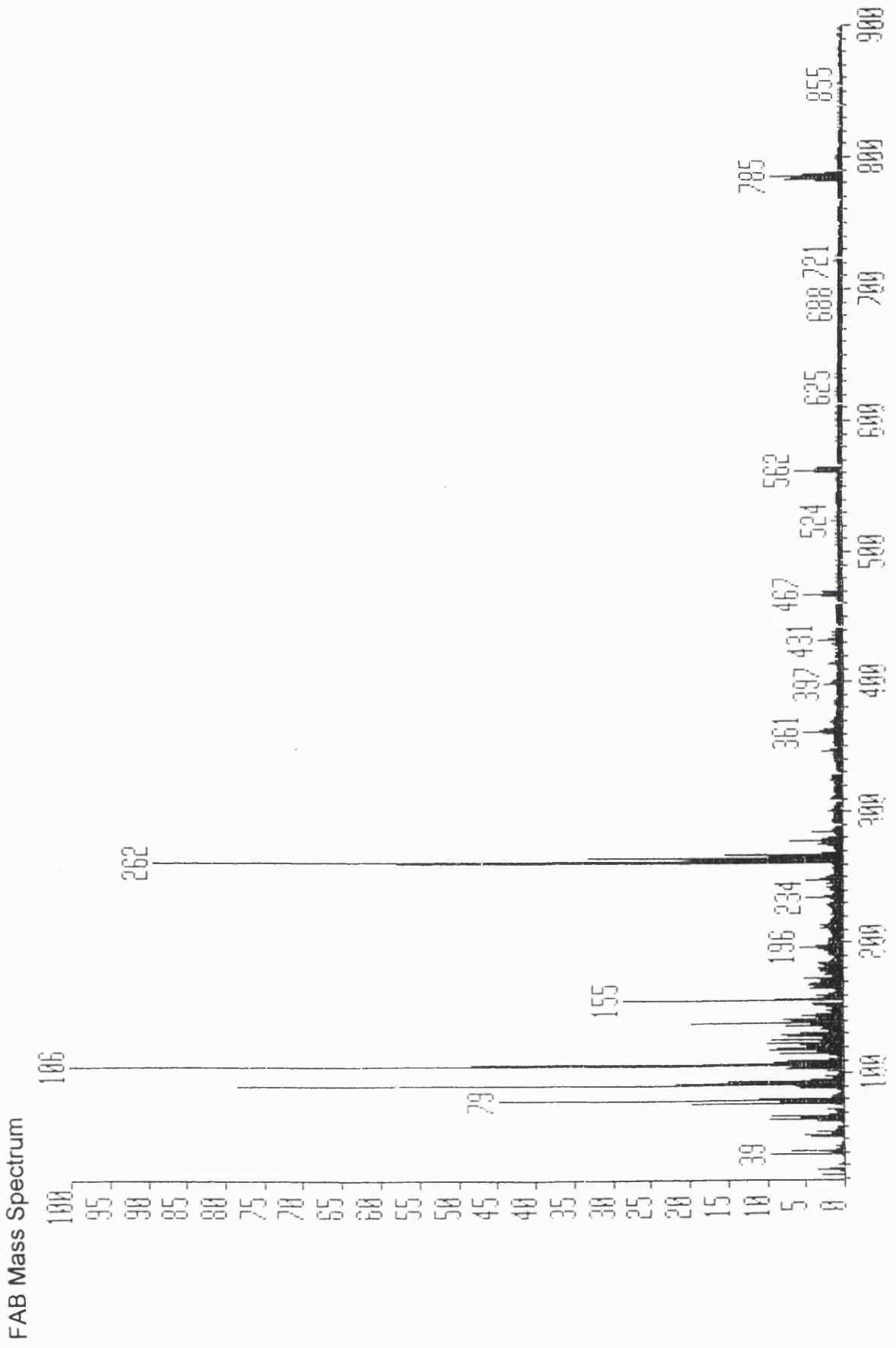
Bond Angles [deg] for [Co(TosNSC(NEt$_2$)SNTos)$_2$]

N(5) -Co(1)-N(2)	117.51(17)	C(37)-N(6) -C(35)	115.7(5)
N(5) -Co(1)-N(4)	92.89(16)	C(6) -C(1) -C(2)	118.1(5)
N(2) -Co(1)-N(4)	115.02(17)	C(6) -C(1) -S(1)	120.6(4)
N(5) -Co(1)-N(1)	124.64(17)	C(2) -C(1) -S(1)	121.2(4)
N(2) -Co(1)-N(1)	92.89(16)	C(3) -C(2) -C(1)	120.0(6)
N(4) -Co(1)-N(1)	115.79(16)	C(2) -C(3) -C(4)	121.8(6)
O(2) -S(1) -O(1)	118.7(2)	C(5) -C(4) -C(3)	118.2(6)
O(2) -S(1) -N(1)	110.7(2)	C(5) -C(4) -C(7)	120.4(7)
O(1) -S(1) -N(1)	105.0(2)	C(3) -C(4) -C(7)	121.4(6)
O(2) -S(1) -C(1)	107.2(3)	C(4) -C(5) -C(6)	120.6(6)
O(1) -S(1) -C(1)	107.9(2)	C(5) -C(6) -C(1)	121.3(5)
N(1) -S(1) -C(1)	106.8(2)	C(13)-C(8) -C(9)	118.7(7)
O(4) -S(2) -O(3)	118.7(3)	C(13)-C(8) -S(2)	121.2(6)
O(4) -S(2) -N(2)	111.0(3)	C(9) -C(8) -S(2)	120.1(5)
O(3) -S(2) -N(2)	105.2(2)	C(8) -C(9) -C(10)	120.0(7)
O(4) -S(2) -C(8)	107.2(3)	C(11)-C(10)-C(9)	122.3(8)
O(3) -S(2) -C(8)	107.7(3)	C(10)-C(11)-C(12)	117.5(9)
N(2) -S(2) -C(8)	106.5(3)	C(10)-C(11)-C(14)	122.2(10)
N(1) -S(3) -C(15)	105.4(2)	C(12)-C(11)-C(14)	120.1(10)
N(2) -S(4) -C(15)	104.4(2)	C(11)-C(12)-C(13)	123.0(9)
O(6) -S(5) -O(5)	118.6(2)	C(8) -C(13)-C(12)	118.4(9)
O(6) -S(5) -N(4)	110.8(2)	N(3) -C(15)-S(4)	120.5(4)
O(5) -S(5) -N(4)	105.0(2)	N(3) -C(15)-S(3)	119.2(4)
O(6) -S(5) -C(20)	107.5(3)	S(4) -C(15)-S(3)	120.3(3)
O(5) -S(5) -C(20)	107.8(3)	N(3) -C(16)-C(17)	112.4(6)
N(4) -S(5) -C(20)	106.5(2)	C(19)-C(18)-N(3)	112.4(6)
O(7) -S(6) -O(8)	118.8(2)	C(21)-C(20)-C(25)	120.0(5)
O(7) -S(6) -N(5)	103.9(2)	C(21)-C(20)-S(5)	119.1(4)
O(8) -S(6) -N(5)	111.6(2)	C(25)-C(20)-S(5)	120.9(5)
O(7) -S(6) -C(27)	110.0(3)	C(20)-C(21)-C(22)	119.8(6)
O(8) -S(6) -C(27)	106.7(2)	C(23)-C(22)-C(21)	121.5(6)
N(5) -S(6) -C(27)	105.0(2)	C(22)-C(23)-C(24)	118.2(6)
N(4) -S(7) -C(34)	104.1(2)	C(22)-C(23)-C(26)	122.3(7)
N(5) -S(8) -C(34)	103.5(2)	C(24)-C(23)-C(26)	119.4(7)
S(1) -N(1) -S(3)	113.8(2)	C(25)-C(24)-C(23)	121.8(6)
S(1) -N(1) -Co(1)	123.4(2)	C(24)-C(25)-C(20)	118.7(6)
S(3) -N(1) -Co(1)	121.1(2)	C(28)-C(27)-C(32)	121.0(5)
S(2) -N(2) -S(4)	114.1(2)	C(28)-C(27)-S(6)	120.4(4)
S(2) -N(2) -Co(1)	127.6(3)	C(32)-C(27)-S(6)	118.6(4)
S(4) -N(2) -Co(1)	118.3(2)	C(27)-C(28)-C(29)	118.7(5)
C(15)-N(3) -C(16)	122.9(5)	C(28)-C(29)-C(30)	121.6(6)
C(15)-N(3) -C(18)	121.4(5)	C(31)-C(30)-C(29)	117.7(5)
C(16)-N(3) -C(18)	115.7(5)	C(31)-C(30)-C(33)	121.5(6)
S(5) -N(4) -S(7)	113.3(2)	C(29)-C(30)-C(33)	120.8(6)
S(5) -N(4) -Co(1)	128.3(2)	C(32)-C(31)-C(30)	121.7(5)
S(7) -N(4) -Co(1)	117.7(2)	C(31)-C(32)-C(27)	119.3(5)
S(6) -N(5) -S(8)	113.4(2)	N(6) -C(34)-S(7)	119.7(4)
S(6) -N(5) -Co(1)	125.7(2)	N(6) -C(34)-S(8)	120.1(4)
S(8) -N(5) -Co(1)	120.3(2)	S(7) -C(34)-S(8)	120.2(3)
C(34)-N(6) -C(37)	122.4(5)	N(6) -C(35)-C(36)	112.4(5)
C(34)-N(6) -C(35)	121.9(5)	N(6) -C(37)-C(38)	111.6(6)

Appendix 2 Spectroscopic Data



^{1}H NMR Spectrum


FAB Mass Spectrum
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
39
72
106
155
196
234
262
361
397
431
467
524
582
625
688
721
785
855
900
800
700
600
500
400
300
200
100