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Dithiocarbamate Stabilized Molybdenum Imido Complexes

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In memory of my loving father

Glynn Forster 1st June 1910 - 1st April 1994

Abstract

This thesis is concerned with the synthesis, reactivity and structure of molybdenum imido complexes stabilized by dialkyldithiocarbamate ligands.

The structure of a series of bis(arylimido) complexes $[Mo(NR)_2(S_2CNEt_2)_2]$ is reported and compared to that of the parent complex $[Mo(NPh)_2(S_2CNEt_2)_2]$. The complexes are prepared via two methods, involving either the thermolysis of $[Mo(O)_2(S_2CNEt_2)_2]$ with an organic isocyanate, or the treatment of $[Mo(NR)_2Cl_2(DME)]$ with $[NH_4][S_2CNEt_2]$.

The former reaction was not as simple as expected, affording $[Mo(NR)_2(S_2CNEt_2)_2]$ only with bulky arylisocyanates, the disulfur complexes $[Mo(NR)(S_2)(S_2CNEt_2)_2]$ being the only compounds formed with all isocyanates. The structure and reactivity of the latter is reported, along with an investigation into the formation of the disulfur ligand, which is proposed to be the result of replacement of an oxo for an imido ligand, and a double sulphur-carbon bond cleavage of an additionally coordinated dithiocarbamate ligand.

Other products from the reaction, although all dimeric, vary with the nature of the isocyanate. As the substituent on the isocyanate is increased in steric bulk the product changes from $[Mo(\mu-NR)(O)(S_2CNEt_2)]_2$ (R=Ph, p-Tol) to $[Mo(NR)(\mu-NR)(S_2CNEt_2)]_2$ (R=o-Tol), with no dimeric products being recovered with very bulky substituents. When bulky alkyl isocyanates are used the second product is the dimeric complex $[\{Mo_2(\mu-S)_2(O)(NR)(S_2CNEt_2)_2\}]_2$.

The reactivity and structures of these complexes is discussed, including the reversible addition of an isocyanate into the bridging imido ligand in $[{Mo(NPh)(\mu-NPh)(S_2CNEt_2)}_2]$ affording $[{Mo(NPh)_2(\mu-PhNC(O)NPh)(\mu-NPh)(S_2CNEt_2)_2}]$.

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Abbreviations

	nmr	Nuclear Magnetic Resonance	DME	1,2-Dimethoxyethane
with reference to nmr spectroscopy			THF	Tetrahydrofuran
			DMA	Dimethylacetylenedicarboxylate
	ppm	parts per million	Ср	Cyclopentadienyl
	s	singlet	Cp*	Pentamethylcyclopentadienyl
	d	doublet	acac	Acetylacetonate
	t	triplet	Ме	Methyl
	q	quartet	Et	Ethyl
	sep	septet	Pr	Propyl
	m	multiplet	ⁱ Pr	<i>i</i> -Propyl
	br	broad	Bu	Butyl
			^t Bu	<i>t</i> -Butyl
	ir	Infrared	Ph	Phenyl
with reference to ir spectroscopy			ру	Pyridine
			Tol	Tolyl
	S	strong	Adm	Adamantyl
	m	medium	Tos	Tosylate
	w	weak		

br broad

Declaration

Except where noted, all the work reported in this thesis was carried out by myself in the Department of Chemistry, University College London, between the 1st October 1991 and the 31st September 1994. Those experiments marked by an asterisk in the experimental section were performed by Miss Thérèse Coffey under my direct supervision as part of her 3rd year project.

Glyn DFORKER

Glvn D Forster

Compound Numbers

- 1.1 $[Mo(NR)_2(S_2CNEt_2)_2]$
- 1.2 $[Mo(O)_2(S_2CNEt_2)_2]$
- 2.1 $[MoCl_2(NR)_2(DME)]$
- 2.2 $[Mo(NR)(S_2)(S_2CNEt_2)_2]$
- 2.3 $[MoO(NR)(S_2CNEt_2)_2]$
- 3.1 $[MoO(S_2)(S_2CNEt_2)_2]$
- 3.2 $[Mo(\mu-S)(O)(S_2CNEt_2)]_2$
- 3.4 $[Mo{PhNC(R)C(R)S}{SC(R)C(R)C(NEt_2)S}(S_2CNEt_2)] (R=CO_2Me)$
- 3.6 $[Mo{SC(R)C(R)S}{SC(R)C(R)SC(NMe_2)}(S_2CNMe_2)](R=CO_2Me)$
- 3.7 $[Mo{SC(R)C(R)S}{SC(R)C(R)SC(NMe_2)}(S_2CNMe_2)](R=CO_2Me)$
- $3.8 \quad [Mo_2(\mu\text{-}S)(\mu\text{-}NPh)(O)_2(S_2CNEt_2)_2]$
- 4.1 $[Mo(\mu-O)(O)(S_2CNEt_2)]_2$
- 4.2 $[Mo_2(\mu-S)(\mu-O)(O)_2(S_2CNEt_2)_2]$
- 4.3 $[Mo_2(\mu-S)_2(S)(O)(S_2CNEt_2)_2]$
- 4.4 $[Mo(\mu-S)(S)(S_2CNEt_2)]_2$
- 4.5 $[Mo(\mu-NR)(O)(S_2CNEt_2)]_2$
- 4.6 $[Mo(\mu-NR)(NR)(S_2CNEt_2)]_2$
- 4.7 $[Mo_2(\mu-NR)\{\mu-RNC(O)NR\}(NR)_2(S_2CNEt_2)_2]$
- 4.8 $[Mo_2(\mu-NR){\mu-RNC(NR)NR}(NR)_2(S_2CNEt_2)_2]$
- 4.9 $[Mo_2(\mu-S){\mu-RNC(O)NR}(NR)_2(S_2CNEt_2)_2]$
- 4.10 $[Mo_2(\mu-S){\mu-RNC(NNHC_6H_3(NO_2)_2)NR}(NR)_2(S_2CNEt_2)_2]$
- 4.11 $[Mo_2(\mu-NR)_2(O)(S_2CNEt_2)_3][BF_4]$
- 4.12 $[Mo_2(\mu-S)_2(O)(NR)(S_2CNEt_2)_2]$

The letter after the compound number indicates the substituent on the imido ligand were appropriate. An apostrophe after a compound number indicates the use of dimethyldithiocarbamate instead of the ethyl substituted ligand a=Ph, b=p-Tolyl, c=o-Tolyl, d=2,6-Me₂C₆H₃, e=2,6-Cl₂C₆H₃, f=2,6-ⁱPr₂C₆H₃, g=Tosylate, h=^tBu, i=Adamantyl.

Introduction

This report is primarily concerned with the synthesis of molybdenum bis(imido) complexes of the type $[Mo(NR)_2(S_2CNR'_2)_2]$ **1.1**. Chelating dithiocarbamate ligands¹, which have been shown to stabilize both high² and low³ oxidation states of molybdenum, being used as innocent spectator groups. These complexes were then to be investigated as potential imido transfer reagents. Although a synthetic route to them is known⁴, it involves the use of organic azides which are highly explosive. Thus, a new safer route was sought, via the use of organic isocyanates as the source of the imido functionality. However during attempts to synthesise a number of bis(imido) complexes the dithiocarbamate ligands became involved in the reaction, acting as a source of either sulfido or disulfur ligands. This general introduction details the reactions of oxo and alkylidene ligands, which are isoelectronic with the imido ligand, towards organic substrates. It then covers the bonding, synthesis and reactivity of known monoimido complexes. A comprehensive review of ligands containing multiple bonds to metals (oxo, imido, nitrido, hydrazido(2-), alkylidene and alkylidyne) was published in 1988⁵.

1.1 Metal-Oxo Complexes

Oxo ligands (O^{2-}), formally doubly deprotonated water molecules, are strong π -donor groups found mainly in high oxidation state metal complexes. For many years such complexes have been utilized in organic synthesis to facilitate many useful reactions.

1.1.1 Epoxidation: The formation of epoxides from alkenes by the use of stoichiometric amounts of a metal-oxo complex such as $[Cr(O)_2(ONO_2)_2]^6$, has received much attention due to the versatility of epoxides as intermediates in organic synthesis.



Figure 1.1 Epoxidation of an alkene

However, although a number of systems have been developed that facilitate this reaction⁷, a complete understanding of the mechanism has not yet been achieved⁸. This has not prevented the development of catalytic iron porphyrin complexes that promote the synthesis of chiral epoxides⁹, and a catalytic porphyrin complex of ruthenium that utilises atmospheric oxygen as the stoichiometric oxidant¹⁰. However, despite the interest in metal oxide complexes as epoxidation catalysts the most widely used catalytic system is that developed by Sharpless^{11,12}, involving the use of titanium tetraisopropoxide, (+) or (-) -diethyl tartrate and *t*-butyl hydroperoxide. This system has been shown to give enantiomeric excesses of greater than 90% for allylic alcohols.

1.1.2 *Cis*-1,2-Dihydroxylation of Alkenes: *Cis*-1,2-dihydroxylation of alkenes is often achieved by the use of $[OsO_4]^{13,14}$. It had been recognized for some time that the rate of this reaction is greatly enhanced by the addition of a tertiary amines¹⁵. For example, the addition of pyridine in greater than stoichiometric amounts was noted to be extremely beneficial, and the isolated osmate esters from reactions carried out in excess pyridine have been shown to contain two molecules of pyridine in the coordination sphere of the osmium¹⁶. An explanation for these observations was offered by Sharpless (Fig 1.2)¹⁷. Coordination of one pyridine to a [OsO₄(alkene)] molecule, leads to the formation of an oxametallacyclobutane intermediate, attack of a second pyridine molecule then induces formation of the observed osmate ester.



Figure 1.2 Sharpless's Mechanism for the Reaction of [OsO₄] with Alkenes in the Presence of Pyridine

More recently, Jörgenson and Hoffman¹⁸ have reported an alternative mechanism supported by a frontier orbital study. They showed that the interaction of an alkene with $[OsO_4]$ would lead to the formation of a disfavoured tetrahedral d²- intermediate $[Os(O)_2{OC(R)C(R)O}]$. However, initial coordination of two pyridine molecules would afford an octahedral complex. In which the oxygen atoms in the equatorial positions are physically closer together, and which has a HOMO and a LUMO of correct symmetry to interact with the π and π^* orbitals of an alkene.



Figure 1.3 Jörgenson and Hoffman's Mechanism for the Reaction of $[OsO_4]$ with Alkene in the Presence of Pyridine

This improved understanding of the mechanism has lead to the development of chiral diamines^{19,20} (Fig 1.4) which allow the asymmetric *cis* - 1,2-dihydroxylation of alkenes with up to 90% enantiomeric excess, by inducing chirality into the osmate ester intermediate.



Figure 1.4 Chiral Diamines used in cis-1,2-Dihydroxylation

1.1.3 Oxo Transfer Reactions: Many metal oxide species have been shown to effect the transfer of an oxo group from the metal to an organic (or inorganic) molecule. A review of such processes by Holm appeared in 1987²¹. Although this reaction has been observed for most of the transition metals, molybdenum has by far the most reported examples. This is due principally to molybdenum being involved in the active site of a number of enzymes that perform oxo transfer chemistry in biological systems²².

Several molybdenum complexes have been developed to transfer oxo groups, one group of such complexes are based on octahedral molybdenum(VI) complexes of the type $[Mo(O)_2(L)_2]$, where L is a monoanionic chelating ligand. These systems have been shown to especially effective for ligands (L) bound via sulphur atoms such as dithiocarbamate (S₂CNR₂).





Although these complexes are good catalytic oxo transfer reagents, due to the oxidation of the molybdenum(IV) species been effected by molecular



Figure 1.6 Bulky Ligand Used By Holm to Prevent Dimer Formation

oxygen. A dimeric molybdenum(V) species can become involved in the reverse oxidation process, complicating the kinetics of the system. Recently Holm and coworkers have overcome this problem by the use of a bulky ligand that chelates though sulphur and nitrogen atoms (Fig 1.6). These complexes have been shown to be the most effective oxo transfer reagents to date^{23,24}.

1.2 Metal-Alkylidene Complexes

Alkylidene ligands ($CR_2^{2^{\circ}}$) are also strong π -donor groups, differing from oxo and imido ligands in that they cannot form a second π -bond with a metal centre. A result of not having a lone pair of electrons on the carbon atom. They are divided into two classes. Fischer alkylidene ligands have a noncarbon bound group attached to the α -carbon atom, such as NR₂ or OR. These ligands are found generally in low oxidation state metal complexes. Schrock alkylidenes do not posses such groups, and are generally found in high oxidation state complexes. For the purposes of this report we will not consider the classes separately.

1.2.1 Cyclopropanation: The implication of alkylidene ligands in cyclopropanation reactions is not as well understood, and there are less clear cut examples of this type of reaction, a review of these reactions was published in 1987²⁵. The classic procedure for cyclopropanation using metal reagents is that reported by Simmons and Smith²⁶. The success of this method depends on the activity of the copper/zinc reagent used, although the reaction

is not believed to proceed via an alkylidene intermediate in the cyclopropanation step, an organo zinc intermediate is believed to be involved.



Figure 1.7 Mechanism of Simmons and Smith Cyclopropanation The role of metal alkylidene species in cyclopropanation is demonstrated by the reactivity of $[Fe(Cp)(dppe)(CH_2OCH_3)]^{27,28}$ (dppe=bis(diphenylphosphino)ethane). Treatment of this complex with trifluoroacetic acid leads to loss of methanol from the coordinated organic fragment, leaving an alkylidene moiety. This intermediate reacts with an alkene leading to formation of a cyclopropane which contains the methylene unit.



This has also been extended to the synthesis of chiral cyclopropanes. Thus, when the chiral substrate $[Cr(CO)_4(PPhPrMe)(CHOMe)]^{29}$ is treated with a prochiral alkene, high enantioselectivity is observed.

Figure 1.8 Cyclopropanation using an Iron Alkylidene Complex



Figure 1.9 Chiral Cyclopropanation Using a Chromium Alkylidene Complex

1.2.2 Ylide Type Reactions: In a reaction that is directly analogous to the phosphorus ylides of Wittig³⁰, alkylidene species react with organic carbonyl compounds, to give the corresponding alkene and a metal oxo species^{31,32}. However unlike the phosphorus ylides, this reaction works for the carbonyl groups in ester and amides functionalities, and even for carbon dioxide.



Figure 1.10 Replacement of an Carbonyl Oxygen by an Alkylidene Group

A reagent for the replacement of a carbonyl oxygen atom by a CH₂ unit has been developed by Grubbs³³, from a titanium system first reported by Tebbe³⁴, which involves a methylidene bridging between titanium and aluminium.



Figure 1.11 Grubbs system for Methylidene Transfer

1.3 Imido Ligands

The first example of an imido complex, namely $[OsO_3(^{t}BuN)]$, was reported by Clifford and Kobayashi in 1956³⁵. Imido ligands are formally doubly deprotonated amines (RN²⁻) and are isoelectronic with oxo (O²⁻), alkylidene (R₂C²⁻), sulfido (S²⁻) and other similar π -donor ligands. As with other π -donor ligands, imido ligands exhibit a strong *trans* influence which **a** ffects the structure of complexes containing them in two ways. The bond to the atom

that is *trans* to the imido ligand is elongated, and the metal atom is shifted out of the plane defined by the ligands *cis* to the imido ligand, towards the imido moiety. Complexes containing imido ligands, of a variety of transition metals in numerous oxidation states have been observed showing five types of coordination to metal complexes.



1.3.1 Terminal Linear: This is observed in the majority of cases were an imido is coordinated to only one metal centre. The lone pair on the nitrogen is involved in bonding to the metal and the ligand is considered to be a fourelectron donor¹, with a bond order of three. The angle about the nitrogen atom is typically greater than ~150°.

1.4.2 Terminal Bent: To date there have been few examples of this type of coordination of an imido ligand characterised crystallographically. As in the terminal linear case the ligand is bound to only one metal centre, but now the lone pair on the nitrogen atom is not formally involved in bonding and so the angle about nitrogen tends to 120°. Normally however, an imido will be considered to be bent if the angle is less than 150°, with angles between that and linearity being rationalised as a result of steric and crystal packing interactions³⁶. The ligand in this bonding mode is formally a two electron

¹ While the imido ligand is best considered as an NR²⁻ fragment, for the purposes of electron counting the diradical nitrene formalisation NR will be utilised throughout.

Chapter I: Introduction

donor, and has a bond order of two. The first example of this form of bonding to be crystallographically characterised was in t h e b i s (i m i d o) c o m p l e x $[Mo(NPh)_2(S_2CNEt_2)_2]$ **1.1a**⁴ which shows both the linear $[169.4(4)^\circ]$ and bent $[135.4(4)^\circ]$ forms of terminal imido ligation.

Recently Minelli and coworkers³⁷ synthesized $[Mo(NC_6H_4S)CI(S_2CNEt_2)_2]$ from 2-aminothiophenol and $[MoOCl_2(S_2CNEt_2)_2]$, which was the first example of a chelating ligand containing an imido moiety. The angle about the



Figure 1.13 X-Ray Crystal Structure of [Mo(NPh)₂(S₂CNEt₂)₂] 1.1a

nitrogen atom at 137.7(7)° is severely bent, although in this case the ligand is forced somewhat into this situation to accommodate the formation of the five membered ring. It is interesting to note that the corresponding diamine does not afford the expected bis(imido) chelating system³⁸, but rather gives an imido with a free amine substituent. Also the corresponding methoxy complex $[Mo(NC_6H_4S)(OCH_3)(S_2CNEt_2)_2]^{39}$ has been observed, again showing bent imido ligation in the chelate ring [136.4(4)°].



Figure 1.14 Example of a Chelating Imido Ligand

1.3.3 Bridging: In this bonding mode the imido ligand bridges a number (2-4) of metal atoms in a cluster, and acts as a four-electron donor. Doubly bridging imido ligands are predominately found for the early transition metals. Here the low oxidation state of the metal, coupled with the tendency of the remaining ligands in the complex to be monodentate anions, leads to the formation of coordinatively unsaturated complexes, which as a consequence form dimers linked via the imido ligands. The bridge is often symmetric, however a number unsymmetrically bridged dimers having been reported^{40,41}. The formation of an unsymmetrically bridged structure has been rationalised as a result of a second order Jahn-Teller distortion in the molecule, thus increasing the HOMO-LUMO gap, which otherwise would be small. Triply and quadruply bridging imido ligands generally are observed for the late transition metals. Here the metal centres have diminished capacity for metal-nitrogen π -bonding, due to the presence of electrons in the metal d-orbitals reducing the number available for π -bonding. The lack of available orbitals causes the imido ligand to interact with multiple metal centres in order to form the appropriate number of bonding interactions.



Figure 1.15 Examples of Doubly⁴², Triply⁴³ and Quadruply Bridging⁴⁴ Imido Ligands

1.4 Synthesis of Imido Ligands

A number of routes to imido complexes have been reported in the literature, more general examples of which, and those pertinent to this report will be detailed below.

1.4.1 Oxidative-Addition: This methodology has been used with success to introduce imido ligands to low-valent metal centres. The source of the imido fragment is usually an isocyanate⁴⁵, leading to an imido carbonyl complex, or an azoalkane⁴⁶⁻⁵¹ derivative leading to the formation of a complex containing more then one imido ligand. Both of these reagents can lead to the formation of a side bound π -complex instead of the cleaved imido containing complex^{52,53,54}.



Figure 1.16 Formation of an Imido Ligand via Oxidative-Addition

In some oxidative-addition reactions only half the cleaved molecule coordinates to the metal centre. As is the case with organic azides. where the dinitrogen fragment remains uncoordinated⁵⁵⁻⁵⁸. The use of azides however, is not widespread due to their explosive nature. Although recently they have been use in the synthesis of novel imido complexes, including the synthesis of linking imido units⁵⁹.

Figure 1.17 Use of Organic Azides in the Synthesis of an Imido Moiety

1.4.2 Alkylation of a Nitrido Ligand: This has limited uses due to difficulty in preparation of the precursor nitrido moiety, which **is** generally not sufficiently nucleophilic to react. It thus only works well for certain groups, in which a substantial positive charge can be generated on one atom, such as Me, H or $Ph_3C^{60.61}$. A complex which can be alkylated by all of these reagents is $[Mo(N)(S_2CNEt_2)_3]^{62}$ which is apparently more nucleophilic than most nitrido complexes.



Figure 1.18 Alkylation of a Nitrido to give an Imido Moiety

1.4.3 Replacement of an Oxo Ligand: A number of reagents have been used to replace oxo ligands by imido moieties. Here we will consider only those methods which have been employed during this study, namely the use of primary amines and organic isocyanates. The reaction of a primary amine with an oxo complex to give an imido ligand and water has been widely used^{63,64}. However, this method can prove problematic due to the formation of water, which can often drive the reaction back to the starting materials. In many cases it has to be removed by the presence of a drying agent. The latter though can sometimes become involved in the reaction leading to different products to those expected⁶⁵.





The use of organic isocyanates in the synthesis of imido ligands is well documented^{66,67,68,69}, and has the advantage over the use of primary amines in such reactions that it generates carbon dioxide as the by product, which is rarely involved further in the reaction. However, organic isocyanates are not available with the same diversity of functional groups as primary amines, and are difficult to synthesise from the corresponding primary amine⁷⁰, although recently a new simpler route has been reported⁷¹.



Figure 1.20 Mechanism of the Replacement of an Oxo by an Imido Ligand Using Organic Isocyanates

The reaction is believed to occur via an initial [2+2] cycloaddition of the isocyanate to the metal-oxygen bond forming a four-membered metallocycle. This can then either break down back to the oxide and the isocyanate, or go on to give the imido and carbon dioxide. Some evidence for this metallocyclic intermediate comes from the reaction of [Cp₂MoO] with phenylisocyanate, which lead to clean formation of the metallocyclic complex [Cp₂Mo{OC(O)NPh}], characterised by X-ray crystallography⁷². However, refluxing this complex in THF did not lead to formation of the corresponding

imido species.



Figure 1.21 Isolation of the Metallocyclic Intermediate

This must be a consequence of the stability of the metallocyclic complex as the imido complex has since been synthesised by Green and co-workers⁷³, via treatment of $[Mo(Cp)(N^tBu)(C_2H_4)CI]$ with NaCp. The reaction of this complex with carbon dioxide however is not reported.

1.4.4 Substitution of Other Ligands: The substitution of ligands such as halides for imido moieties has been frequently used, and utilizes a number of reagents as the source of the imido moiety. A typical synthesis involves the replacement of two halide ligands by an imido group. This is achieved by treatment of the metal dichloride with two equivalents of a mono alkylated amide (LiRNH) to give the bis(amide) complex via substitution. Which then undergoes an elimination reaction, giving the required imido complex and an amine⁷⁴. The use of the lithiated amide is not always required to replace halide ligands by imido ligands, with some syntheses requiring only the primary amine to be used⁷⁵.



Figure 1.22 Formation of an Imido Ligand Via the use of Lithium Amide

Silyl amines have also been utilized to replace an oxo ligand and a halide ligand, by an imido ligand and a silyloxy moiety. The driving force for this reaction is the strength of the silicon-oxygen bond formed⁷⁶.



Figure 1.23 Mechanism of the Reaction of RNHSiMe₃ with M(O)X Species

1.5 Reactivity of Imido Complexes

1.5.1 Reactions of Co-Ligands: The replacement of other ligands in the coordination sphere of imido complexes is often seen due to the stability of a large number of imido complexes. Complexes where the imido ligand has been shown to be inert to a number of reagents include $[Mo(MeCp)(NR)(Cl)_2]$ (R=Ph, ^tBu)⁷⁷.



Figure 1.25 Reactions of [Mo(MeCp)(NR)(Cl)₂] (R=Ph, 'Bu)

Treatment with sodium amalgam in the presence of neutral ligands (MeC_2Me, C_2H_4, PMe_3) , leads in all cases to retention of the imido moiety, even though when trimethylphosphine is used the usually substitutional inert cyclopentadienyl ligand is replaced.

A more interesting example is the formation of carbon-carbon bonds when $[TaCl_3(py)_2(2,6^{-i}Pr_2C_6H_3N)]$ is treated with ^tBuCCH affording a metallocyclopentane⁷⁸.



Figure 1.26 Reaction of [TaCl₃(py)₂(2,6-ⁱPr₂C₆H₃N)] with 'BuCCH

The use of imido ligands to stabilise a metal centre while reaction occurs elsewhere in the molecule, has been utilised extensively in the complexes $[M(NAr)(CR')(OR'')_2]$ [M=Mo,W] shown to be effective ring opening metathesis polymerisation (ROMP) catalysts⁷⁹. In a ROMP reaction the catalyst promotes molecules containing endocyclic alkene groups to ring open and form polymers.



Figure 1.27 Mechanism of Polymerisation Using ROMP Catalysts

The mechanism by which this occurs is an extension of alkene metathesis by alkylidene species, and is driven by the release of ring strain in the organic molecule. ROMP catalysts have shown a variety of advantages over conventional polymerisation techniques, such as high control over tacticity, a simplification in preparation of block co-polymers due to the living nature of the system, and the ability to withstand a number of functionalities and substituents on the ring⁸⁰.

1.5.2 C-H Bond Activation by Imido Ligands: The activation by imido ligands of C-H bonds has been mainly observed for complexes of the early transition elements^{81,82,83}. An example of this type of behaviour is in the reaction between $[({}^{t}Bu_{3}SiNH)_{2}Zr(NSi{}^{t}Bu_{3})]$ and PhH⁸⁴, to give $[({}^{t}Bu_{3}SiNH)_{3}ZrPh]$.



Figure 1.28 C-H Bond Activation by [('Bu₃SiNH)₂Zr(NSi'Bu₃)]

Recently an analogous vanadium system has been reported that activates a wide range of C-H bonds including those in methane, as shown by the addition of ¹³C labelled methane⁸⁵. Although this reaction appears to only involve the substitution of the methyl in the starting complex for another alkyl group, the intermediate bis(imido) complex can be trapped by the addition of coordinating solvents (THF, pyridine or ether).



Figure 1.29 C-H Bond Activation by [('Bu₃SiNH)₂V(NSi'Bu₃)Me]

1.5.3 Insertion of Unsaturated Organic Molecules: The insertion of unsaturated organic molecules such as alkenes, alkynes and heterocumulenes

has been observed for imido complexes from both ends of the transition series, although the greatest? diversity of reactions is observed for the 'pogostick' complexes of osmium and iridium.

Where as zirconium⁸⁶ and vanadium⁸⁷ imido complexes have only been shown to add alkynes, osmium⁷⁴ and iridium^{88,89,90} imido complexes such as [(Cp*)Ir(N^tBu)] have been shown to add a variety of reagents across the metal nitrogen bond (Fig 1.30).

For example, treatment with the activated alkyne DMAD leads to the insertion of two molecules of alkyne to give a coordinated pyrrole fragment. This is believed to be formed by the mechanism shown in Figure 1.31. Initial insertion of one alkyne affords a metallocyclobutane ring, which undergoes a second insertion to give a metallocyclohexane. This then proceeds via a carbon-carbon bond formation to give the observed product (Fig 1.31).



Figure 1.30 Reactions of [(Cp*)Ir(N'Bu)]



Figure 1.31 Mechanism of the Reaction of [(Cp*)Ir(N'Bu)] with DMAD

These types of reactions are not limited to mononuclear complexes or indeed to terminal imido moieties, a number of iron and ruthenium trimetallic clusters containing triply bridging imido ligands has been reported to react with alkynes to give a variety of complexes containing new N-C bonds^{91,92,93}

1.5.4 Imido Transfer Reactions: There have been a few examples of the transfer of a NR group in the literature that utilize either metal catalysts or stoichiometric metal-imido species. Treatment of $[Mn(TPP)(OCOCF_3)(NTos)]$ (TPP=tetraphenylporphrin) with an alkene affords the corresponding aziridene⁹⁴. The reaction is however highly water sensitive, with the rest of the alkene been recovered as the epoxide. This is probably due to hydrolysis of the imido complex to the corresponding oxide, which quantitatively converts the alkene to the epoxide⁹⁵.



Figure 1.31 Reaction of [Mn(TPP)(OCOCF₃)(NTos)] with Cyclooctene Recently, Evans and co-workers have shown that copper(I) triflate converts alkenes to the corresponding chiral aziridenes in the presence of 4,4'-

disubsituted bis(oxazolines) and a source of NR (PhI=NTos) (Fig 1.32) in yields up to 89% and in up to 89% enantiomeric excess⁹⁶. Although the nature of the active catalyst is not known, it is interesting to note that copper(II) triflate also gives comparable yields and enantiomeric excesses.



Figure 1.32 Catalytic Aziridination Using Copper(I) Triflate

1.5.5 Reactivity of the Aryl Ring: There have been few reports of reactivity of the alkyl or aryl substituent of imido complexes⁹⁷. One such example is the reactivity of the dirhodium complex $[Rh_2(\mu-dppm)_2(\mu-4-MeC_6H_4N)(CO)_2]^{98,99}$, in which the carbon in the phenyl ring that has the methyl group attached to it, is susceptible to electrophilic attack. Thus, treatment with methyliodide gives the complex $[Rh_2(\mu-dppm)_2(\mu-4,4-Me_2C_6H_4N)(CO)_2][I]$.



Figure 1.33 Reaction of [Rh₂(µ-dppm)₂(µ-4-MeC₆H₄N)(CO)₂] with MeI

1.6 Summary

During this introduction metal-oxo and metal-alkylidene complexes have been shown to display a variety of substitution and transfer reactions. With oxo ligands these tend to occur in polyoxo complexes such as $[OsO_4]$. In contrast, with alkylidene ligands reactions tend to occur with monoalkylidene complexes. With the imido ligand, which is isoelectronic to both oxo and alkylidene ligands, complexes that contain one imido ligand are substitutional inert in the majority of cases. In the next chapter it will be shown that bis(imido) complexes show greater reactivity, with one of the imido ligands becoming easier to displace.

Molybdenum(VI) Bis(Imido) Complexes

2.1 Introduction

Mononuclear bis(imido) complexes have been of great interest as catalysts since Sharpless synthesised the first such complex $[Os(O)_2(N^tBu)_2]$ in 1977¹⁰⁰, which was shown to effect the transformation of alkenes into geminal diamines. The first reported example of a bent imido ligand was also a bis(imido) complex, namely $[Mo(NPh)_2(S_2CNEt_2)_2]^4$ **2.1a**. Bent imido ligands are expected to show a greater nucleophilicity and reactivity than linear imido linkages, due to the formal presence of a lone pair on nitrogen. While loss of one of the imido ligands will cause the second to become a stronger π -donor, thus stabilising the complex, known as the spectator effect^{101,102,103,104}.



Figure 2.1 Geminal Diamination by [Os(O)₂(N^tBu)₂]

Bis(imido) complexes are now known for a number of the transition metals V⁸⁵, Ta^{105,106}, Re^{107,108,109}, Ru¹¹⁰, Rh¹¹¹, Os¹¹², Cr¹¹³, Mo¹¹⁴, W¹¹⁵. Here we will consider only those of the group six transition metals. Bis(imido) complexes of this group are found with a wide range other ligands in the coordination sphere, and in general have a d⁰ metal configuration. They generally display either tetrahedral or octahedral (usually distorted) geometry. However, Gibson and co-workers have synthesised the five coordinated complex [Mo(2,6-ⁱPr₂C₆H₃N)₂(2,6-(OCPh₂CH₂)₂C₅H₃N)], which displays distorted trigonal bipyramidal geometry¹¹⁶, and contains both linear and bent forms of terminal imido ligation [164.7(4)°, 144.8(5)°].

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Figure 2.2 Preparation and Molecular Geometry of $[Mo(2,6^{-i}Pr_2C_6H_3N)_2(2,6\text{-}(OCPh_2CH_2)_2C_5H_3N)]$

The first group six bis(imido) complex was reported by Nugent and coworkers^{117,118} in 1979, the synthesis of the chromium complex $[Cr(N'Bu)_2(OSiMe_3)_2]$ proceeded in good yield from the treatment of $[CrO_2Cl_2]$ with *t*-butyl(trimethylsilyl)amine. Since then, the alkoxide complexes of the heavier group six metals have attracted much attention, due to their intermediacy in the synthesis of ROMP catalysts of the type $[M(NR)(CR_2)(OR)_2]^{119}$ (M=Mo,W). The precursors to these complexes $[M(NR)_2Cl_2L]$ (where L is typically DME or 2,2'-bipyridine) provide an easy route to a wide range of bis(imido) complexes of molybdenum, due to the ease of displacement of the chlorides and the neutral ligand, upon treatment with anionic ligands such as alkoxide.



Figure 2.3 Synthesis of [Mo(NR)₂Cl₂(DME)] 2.1

Although the corresponding tungsten complexes $[W(NR)_2Cl_2L]$ have been reported^{120,121,122,123}, they have not been studied as greatly as their molybdenum counterparts. This is because the synthesis of these complexes is not as simple as in the molybdenum system, and more convenient ways to the ROMP catalysts have been employed¹²⁴ that do not involve the use of bis(imido) complexes.



Figure 2.4 Preparation of the Alkoxide Complexes from [Mo(NR)₂Cl₂(DME)] 2.1

The substitution reactions of the dichloro complexes has recently been taken a stage further by Sundermever and co-workers¹²⁵, who treated the analogous unsolvated complexes with carbonyl metallates such as $[Mo(CO)_3Cp]$ and $[Co(CO)_4]$ to form a variety of homo and hetero trimetallic complexes (Fig 2.5).



Figure 2.5 Formation of Heterotrimetallic Species from [Mo(NR)₂Cl₂]

The alkoxide complexes themselves can be used to prepare new bis(imido) complexes. The trimethylsilyloxy ligands in $[Cr(N^tBu)_2(OSiMe_3)_2]$ can be replaced by organic σ -bound ligands upon treatment with two equivalents
of RMgBr to give $[Cr(N^tBu)_2R_2]$ (R=2,6-Me₂C₆H₃, 2,4,6-Me₃C₆H₂)¹²⁶. The mesityl derivative being the first bis(imido) chromium complex to be characterized by X-ray crystallography.



Figure 2.6 Preparation of $[Cr(N^{t}Bu)_{2}R_{2}]$ (R=2,6-Me₂C₆H₃, 2,4,6-Me₃C₆H₂)

Attempts by Nugent and co-workers to synthesise similar complexes with less sterically demanding aryl groups, via treatment of $[Cr(N^{t}Bu)_{2}(OSiMe_{3})_{2}]$ with diphenylzinc⁷⁶, led only to recovery of *t*-butyl-phenylamine and biphenyl. These products are believed to be formed by the expected replacement of one of the trimethylsiloxy groups by a phenyl to form $[Cr(N^{t}Bu)_{2}(OSiMe_{3})Ph]$. The latter can now either undergo another substitution to give the bis(phenyl) complex which then eliminates biphenyl, or undergoes a phenyl migration to the electron deficient imido nitrogen leading to formation of an amido, subsequently lost as the amine (Fig 2.7).



Figure 2.7 Reaction of $[Cr(N^tBu)_2(OSiMe_3)_2]$ with Diphenyl Zinc This mechanism was also shown to occur for the bis(mesityl)

complexes¹²⁷, which after insertion of carbon monoxide into both of the chromium carbon bonds affords the thermally unstable bis(acyl) complex. The latter decomposing via migration of the acyl groups to the imido ligands to give $HN(^{1}Bu)COC_{6}H_{2}Me_{3}$.



Figure 2.8 Reaction of [Cr(N^tBu)₂(2,4,6-Me₃C₆H₂)₂] with Carbon Monoxide

The tetrahedral molybdenum alkoxide complexes display varied reactivity of the imido ligands¹²⁸. For example, treatment of $[Mo(O'Bu)_2(N'Bu)_2]$ with two equivalents of 2,6-diisopropylamine leads to exchange of the imido ligands with the amine to give $[Mo(O'Bu)_2(2,6-Pr_2C_6H_3N)_2]$ and *t*-butylamine.



Figure 2.9 Imido Ligand Exchange at a Molybdenum(VI) Centre

These complexes also undergo ligand exchange reactions with complexes containing other π -donor ligands such as $0x0^{129}$. Thus, treatment of $[Mo(O'Bu)_2(2,6-Pr_2C_6H_3N)_2]$ with $[Mo(O'Bu)_2(O)_2]$ gives the mixed ligand species $[MoO(O'Bu)_2(2,6-Pr_2C_6H_3N)]$. The reaction proceeding via a [2+2] cycloaddition intermediate.



Figure 2.10 Reaction of $[Mo(O'Bu)_2(2,6-Pr_2C_6H_3N)_2]$ with $[Mo(O'Bu)_2(O)_2]$ Prior to the work described herein, two known molybdenum bis(imido) complexes containing dithiocarbamate ligands had been reported. They were prepared by the treatment of $[Mo(CO)_2(S_2CNEt_2)_2]$ with organic azides^{4,130}.



Figure 2.11 Preparation of $[Mo(NR)_2(S_2CNEt_2)_2]$ **1.1** from $[Mo(CO)_2(S_2CNEt_2)_2]$ and Organic Azides

However, unlike the previous complexes where co-ligand replacement is often observed, the chemistry of the complexes $[Mo(NR)_2(S_2CNEt_2)_2]$ (R=Ph **1.1a**, Tos **1.1g**) is dominated by the reactivity of one of the imido ligands, which undergoes a number of substitution reactions¹³¹. Treatment of this complex (**1.1a**) with coordinating acid media such as HX (X=CI, Br, I) causes the loss of one imido group (recovered as the acid salt of the amine) and the coordination of the counterion to the metal (Fig. 2.12). A similar reaction occurs with methyliodide giving trimethylphenylammonium iodide and [Mo(NPh)I₂(S₂CNEt₂)₂].



Figure 2.12 Elimination of One Imido via Electrophilic Attack at the Nitrogen

When the complex is treated with none coordinating acid media, such as tetrafluoroboric acid, the lost imido ligand is replaced by another dithiocarbamate, a reaction that also occurs for the oxo analogue $[Mo(O)_2(S_2CNEt_2)_2]$ **1.2**. Presumably the extra dithiocarbamate ligand must have been scavenged from another molecule of the starting material. However, no other molybdenum containing species has been isolated from either of these reactions.



Figure 2.13 Lability of Dithiocarbamates in None Coordinating Acid Media

The reactivity of the imido ligand in complexes of this type was developed further by Holm¹³⁰, who synthesised the tosylate derivative by a variety of routes. The reactivity of **1.1g** towards phosphines was investigated and it was shown that like the corresponding oxo complex, this complex transfers imido groups to the phosphine giving rise to the reduced metal species [Mo(NTos)(S₂CNEt₂)₂] and the phosphorus imine.



Figure 2.14 Imido Group Transfer to a Phosphine

2.1.1 Structure: The structure of bis(imido) complexes poses something of a problem. Typically the metal ligand fragment, that the two imido moieties are coordinated to, already has twelve valence electrons and thus only requires another six from the two imido ligands. This theoretically could be achieved with one imido being linear and acting as a four electron donor, and the other bent, and a two electron donor. However, this is only observed in a minority of cases. **1.1a**⁴ being the first such complex reported, containing an extremely bent imido ligand [139.4(4)°].

In the majority of cases though the imido ligands in such systems are bent to a comparable degree, usually about 160°. If both imido ligands are considered to be four electron donors, then the molecule is a 20-electron species. This is unlikely, as molecular orbital calculations¹³² have shown that an octahedral metal centre only has three orbitals of appropriate symmetry that can interact with two π -donor ligands in a *cis* configuration. Thus they can only form a total of three π -bonds to the metal, and so both the imido ligands cannot be four electron donors.

It is however, possible for both imido ligands to be equivalent. Molecular orbital calculations¹³³ on the tetra(imido) complex $[MoCp(\mu-NH)(NH)]_2$, formally a 38-electron species before its metal-metal interaction is considered, have shown that the two HOMO's of the molecule contain approximately equal contributions from both the terminal and bridging imido ligands, and are non-bonding with respect to the metal. Thus, one electron per imido ligand is not

involved in metal-ligand π -bonding and the imido ligands act as three electron donors. Consequently, both imido ligands in a bis(imido) complex can formally be three electron donors, giving them a bond order intermediate between two and three.

During this introduction it has been shown that bis(imido) complexes show a wider range of substitution reactions compared to mono(imido) complexes. Also, although bent imido ligands are expected to show greater reactivity than their linear counterparts, very few examples of this form of ligation have been characterised. The rest of this chapter details attempts to synthesise complexes analogous to one of the molecules known to contain a bent imido ligand $[Mo(NPh)_2(S_2CNEt_2)_2]$ **1.1a**⁴.

2.2 Synthesis of [Mo(NR)₂(S₂CNR'₂)₂] 1.1 Complexes

2.2.1 From [Mo(O)₂(S₂CNR'₂)₂] 1.2 and Organic Isocyanates: Treatment of 1.2 or 1.2' with phenyl and other sterically undemanding isocyanates did not give any of the corresponding bis(imido) complexes upon workup. Instead, complexes of the type $[Mo(NR)(S_2)(S_2CNR'_2)_2]$ **2.2** were obtained (Chapter 3), together with a range of molybdenum(V) dimers (Chapter 4). However, the use of isocyanates containing bulky substituents in the two and six positions of the phenyl ring did lead to the formation of bis(imido) complexes in moderate yield along with 2.2. The reaction of 1.2 with 2,6-R₂C₆H₃NCO (R=Me, Cl, ⁱPr) in refluxing toluene lead to the formation of brown [Mo(2,6-R₂C₆H₃N)₂(S₂CNR'₂)₂] **1.1d-f** in moderate yield after purification by column chromatography. These complexes are typically characterised by the absence of a band in the region of the ir spectra associated with Mo=O (900-1000 cm⁻¹)¹³⁴, the presence of bands assignable to Mo=N (~1250 cm⁻¹) and C=N (~1510 cm⁻¹), and broad ¹H nmr spectra due to dynamic behaviour in solution. Increased reaction times did not lead to increased yields of the bis(imido) product, and indeed in the case of 1.1d lead to a reduction. Reaction with only one equivalent of isocyanate in yield

gave a reduced yield of the bis(imido) complex, as opposed to isolation of the mixed oxo/imido species $[Mo(2,6-R_2C_6H_3N)(O)(S_2CNR'_2)_2]$ (R=ⁱPr **2.3f**). This suggests that replacement of one of the oxo ligands by an imido activates the second oxo towards substitution, or that the oxo/imido complex is not stable under these conditions.



Figure 2.15 Thermolysis of 1.2 or 1.2' with $2,6-R_2C_6H_3NCO$ (R=Me, Cl, ⁱPr)

Although thermolysis of a toluene solution of **1.2** in the presence of otolylisocyanate did lead to the formation of the complex [Mo(2- $MeC_6H_4N)_2(S_2CNEt_2)_2$] **1.1c**, shown by a brown band that (like the others complexes of this type) moves down a chromatography column in 20% dichloromethane in petrol. Unlike the other complexes which are stable on the column, this underwent extensive decomposition making purification difficult.

In order to further investigate complexes of this type with sterically undemanding groups, a new route was required to prepare them by. The synthesis would need to carried out at low temperatures, due to some of these complexes being thermally unstable, as noted by the reduced yield of **1.1d** with longer reaction times. Also affording the complexes in high yield would be preferable in order to aid purification.

2.2.2 Synthesis from $[MoCl_2(NR)_2(DME)]$ **2.1** Complexes: As previously noted (2.1), complex **2.1** is easily prepared with a range of imido substituents. Undergoing rapid substitution reactions with monoanionic monodentate ligands, such as alkoxides, to give four coordinate complexes of the type $[Mo(NR)_2(X)_2]^{128}$.



Figure 2.16 Formation of $[Mo(NR)_2(S_2CNEt_2)_2]$ **1.1** from $[MoCl_2(NR)_2(DME)]$ **2.1**

A simple extension of this known chemistry would be the use of monoanionic bidentate ligands such as dithiocarbamate, affording the analogous six coordinate complexes. This would provide a convenient, low temperature synthesis utilising amines instead of isocyanates, the later being available with a greater diversity of functional groups. A further advantage of this method is the availability of precursors with two different imido groups, thus opening the way for systems in which competitive π -donation between two imido ligands can be observed¹³⁵.

Treatment of $[MoCl_2(2,6-R_2C_6H_3N)_2(DME)]$ (R=Me, Cl, ⁱPr) **2.1d-f** with two equivalents of $[NH_4][S_2CNEt_2]$ leads to the formation of $[Mo(2,6-R_2C_6H_3N)_2(S_2CNEt_2)_2]$ **1.1d-f** in high yield. Purification by chromatography gave yields of ~95%, except for **1.1e** which showed appreciable decomposition and smeared on the column. Unlike the previous method this can be extended to none sterically demanding aryl groups such as phenyl. Shown by a colour change from red to brown when $[MoCl_2(NPh)_2(DME)]$ was treated with $[NH_4][S_2CNEt_2]$, and the ¹H nmr spectrum of the crude product which indicated the presence of a complex containing sets of resonances attributable to phenyl protons (δ 7.69, 7.16, 6.76) and ethyl groups on dithiocarbamates (δ 3.89-3.05, 1.43-1.20), along with peaks to other minor unidentified products. However this data is not consistent with that reported in 1978⁴, and further purification of this complex proved problematic due to high water-sensitivity.

Bis(alkylimido) molecules can also be prepared via this method when bulky groups such as *t*-butyl are used. Thus, treatment of $[MoCl_2(N^tBu)_2(DME)]$

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2.1h with $[NH_4][S_2CNEt_2]$ gave the expected bis(alkylimido) complex **1.1h**. Although this complex is also air-sensitive, purification was achieved by recrystallisation from cold ether, affording an orange powder. The ¹H nmr spectrum of this complex at room temperature does not indicate any fluxional behaviour in the complex, showing a single sharp signal at δ 1.37 for the ¹Bu groups, and a sharp quartet (δ 3.80) and a triplet (δ 1.23) for the ethyl groups on the dithiocarbamate ligands. This is in contrast with the aryl complexes which all show broad peaks in their ¹H nmr spectra, and indicates that the fluxional process in the latter is linked to the phenyl rings. The ¹H nmr spectra of these complexes, and the fluxional processes present, will be discussed in more detail in section 2.4.

2.3 Crystal and Molecular Structures

The crystal structures of $[Mo(2,6-R_2C_6H_3N)_2(S_2CNEt_2)_2]$ (R=Me, CI, ⁱPr) **1.1d-f** are of interest so that they can be compared to that of the parent complex $[Mo(NPh)_2(S_2CNEt_2)_2]$ **1.1a⁴** which shows both linear and bent imido ligation. X-ray crystallography was performed on all three complexes. (important crystallographic parameters are summarised in Appendices 1.1-3). Like the structure of **1.1a**, the imido ligands in all three structures are in an approximately octahedral coordination sphere about molybdenum, with the two dithiocarbamate ligands, and show the expected *cis*-configuration. However unlike the structure of **1.1a**, they all display linear imido ligands [169.9(2)°] are symmetry related by a \mathcal{L}_2 rotation axis that passes through the molybdenum centre.

On going from **1.1f** (R=Pr) to **1.1d** (R=Me) a number of changes take place. Although the complex still has two linear imido moieties [162.8(6)° and 162.0(6)°], they are no longer symmetry related to each other. There is also a large decrease in the angle between the phenyl rings which have moved

Mo(1)-S(1)	2.464 (1)
Mo(1)-S(2)	2.672 (1)
Mo(1)-N(2)	1.766 (2)
S(1)-Mo(1)-S(2)	68.6 (1)
S(1)-Mo(1)-N(2)	100.5 (1)
S(2)-Mo(1)-N(2)	90.2 (1)
S(1)-Mo(1)-S(1A)	148.0 (1)
S(2)-Mo(1)-S(1A)	86.2 (1)
N(2)-Mo(1)-S(1A)	98.9 (1)
S(2)-Mo(1)-S(2A)	77.0 (1)
N(2)-Mo(1)-S(2A)	162.4 (1)
N(2)-Mo(1)-N(2A)	104.7 (1)
Mo(1)-N(2)-C(11)	169.9 (2)



X-ray Crystal Structure of [Mo(2,6-ⁱPr₂C₆H₃N)₂(S₂CNEt₂)₂] **1.1f**, with Selected Bond Lengths (Å) and Bond Angles (°)



X-ray Crystal Structure of [Mo(2,6-Me₂C₆H₃N)₂(S₂CNEt₂)₂] **1.1d**, with Selected Bond Lengths (Å) and Bond Angles (°)



X-Ray Crystal Structure of [Mo(2,6-Cl₂C₆H₃N)₂(S₂CNEt₂)₂] **1.1e**, with Selected Bond Lengths (Å) and Bond Angles (°)

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closer together upon removal of the isopropyl groups. These changes in structure could be attributed to one of two factors; either the large steric bulk of the isopropyl groups forcing the imido ligands to be linear, or that the electron releasing properties of these groups effects the electron donor properties of the imido ligands.

By studying the complex **1.1e**, we gain further insight into the causes of these effects, due to chlorine having a similar Van der Waals radius to a methyl group but different electronic properties. As the structures of **1.1e** and **1.1d** are very similar, we assume that the effect must be caused by the steric requirements of the substituents in the two and six positions on the ring. However, in the case of **1.1d**,**e** the imido ligands do have the freedom to become bent. As can be seen in the space filling diagram (Fig 2.17) there is a significant amount of space for the imido ligands to move into by bending away from the other imido ligand. There is however a trend in the two known bent imido ligand structures^{4,116}, for the substituents on the imido ligands to bent towards each other (Fig 2.18), an effect that presumably is dependent upon increased π -overlap between the ligands and the metal centre. This preference for imido ligands to bent towards each other can be see occurring in this system, as upon going from **1.1f** (R=ⁱPr) to **1.1d** (R=Me) the two aryl rings move closer together. Chapter II: Molybdenum(VI) Bis(Imido) Complexes



Figure 2.17 Space Filling Diagram of [Mo(2,6-Me₂C₆H₃N)₂(S₂CNEt₂)₂] 1.1d



Figure 2.18 X-ray Crystal Structure of [Mo(NPh)₂(S₂CNEt₂)₂] **1.1a**. Showing the Bending of the Imido Ligands Towards Each Other

The occurrence of two linear imido ligands in these structures, poses the problem previously eluded to that these complexes are formally twenty electron species, and in order to maintain an eighteen count the two imido ligands should have a bond order of 2.5, donating three electrons each. Consideration of the bond lengths provides evidence to support this theory.

The Mo-N bond distances in the imido ligands do not generally give a

good measure of the bond order, as such lengths vary by only 0.1 Å in all known molybdenum imido complexes¹³⁶. However, in **1.1f** this bond at 1.766(2) Å does fall between the two bond lengths from the parent complex, where the linear imido-molybdenum interaction is 1.754(4) Å, while that to the bent ligand is 1.789(4) Å. This appears to imply that the metal-nitrogen bond order in **1.1f** is intermediate between these two extremes. In the other two structures (**1.1d-e**) definite assignment of bond order is not possible due to the large errors on these lengths, a result of the thermal motion of the ring. So even though the bonds are different, **1.1d** [1.770(6) and 1.756(6) Å], **1.1e** [1.769(7) and 1.760(7) Å] they are not significantly different.

Table 1 Comparison of bond lengths (Å) and bond angles (°) in the complexes [Mo(NR)₂(S₂CNEt₂)₂]

	Ph 1.1a	Tos 1.1g	'Pr₂C₀H₃ 1.1f	Me ₂ C ₆ H ₃ 1.1d	Cl ₂ C ₆ H ₃ 1.1e
Mo(1)-N(4)	1.754(4)	1.790(8)	1.766(2)	1.756(6)	1.769(7)
Mo(1)-N(3)	1.789(4)	1.797(7)		1.770(6)	1.760(7)
N(3)-Mo(1)-N(4)	103.5(2)	104.0(4)	104.7(1)	102.5(3)	101.4(3)
Mo(1)-N(4)-C(11)	169.4(4)	165.1(5)	169.9(2)	162.8(6)	162.9(7)
Mo(1)-N(3)-C(21)	139.4(4)	156.8(5)		162.0(6)	162.2(7)
Mo(1)-S(1)	2.755(2)	2.559(3)	2.672(1)	2.685(2)	2.648(3)
Mo(1)-S(3)	2.602(2)	2.550(3)		2.684(2)	2.651(3)
Mo(1)-S(2)	2.453(2)	2.444(3)	2.464(1)	2.462(2)	2.452(3)
Mo(1)-S(4)	2.461(2)	2.452(3)		2.452(2)	2.448(2)

The Mo-S bond *trans* to an imido ligand in these complexes can give a better insight into the bond order, being greatly **a**ffected by the number of electrons the ligand donates to the metal. Thus, in the parent complex the Mo-S bond vary by 0.15 Å, that *trans* to the linear imido ligand at 2.602(2) Å being significantly shorter than that *trans* to the bent imido of 2.755(2) Å, while both are considerably longer than the two Mo-S bonds that are *trans* to each other [2.453(2), 2.461(2) Å].

The Mo-S bond *trans* to the imido ligands in **1.1d-f** are 2.672(1) Å **1.1f**, 2.684(2) and 2.685(2) Å **1.1d**, 2.648(3) and 2.651(3) Å **1.1e** approximately midway between the two values from the parent complex. This provides further evidence that the imido ligands in **1.1d-f** do behave as three electron donors giving the complexes an eighteen electron count.

2.4 NMR Studies

It is believed that these structures are maintained in solution, as the protons on the phenyl rings remain equivalent in the ¹H nmr spectrum as the temperature is varied (253 K to 373 K) **1.1f**. However, it does show at low temperature two triplets (δ 0.81, 0.74) for the methyls on the dithiocarbamates and two doublets (δ 1.28, 1.16) for the methyls on the isopropyl groups on the aryl ring (Fig 2.19). Upon warming these signals broaden and coalesce, until at 373 K only one signal for each of the types of methyl is observed (δ 0.96, t, 1.19, d). It is believed that this fluxionality is due to a geared rotation of the two phenyls rings. As can be seen from the space filling diagram (Fig 2.20), while one of the isopropyl groups on one of the imido ligands lies above the phenyl ring of the other imido moiety, the second lies away from the other ring. So as the rings rotate these two sites exchange. A similar process is believed to occur in **1.1d**.

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Figure 2.19 Variable Temperature ¹H nmr Spectra of 1.1f



Figure 2.20 Space Filling Diagram for 1.1f

The complex with the next smallest amount of steric bulk in the two and six positions of the ring is the o-tolyl derivative. This complex has been prepared from $[Mo(2-MeC_6H_4N)_2Cl_2.DME]$ **2.1c** and $[NH_4][S_2CNEt_2]^{137}$, and although the crystal structure has not been determined, it has been shown by ¹³C{¹H} CPMAS nmr spectroscopy to contain one linear and one bent imido

linkage. However this structure in not maintained in solution, as even at low temperature the ¹³C{¹H} nmr spectrum contains only one signal for the ipso carbon in the phenyl rings, showing the rings to be equivalent. This is believed to be a result of the rapid interconversion of the imido ligands between bent and linear forms of ligation.



Figure 2.21 Interconversion Between Bent and Linear Forms of Imido Ligation in Bis(Imido) Complexes

In the light of this the ¹H nmr spectrum of $[Mo(N^{t}Bu)_{2}(S_{2}CNEt_{2})_{2}]$ **1.1h** which only shows one signal for the *t*-butyl groups, does not necessarily have to contain two linear imido ligands. It could also have a linear bent structure with rapid interconversion on the nmr time scale at room temperature. This hypothesis is also supported by the air and moisture sensitivity of **1.1h**. As this feature of these complexes has only been manifested in those that contain bent imido ligands. The lack of fluxionality in **1.1h** is however, more likely due to the absence of aryl rings, further reinforcing the theory that the fluxionality in the aryl substituted complexes is a result of a geared ring rotation.

2.5 Reactivity of Bis(Imido) Complexes

2.5.1 Thermolysis of $[Mo(2,6-R_2C_6H_3N)_2(S_2CNEt_2)_2]$ (R=Me 1.1d, ⁱPr 1.1f): As noted earlier, with certain substituents (R=Me), prolonged reaction times in the preparation of these complexes from $[Mo(O)_2(S_2CNEt_2)_2]$ 1.2, leads to lower yields of the bis(imido) product. Thus the thermal stability of these complexes was investigated to discern if any of the other products from the initial thermolysis reaction originate from the thermal decomposition of 1.1.

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Heating a toluene solution of $[Mo(NR)_2(S_2CNEt_2)_2]$ (R=2,6-Me₂C₆H₃) **1.1d** for 18 hours lead to no noticeable change in colour. However, chromatography revealed the formation of the disulfur complex $[Mo(NR)(S_2)(S_2CNEt_2)_2]$ **2.2d** in 29% yield, with starting material being recovered in 50% yield. This is not common to all bis(imido) complexes of this type. When **1.1f** is used, only unreacted **1.1f** is recovered after prolonged thermolysis in toluene (3 days). This rules out the bis(imido) complexes **1.1** as general intermediates in the formation of the imido disulfur complexes, although in some cases part of the recovered yield of the latter probably arises from this route.



Figure 2.22 Thermolysis of $[Mo(2,6-R_2C_6H_3N)_2(S_2CNEt_2)_2]$ (R=ⁱPr, Me) 1.1d,f

2.5.2 Reaction with Methyliodide: The reaction of the parent bis(imido) complex **1.1a** with methyl iodide has been reported in the literature, the products being $[Mo(NPh)I_2(S_2CNEt_2)_2]$ and $PhNMe_3I^{131}$. These are formed as a result of the methylation of one of the two imido groups, which is recovered as the quaternary salt of the amine. The molybdenum replaces the lost imido in the coordination sphere by the two iodide ions formed as a result of the methylation. The corresponding reaction was performed with the bulky diisopropyl substituted complex, which displayed no evidence of reaction. This can be attributed to either the steric bulk of the imido ligands preventing attack of the methyl iodide at the nitrogen, or that the loss of the bent imido has decreased reactivity.

2.5.3 Reaction with the Activated Alkyne DMAD: The reaction of **1.1f** with the activated alkyne DMAD was performed in order to see if any aziridination occurred. Again the only complex recovered after stirring a solution of **1.1f** and DMAD for 18 hours was the starting material.



Figure 2.23 Proposed Reaction of 1.1f with DMAD

2.6 Summary

In this chapter it has been shown that while bis(imido) complexes are easier to synthesise with bulky imido ligands. This steric bulk prevents the complexes from exhibiting further reactivity. The structures of a series of complexes (**1.1d-f**) have been determined, and show two linear imido ligands. A sharp contrast to the parent complex **1.1a** which shows both bent and linear forms of imido ligation. This change has been attributed to the increase in steric bulk in the two and six positions of the rings, which prevents the two rings from bending towards each other.

Although the initial method of synthesis failed in the majority of cases, a second route has shown to be more convenient, affording the complexes in high yield. Thus, allowing for further investigations into this system. In the next chapter $[Mo(NR)(S_2)(S_2CNR_2)_2]$ **2.2**, the only product to be isolated from all reaction of $[Mo(O)_2(S_2CNR_2)_2]$ (R=Et **1.2**, Me **1.2**') with organic isocyanates, will be discussed.

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Molybdenum(VI) Imido Disulfur Complexes

3.1 Introduction

Metal complexes containing disulfur ligands have been widely reported in the literature. The ligand, which occurs naturally in the mineral patronite^{138,139} where it displays bridging disulfur ligation between vanadium atoms, has recently attracted some attention due to the implication of some metal complexes in fossil fuel hydrodesulfurization¹⁴⁰. This introduction will be primarily concerned with terminal disulfur ligation, although some examples of bridging ligation will be considered. Reviews of transition metal complexes containing polychalcogenide ligands such as dioxygen^{141,142,143,144}, higher sulfides¹⁴⁵, diselenium and ditellurium¹⁴⁶ ligands have been published.



Figure 3.1 Structure of Patronite

3.1.1 Bonding Mode of Disulfur Ligands: Disulfur ligands show a wide variety of bonding modes to metal centres, which can be simplified by considering them as extensions of four basic structural units.



Figure 3.2 The Four Basic Structural Units of Disulfur ligation

Bonding mode (Ia) involves simple side on coordination to a single metal centre. Modes (IIa) and (IIb) are bridging coordination modes, in which either a *cis* or *trans* configuration of the metals is adopted. Mode (III) is again a bridging mode in which both the sulfur atoms are now bound to both of the metals, and finally (IV) is a bridging mode where one of the sulfur atoms is bound to both metals and the other is not.

These basic units are expanded to cover all the known bonding modes by addition of one or more metal atoms to the disulfur ligand¹⁴⁷. The choice of which bonding mode is adopted when more than one metal centre is present is often dependant upon the oxidation state of the metal complex, and the number of electrons the ligand needs to donate. This is shown in the iron(III) complex [Fe₂(MeCp)₂(μ - η^2 : η^2 -S₂)(μ - η^1 : η^1 -S₂)]^{148.149,150}, in which one of the two bridging disulfur ligands undergoes a change in bonding mode, upon oxidation, to the iron(IV) complex [Fe₂(MeCp)₂(μ - η^2 : η^2 -S₂)₂]²⁺. This process is reversible, and upon reduction the ligand reverts back to its original bonding mode.



Figure 3.3 Changes in Bonding Mode upon Oxidation of the Complex $[Fe_2(MeCp)_2(\mu-\eta^2:\eta^2-S_2)(\mu-\eta^1:\eta^1-S_2)]$

3.1.2 Preparation

Addition of elemental sulfur: The treatment of low valent metal complexes with elemental sulfur often leads to incorporation of sulfur into the molecule to give a polysulfide ligand^{151,152,153}, although the chain length is often greater than two. The latter can be controlled by changing the steric requirements of the ligands already coordinated to the metal. For example, treatment of vanadocene with elemental sulfur leads to exclusive formation of the pentasulfur complex^{154,155,156}. However, when the more sterically demanding

pentamethylcyclopentadienyl complex is used the disulfur complex is isolated¹⁵⁷.



Figure 3.4 Steric Control over Length of the Polysulfide Chain

Abstraction of Sulfur from Organics: The formation of disulfur ligands via sulfur abstraction can be broadly divided into two reaction types. In the first, the sulfur containing molecule is a ligand, which is either already coordinated to the metal centre, (on which some other reaction is being performed), or is being added to the metal complex in order to coordinate to it. During the course of the reaction a sulfur atom(s) are abstracted from the ligand and remain in the coordination sphere of the metal in the form of a disulfur ligand. The rest of the desulfurised ligand can sometimes remain in the coordination sphere but is often lost. A recent example of this type of reaction is the interaction of MeCS₂H with [NbCp(η -C₇H₇)] to give the disulfur complex [NbCp(S₂)(S₂CMe)₂]¹⁵⁸.



Figure 3.5 Abstraction of Sulfur from $MeCS_2H$ In the second type of reaction, the sulfur containing molecule is used

primarily as a source of sulfur, with the rest of the molecule not usually becoming involved in coordination to the metal centre¹⁵⁹. Common reagents used for this purpose are propylene sulfide¹⁶⁰, $S_2Cl_2^{161}$, $P_4S_{10}^{162}$, $H_2S^{163,164,165}$ and Na_2S^{166} .



Figure 3.6 Use of S₂Cl₂ in the Synthesis of Disulfur Ligands

3.1.3 Reactivity

Oxidation: When a disulfur complex is treated with mild oxidants such as 3-chloroperoxybenzoic acid¹⁶⁷, sodium periodate¹⁶⁸ or in one case atmospheric oxygen¹⁶⁹, the ligand is partially oxidised to S_2O^2 . This moiety can the undergo further reaction, thus treatment with a further equivalent of sodium periodate affords the moiety $S_2O_2^2$, were total oxidation of the sulfur atoms has occurred.



Figure 3.7 Oxidation of a Disulfur Ligand

Desulfurisation: Treatment of a disulfur complex with nucleophilic reagents such as phosphines and cyanide, has been shown to lead to removal of one

sulphur atom from the ligand, leaving the charge on the metal unchanged. The newly formed metal sulfide species is usually highly reactive. Recently it has been shown that these species can be trapped by treatment of the reaction mixture with a heterocumulene such as phenylisothiocyanate¹⁷⁰ or di-p-tolylcarbodiimide¹⁷¹. There have also been a number of examples reported that involve the complete desulfurisation of a disulfur ligand¹⁷², again leaving a reactive, coordinatively unsaturated molecule.



Figure 3.8 Reaction of a Heterocumulene with a M=S Fragment Formed as a Result of the Desulfurisation of a Disulfur Complex

Addition across the disulfur bond: A number of reagents have been shown to add across the sulfur-sulfur bond of disulfur ligand in both bridging and terminal bonding modes. Treatment of $[{Mo(MeCp)(\mu-S)}_2(\mu-S_2)]$ with hydrogen leads to cleavage of the sulfur-sulfur bond to give $[{Mo(MeCp)(\mu-S)(\mu-SH)}_2]$. This in turn reacts with azobenzene leading to recovery of the starting disulfur complex and hydrogenation of the azobenzene¹⁷³.



Figure 3.9 Catalytic Hydrogenation by a Bridging Disulfur Complex

A more common reaction is the insertion of the activated alkyne, DMAD. This usually reacts cleanly with terminal disulfur ligands by inserting into either the sulfur-sulfur¹⁷⁴ bond to give a dithiolene ligand, or into an metal-sulfur¹⁷⁵ bond to give a vinyldisulfide ligand.



Figure 3.10 Insertion of DMAD into the Sulfur-Metal Bond of a Disulfur Ligand



Figure 3.11 Insertion of DMAD into the Sulfur-Sulfur Bond of a Disulfur Ligand

The reaction of disulfur complexes with other unsaturated molecules such as carbon disulfide has also been reported^{176,177,178}, although in this case it is difficult to determine whether the sulfur-sulfur bond or the metal-sulfur bond has been cleaved, as the carbon atom is not bound to the metal.



Figure 3.12 Insertion of CS₂ Into a Disulfur Ligand

During this introduction the diversity of bonding and reactivity of disulfur ligands has been demonstrated. However, the rest of the chapter will focus on the formation of one series of disulfur containing complexes $[Mo(NR)(S_2)(S_2CNR'_2)_2]$ **2.2**, which were obtained fortuitously from the thermolysis of $[Mo(O)_2(S_2CNR'_2)_2]$ **1.2** with organic isocyanates. At the end of the chapter a number of reactions of these complexes are discussed.

3.2 Synthesis

3.2.1 Synthesis from $[Mo(O)_2(S_2CNR'_2)_2]$ (R'=Et 1.2, R'=Me 1.2'): As mentioned in the previous chapter, treatment of 1.2 or 1.2' with organic isocyanates in refluxing toluene leads to isolation of the corresponding imido disulfur complexes $[Mo(NR)(S_2)(S_2CNR'_2)_2]$ (R'=Me, Et; R=Ph, p-tolyl, o-tolyl, 2,6-Me_2C_6H_3, 2,6-Cl_2C_6H_3, 2,6-ⁱPr_2C_6H_3, Adm, ^tBu) **2.2a-j, 2.2a', 2.2h'**. These complexes are obtained in moderate yield (~30%) from these reactions after purification by column chromatography, and are easily recrystallised by slow diffusion of methanol into a dichloromethane solution.





The colour of the complexes vary depending upon the substituent on the imido ligand. Thus, when aryl imido groups are present the complexes are purple, and when an alkyl imido is present they are red. They all show a weak band at ~550 cm⁻¹ in their ir spectra assignable to the stretching of the sulfur-sulfur bond^{179,180}, as well as bands due to the Mo=N stretch of the imido ligand at ~1275 cm⁻¹ and the C=N stretch of the dithiocarbamate ligand at ~1510 cm⁻¹.

The lack of any oxo ligands is confirmed by the absence of any strong bands in the region of the ir spectra were Mo=O stretches occur (950-880 cm⁻¹). The ¹H nmr spectra of these complexes contain four different methyl resonances, one of these been shifted upfield with respect to the other three.



In the complexes $[MoO(S_2)(S_2CNR_2)_2]$ (R=Me 3.1', Et 3.1), which exhibit similar ¹H nmr spectra¹⁶⁰, this shielded signal was assigned to the alkyl group on the spanning ligand which resides closest to the Mo=O vector, and is a result on the anisotropy of this bond.

An attempt to probe the sensitivity of the reaction to the substituent on the dithiocarbamate ligand, was carried out using the methyl substituted complex **1.2'**. However, this had little effect on the yields of the products, indicating that the substituent of the dithiocarbamate has no effect on the reaction. Although the methyl substituted complexes have simpler nmr spectra compared to their ethyl counterparts, their lack of solubility in common solvents rendered further study impractical.

The reactions with allyl and *i*-propyl isocyanate, are believed to form the corresponding imido disulfur complexes, as the solutions acquire a deep red colour associated with alkyl substituted complexes of this type. However, attempts to purify these complexes by chromatography lead to extensive decomposition, and purification by crystallisation was hampered by the large number of products typically obtained from these reactions. This instability is

believed to be due to the increased acidity of imido complexes which contain protons attached to the α -carbon¹⁸¹.

The formation of the disulfur ligand in this reaction poses something of a problem. The reagents used were checked for purity by microanalysis, and were shown to contain the correct amount of sulfur. Thus, the only source of sulfur in this reaction was the dithiocarbamate ligands. In an attempt to improve the yield of **2.2**, phenylisothiocyanate was used instead of phenylisocyanate in order to provide another source of sulfur in the reaction. However, the yield of **2.2a** was lower in this case indicating that the disulfur ligand is formed primarily from a third molecule of dithiocarbamate, which is believed to coordinate to the metal centre before cleavage occurs. Once coordinated it undergoes cleavage of both of the sulfur-carbon bonds to from a disulfur moiety.

Figure 3.15 Formation of the Disulfur Moiety

The cleavage of dithiocarbamate ligands in this way is not uncommon and a number of examples of this type of reaction have been reported¹⁸²⁻¹⁹³. The first of these was in 1972, when in an attempt to synthesise the dithiocarbamate analogue of the complex $[Mo_2(\mu-MeCOO)_4]$, Weiss and coworkers¹⁸² treated $[Mo_2(\mu-MeCOO)_4]$ with NaS_2CNPr_2 . The isolated complex from this reaction, $[Mo(\mu-S)(SCNPr_2)(S_2CNPr_2)]_2$, is formed as a result of the cleavage of one of the S-C bonds of a dithiocarbamate and coordination of both the cleaved fragments to the dimolybdenum centre.



Figure 3.16 Addition of NaS₂CNPr₂ to [Mo₂(µ-MeCOO)₄]

However, it was not until Deeming and co-workers¹⁹³ reported the reaction of $[Ru(CO)_2(S_2CNEt_2)_2]$ with $[Ru_3(CO)_{12}]$ that conclusive evidence for the cleavage of both of the sulfur-carbon bonds in a dithiocarbamate was provided. The product of the latter is a pentaruthenium cluster that contains two diethylaminomethylidyne ligands, which bridge diruthenium centres. These ligands are the remains of a dithiocarbamate ligand that has lost both of its sulfur atoms, although only two of the four sulfur atoms from these ligands remain in the cluster.



Figure 3.17 Reaction of $[Ru(CO)_2(S_2CNEt_2)_2]$ with $[Ru_3(CO)_{12}]$. Carbonyls Omitted From the Pentaruthenium Product for Clarity

3.2.2 Synthesis from $[MoO(S_2)(S_2CNEt_2)_2]$ **3.1:** The known complex **3.1**¹⁶⁰ was considered to be a possible intermediate in the formation of $[Mo(NR)(S_2)(S_2CNEt_2)_2]$ **2.2**, requiring only to interact with a molecule of isocyanate in order to undergo the transformation. This route was also expected to provide a higher yield of **2.2**, as the disulfur unit is already present in the molecule, and thus formation of **2.2** does not require there to be scavenging of sulfur from dithiocarbamate ligands.



Figure 3.18 Reaction of 3.1 with Isocyanates

Treatment of **3.1** with one equivalent of phenylisocyanate in refluxing toluene gave the expected product **2.2a** in 95% yield after purification by chromatography. However, the corresponding reaction with *t*-butylisocyanate did not give any of the expected product **2.2h**, $[Mo(\mu-S)(O)(S_2CNEt_2)]_2$ **3.2** and starting material being the only observed products. Previously **3.2** has been detected as a product in the thermal gravimetric analysis of **3.1**¹⁶⁰. The inability of alkyl substituted isocyanates to afford imido complexes from the corresponding oxo species, even when an aryl isocyanate does, has been noted before¹⁹⁴. The lack of any reaction in this case with alkyl isocyanates eliminates **3.1** as a possible general intermediate in the formation of disulfur complexes during the thermolysis reaction of $[Mo(O)_2(S_2CNEt_2)_2]$ **1.2**.

3.3 Structure

X-ray crystallography was performed on three of these complexes $[Mo(NPh)(S_2)(S_2CNEt_2)_2]$ **2.2a**, $[Mo(2,6-Pr_2C_6H_3N)(S_2)(S_2CNMe_2)_2]$ **2.2f**' and

 $[Mo(N^{t}Bu)(S_{2})(S_{2}CNMe_{2})_{2}]$ **2.2h**'. (Important crystallographic parameters are summarised in Appendices 1.4-6). All show the expected seven coordinate molybdenum atom in a pentagonal bipyramidal geometry. The equatorial sites are composed of the two sulfur atoms of the disulfur ligand, both the sulfur atoms from one dithiocarbamate, and one of the sulfur atoms from the second dithiocarbamate. The second sulfur from this dithiocarbamate occupies one of the axial sites and lies trans to the imido ligand in the other axial site. The molybdenum atom lies above the plane defined by the five equatorial sulfur atoms an effect caused by the trans influence of the imido ligands. This effect also causes the molybdenum-sulfur vector of the sulfur atom in the other axial site, which is trans to the imido, to be lengthened (~0.11 Å) with respect to those in the equatorial sites. The overall geometry of these complexes is identical to that of the known oxo complex $[MoO(S_2)(S_2CNEt_2)_2]$ **3.1**¹⁹⁵, the only major difference been in the length of the molybdenum-sulfur bond trans to the π -donor ligand, with that in **3.1** being longer than those in **2.2** [**3.1** 2.663(6), 2.2a 2.605(1), 2.2f' 2.612(1), 2.2h' 2.636(1) Å]. The cause of these differences is believed to be the differing π -donor properties of the ligands. The disulfur ligands are bound approximately symmetrically to the metal centre and the sulfur-sulfur bonds at [2.033(2) 2.2a, 2.011(2) 2.2f', 2.035(2) Å 2.2h'] are typical of such ligands¹⁹⁶.

The angle about the nitrogen atom in the imido ligands decreases upon increasing the steric bulk of the substituent on the imido. Thus, although there is some degree of deviation from linearity in **2.2a** (R=Ph) [165.2(3)°], in **2.2f'** (R=2,6-ⁱPr₂C₆H₃) no significant deviation from linearity is observed [179.1(3)°]. The angle in **2.2h'** (R='Bu) is intermediate between these two values at [168.7(2)°]. This is probably caused by the bulkier substituents forcing the angle at the nitrogen to become more linear, thus avoiding unfavourable steric interactions with the atoms that lie in the equatorial plane of the molybdenum. Thus, explaining the difference between **2.2f'** (R=2,6-ⁱPr₂C₆H₃) and **2.2h'** (R='Bu), with **2.2f** containing more steric bulk directed towards the metal centre.





X-ray Crystal Structure of $[Mo(NPh)(S_2)(S_2CNEt_2)_2]$ 2.2a, with Selected Bond Lengths (Å) and Bond Angles (°)

Mo(1)-S(1)	2.484 (1)
Mo(1)-S(2)	2.452 (1)
Mo(1)-S(3)	2.497 (2)
Mo(1)-S(4)	2.612 (1)
Mo(1)-S(5)	2.384 (2)
Mo(1)-S(6)	2.402 (1)
Mo(1)-N(3)	1.734 (3)
S(5)-S(6)	2.011 (2)
S(1)-Mo(1)-S(2)	69.4 (1)
S(3)-Mo(1)-S(4)	68.1 (1)
S(1)-Mo(1)-S(4)	84.0 (1)
S(2)-Mo(1)-S(4)	86.5 (1)
S(4)-Mo(1)-S(5)	88.8 (1)
S(4)-Mo(1)-S(6)	84.0 (1)
S(5)-Mo(1)-S(6)	49.7 (1)
S(1)-Mo(1)-N(3)	91.5 (1)
S(2)-Mo(1)-N(3)	102.2 (1)
S(3)-Mo(1)-N(3)	100.2 (1)
S(5)-Mo(1)-N(3)	100.8 (1)
S(6)-Mo(1)-N(3)	96.8 (1)
S(4)-Mo(1)-N(3)	168.1 (1)
Mo(1)-N(3)-C(7)	179.1 (3)



X-ray Crystal Structure of $[Mo(2,6-{}^{i}Pr_{2}C_{6}H_{3}N)(S_{2})(S_{2}CNMe_{2})_{2}]$ 2.2f', with Selected Bond Lengths (Å) and Bond Angles (°)



X-ray Crystal Structure of [Mo('BuN)(S₂)(S₂CNMe₂)₂] 2.2h', with Selected Bond Lengths (Å) and Bond Angles (°)

C(3)

3.4 Reactivity

Due to the ease of preparation of a wide variety of substituted disulfur complexes of the type $[Mo(NR)(S_2)(S_2CNR'_2)_2]$ **2.2** a number of reactions were studied of $[Mo(NPh)(S_2)(S_2CNR'_2)_2]$ **2.2a**.

3.4.1 Treatment of [Mo(NPh)(S₂)(S₂CNEt₂)₂] 2.2a with DMAD: As noted in the introduction to this Chapter, disulfur ligands have been shown to insert the activated alkyne DMAD. Thus, treatment of **2.2a** with two equivalents of DMAD lead to a colour change from purple to turquoise. Purification by column chromatography gave orange **3.3**, blue **3.4** and green **3.5** complexes, all of which were shown to contain DMAD molecules by the presence of ir bands assignable to carbonyls moieties (1650-1750 cm⁻¹).

The ¹H nmr spectrum of **3.4** shows the presence of two inequivalent dithiocarbamate ligands (δ 1.42, 1.41, 1.26, 1.24, all triplets), and two inequivalent DMAD molecules (δ 3.82, 3.71, 3.69, 3.47). The presence of the latter was confirmed by the ir spectrum which showed four peaks in the carbonyl region (1731, 1718, 1701, 1685 cm⁻¹). An attempt to elucidate the structure of this complex by X-ray crystallography was only partially successful. This was due to a disorder in one of the dithiocarbamate ligands and unacceptable thermal parameters in the rest of the molecule, making full refinement impossible. However, it did give an indication of the molecular structure, which is shown in Fig 3.19.


Figure 3.19 Molecular Structure of

$[Mo{PhNC(R)C(R)S}{SC(R)C(R)C(NEt_2)S}(S_2CNEt_2)] (R=CO_2Me) 3.4$

As can be seen, the molecule does indeed contain two molecules of the acetylene, one having inserted into the sulfur-carbon bond of a dithiocarbamate ligand. The double bond formed by this insertion is also involved in a π -interaction with the metal centre, causing a severe puckering of the six membered ring (Mo-S-C=C-C-S), indicating that the π -interaction stabilises the complex more than π -overlap between the exocyclic double bond (C=N) and the endocyclic double bond (C=C). The second molecule of acetylene is bridging one of the sulfur atoms from the disulfur moiety and the imido ligand, the other sulfur atom of the disulfur moiety having been lost from the molecule.

Elucidation of the nature of **3.3** and **3.5**, however, remained problematic due to difficulty in obtaining pure crystalline samples. Their ¹H nmr spectra indicate that both of these complexes contain DMAD molecules, dithiocarbamate ligands and phenyl groups. The DMAD moieties are nonequivalent, as shown by the presence of multiple peaks due to the methyl

groups on these moieties (**3.3** δ 3.96, 3.90, 3.84, 3.80, 3.74, 3.66, 3.51. **3.5** δ 3.92, 3.84, 3.77, 3.67, 3.65, 3.43). The dithiocarbamate ligands are also none equivalent, with both complexes exhibiting complex multiples at δ ~1.2 Their ir spectra contain a broad band (**3.3** 1711 cm⁻¹, **3.5** 1718 cm⁻¹) due to the carbonyl moieties in the DMAD molecules.

Recently Young and co-workers¹⁹⁷ have reported the reaction of $[MoO(S_2)(S_2CNMe_2)_2]$ **3.1**' with DMAD which leads to the formation of orange **3.6**' and green **3.7**' products, that were characterized by X-ray crystallography.



Figure 3.20 Products from the Reaction of DMAD with $[MoO(S_2)(S_2CNMe_2)_2]$

Green $[Mo{SC(R)C(R)S}{SC(R)C(R)C(NMe_2)S}(S_2CNMe_2)]$ 3.7' also results from an alkyne insertion into the carbon-sulfur bond of one of the dithiocarbamate ligands. Now however, instead of the second DMAD bridging the imido and one of the sulfur atoms of the disulfur ligand, it bridges both the atoms of the disulfur ligand to give a dithiolene ligand.

The orange isomer $[Mo{SC(R)C(R)S}{SC(R)C(R)SCMe_2}(S_2CNMe_2)]$ **3.6'**, shows a different mode of insertion into the dithiocarbamate ligand. Where as before it inserted into the sulfur-carbon bond, here it bridges between the two sulphur atoms, with one of the sulfur-carbon bonds being cleaved. It also has the second DMAD molecule bridging the two sulfur atoms of the disulfur ligand to give a dithiolene ligand.

Although it is possible that similarities exist between these complexes and those reported herein, **3.6**' and **3.7**' are not the identical to **3.3** and **3.5** due to the presence of phenyl groups in the latter where none are present in the former. These are believed to be occur as a result of NR groups being present instead of sulfur atoms in the five membered dithiolene ligands. The similarities arise as a result of the ligands that contain only dithiocarbamate and DMAD fragments. Thus, all of the characterised complexes contain one dithiocarbamate ligand and one ligand that results from the insertion of a DMAD molecule into a dithiocarbamate ligand, and it is believed that **3.3** and **3.5** also contain both of these types of ligand, differing only in the mode of insertion of the DMAD into the dithiocarbamate ligand.



Figure 3.21 Two Different Modes of Insertion of DMAD into a Dithiocarbamate Ligand

Attempts to elucidate which mode of insertion is displayed by each complex by comparison of their ¹H nmr with those reported by Young and coworkers, indicates that **3.5** also shows insertion mode(I). Although it displays six DMAD resonances in its ¹H nmr spectra, as opposed to four for **3.7**', four of these match those of **3.7**' well (**3.7**' δ 3.94, 3.88, 3.87, 3.58; **3.5** δ 3.92, 3.84, 3.77, 3.65). This means that **3.5** contains the same structural elements as **3.4**, and thus are isomers. There is great deal of scope for both stereo and structural isomerisation in these complexes. Stereo isomers occurs as a result of a chiral metal centre, and both of the carbon atoms from the alkene

involved in π -donation to the molybdenum being chiral. Structural isomers occur due to the presence of two asymmetric chelating ligands, which can arrange themselves around the metal centre in four different combinations.



Figure 3.22 Four Different Possible Structural Isomers

The presence of these different isomers may explain the complex ¹H nmr spectra observed for the non- crystalline complexes, resulting from the presence of more that one isomer in solution. This problem may have been overcome in the case of the crystalline sample of **3.4** due to preferential crystallisation of one isomer.

Identification of the mode of insertion in **3.3** is not as simple. It shows seven DMAD resonances in its ¹H nmr spectra, none of which correspond well with the four of **3.7**' or the two DMAD resonances shown by **3.6**' (δ 3.94, 3.84). An analysis of the colours of the complexes identified so far indicates that **3.3** may display insertion mode(II), as the complexes that show insertion mode(I) (**3.4**, **3.5** and **3.7**') are all green or blue, where as **3.6**' which shows insertion mode(I) and **3.3** are both orange. The more complicated ¹H nmr spectra of **3.3** can also be explained as a result of the presence of multiple isomers in solution.



Figure 3.23 Proposed Structures for 3.3 and 3.5

Although there is a significant amount of similarity between the complexes obtained by Young and co-workers (**3.6**' and **3.7**'), and those reported herein (**3.3-5**), in that they all show insertion reactions into dithiocarbamate ligands, one major difference does occur between the complexes. In the latter the initially π -bound ligand (ie the imido) is retained in the product, whereas in the former it is lost. A greater understanding of the mechanism of this reaction may explain the reason why this is so, however, very little has been reported on this matter except that it is possible to convert **3.7**' into **3.6**' upon heating. This lead Young and co-workers to postulate that the initial step in the formation of the dithiocarbamate/alkyne ligands, is attack of one of the sulfur atoms of a dithiocarbamate ligand on the alkyne, followed by sulfur-carbon bond cleavage. Conversion would then occur via the migration of the R₂CN fragment from its initial position spanning a molybdenum-sulfur bond, to inserting into the remaining sulfur-carbon bond.



Figure 3.24 Conversion of 3.6' into 3.7'. Other Ligands Omitted for Clarity

The loss of the π -donor ligand must occur before this, presumably during the formation of the dithiolene ligand. When an oxo ligand is present in the molecule the alkyne shows a preference for bridging between the two sulfur atoms of the disulfur unit. However, when an imido moiety is present the alkyne shows a preference for bridging between this and one of the sulfur atoms (although we have not characterised any complexes that do not contain the NR fragment, their formation cannot be ruled out). The reason for this change is not clear, although it is more likely to be an electronic effect rather than an steric one, as if steric factors dominated then it might be expected that oxo ligands would be incorporated in the molecules rather than imido ligands, due to the increased steric properties of the latter over the former.

3.4.2 Treatment of [Mo(NPh)(S₂)(S₂CNEt₂)₂] 2.2a with P(OEt)₃: It has previously been reported¹⁷² that treatment of $[MoO(S_2)(S_2CNEt_2)]$ **3.1** with two equivalents of triethylphosphite leads to complete desulfurisation, affording the reduced metal complex $[MoO(S_2CNEt_2)_2]$, while it has also been shown that the analogous imido complex $[Mo(NPh)(S_2CNEt_2)_2]$ reacts with atmospheric oxygen to give the mixed oxo-imido complex $[MoO(NPh)(S_2CNEt_2)_2]$ **2.3a**¹⁹⁸. It was therefore believed that initial desulfurisation of $[Mo(NPh)(S_2CNEt_2)_2]$ **2.2a**, may afford $[Mo(NPh)(S_2CNEt_2)_2]$, which upon oxidation would generate the mixed oxo-imido complex **2.3a**.



Figure 3.25 Proposed Formation of $[MoO(NPh)(S_2CNEt_2)_2]$ 2.3a From $[Mo(NPh)(S_2)(S_2CNEt_2)_2]$ 2.2a

Treatment of 2.2a with two equivalents of triethylphosphite lead to a

colour change from purple to brown, as was expected for formation of the reduced complex. Exposure of this stirred solution to the atmosphere gave a further change, initially to red and then finally orange. Removal of the solvent from this solution afforded a orange oil, which was washed with petrol to removed any residual phosphine. Yellow crystals of 3.8a (60% yield) were grown by slow diffusion of methanol into a dichloromethane solution of the oil. Spectroscopic data collected the crystals were not completely in accordance with the compound being [MoO(NPh)(S₂CNEt₂)₂] **2.3a**. Thus in the ¹H nmr spectrum, signals assignable to one phenyl ring and two dithiocarbamate ligands were observed, and in the ir spectra absorbtion bands assignable to Mo=O (953, 941 cm⁻¹), Mo=NR (1279 cm⁻¹) and C=N (1530 cm⁻¹) were present. The appearance of two bands for Mo=O indicated the presence of two terminal oxo ligands. An elemental analysis obtained from crystals of the complex was low in carbon, hydrogen and nitrogen, although the ratio of the elements was correct. The analysis for sulfur was higher than expected, again indicating the possibility of a dimeric complex.

A X-ray structure determination performed on this complex (important crystallographic parameters are summarized in Appendix 1.7), showed that the complex was indeed dimeric $[Mo_2(\mu-S)(\mu-NPh)(O)_2(S_2CNEt_2)_2]$ **3.8a**. The molecule shows a *cis* configuration of the dithiocarbamate ligands, the configuration seen in all dimers of this type. The two bridge sites are occupied by sulfido and phenyl imido ligands both of which bridge, approximately symmetrically, the dimetallic centre [Mo(1)-N(3) 1.974(4), Mo(2)-N(3) 1.979(5), Mo(1)-S(5) 2.334(2), Mo(2)-S(5) 2.315(2) Å]. The terminal sites on both the molybdenum atoms are occupied by oxo ligands [Mo(1)-O(1) 1.681(4), Mo(2)-O(2) 1.681(5) Å]. The distance between the two metal centres at 2.732(1) Å is within the range for molybdenum-molybdenum single bonds. This appears to be controlled by the nature of the bridging ligands in the system. Thus, with a mixed bridging system of an sulfido ligand and an imido ligand, the bond is intermediate between that of the tetrasulfido complex [2.801(2) Å]¹⁹⁹ and the tetraimido species [2.633(1) Å] (this structure is reported in Chapter 4). The

Mo(1)-Mo(2)	2.732 (1)
Mo(1)-S(1)	2.465 (2)
Mo(1)-S(2)	2.481 (2)
Mo(2)-S(3)	2.491 (2)
Mo(2)-S(4)	2.460 (2)
Mo(1)-S(5)	2.334 (2)
Mo(2)-S(5)	2.315 (2)
Mo(1)-N(3)	1.974 (4)
Mo(2)-N(3)	1.979 (5)
Mo(1)-O(1)	1.681 (4)
Mo(2)-O(2)	1.681 (5)
S(1)-Mo(1)-S(2)	70.9 (1)
S(3)-Mo(2)-S(4)	70.8 (1)
Mo(1)-S(5)-Mo(2)	72.0 (1)
Mo(1)-N(3)-Mo(2)	87.4 (2)
Mo(2)-Mo(1)-O(1)	106.1 (2)
Mo(1)-Mo(2)-O(2)	106.1 (1)



X-ray Crystal Structure of [Mo₂(µ-S)(µ-NPh)(O)₂(S₂CNEt₂)₂] 3.8a, with Selected Bond Lengths (Å) and Bond Angles (°)

methyl groups at the ends of the dithiocarbamate ligands are, however, not in the expected configuration, that being the case where they point in opposite directions. The reason for this becomes clear when the packing of the molecules is studied. As can be seen the molecules pack closely into layers, an effect that would not be possible if the substituents on the dithiocarbamate ligands pointed in opposite directions, indicating that this is caused by crystal packing forces.



Figure 3.26 Packing Diagram for $[Mo_2(\mu-S)(\mu-NPh)(O)_2(S_2CNEt_2)_2]$ 3.8a

The mechanism by which the dimer is formed is not clear, and it cannot be ruled out that it results from the decomposition of target complex, no such problems reported¹⁹⁸. It was speculated that because of the stepwise nature of the desulfurisation reaction, the first intermediate in the reaction is $[MoS(NPh)(S_2CNEt_2)_2]$ **3.9a**, formed by the loss of one sulfur atom form **2.2a**. The analogous oxo complex $[MoS(O)(S_2CNEt_2)_2]$ has been reported to be highly reactive, and has yet to be isolated¹⁷². Thus, it is believed that **3.9a** attacks either another molecule of **3.9a** or a unreacted molecule of **2.2a**, affording a dimeric molecule such as $[Mo_2(\mu-S)(\mu-NPh)(X)(X')(S_2CNEt_2)_2]$ (X, X' = NPh, S) after **lo**sing two dithiocarbamate ligands. This can then undergo replacement of any terminal imido or sulfido ligands via hydrolysis at these positions.



Figure 3.27 Proposed Mechanism for the Formation of

 $[Mo_2(\mu-S)(\mu-NPh)(O)_2(S_2CNEt_2)_2]$ 3.8a

In order to try to prevent any dimerisation reactions from occurring, and to give **2.2a** time to completely desulfurise, the reaction was repeated by slowly adding a solution h_2 **2.2a** to one of triethylphosphite at high dilution. However, similar colour changes were observed, with **3.8a** being the only complex isolated from the reaction. This indicates that $[Mo(S)(NR)(S_2CNEt_2)_2]$ **3.9a** does not play a part in the reaction as it is unlikely to have a long lifetime in the above reaction.

3.4.3 Thermolysis of [Mo(NR)(S₂)(S₂CNR'₂)₂] 2.2: It was considered that the thermolysis of $[Mo(NR)(S_2)(S_2CNR'_2)_2]$ **2.2** might lead to some of the other dimeric products observed from the initial reaction. However, after the thermolysis of two of these complexes **2.2a** (R=Ph, R'=Et) and **2.2h'** (R=¹Bu, R'=Me) in refluxing toluene for three days, analysis of the sample by ¹H nmr spectroscopy showed only starting material to be present. This, indicates that these complexes are not involved further in the thermolysis reaction, being stable at elevated temperatures.

3.4.4 Protonation of [Mo(NPh)(S_2)(S_2CNEt_2)_2] 2.2a with HBF₄: The protonation of 2.2a was preformed in order to determine whether the disulfur unit was more nucleophilic that the imido ligand. Upon addition of a few drops

of HBF₄ to a dichloromethane solution of **2.2a** an immediate colour change from blue to brown was observed. The solvent was removed on a rotary evaporator, and the resulting brown oil was washed with ether to remove any unreacted acid. The ¹H nmr spectrum of this oil contained a large number of peaks corresponding to phenyl rings and the ethyl groups of the dithiocarbamate ligands, and was believed to be due to a large number of complexes present in the solution. Attempts to purify this oil by either recrystallisation or extraction methods met with failure.

3.4.5 Oxidation of [Mo(NPh)(S2)(S2CNEt2)2] 2.2a: As was discussed in the introduction to this chapter (3.1.3), the oxidation of disulfur ligands is a well known process. However, while treatment of 2.2a with either one or two equivalents of 2-chloroperoxybenzoic acid (a typical reagent for such reactions) did give a colour change from blue to green, difficulty was encountered in attempts to obtain crystalline samples of the complexes. The ¹H nmr and ir spectra of the green solid obtained from this solution after removal of the solvent showed a number of complexes to be present. An attempt to purify this mixture via column chromatography lead to extensive decomposition of the products, shown by a colour change from green to yellow. The majority of the material remained stuck to the column after it decomposed, however, a small amount of a yellow complex was obtained upon elution with 90% dichloromethane in petrols. This was identified as $[Mo(\mu-S)(\mu-NPh)(O)_2(S_2CNEt_2)_2]$ **3.8a** (5%) by comparison of ¹H nmr and ir with that of an authentic sample. The processes via which this dimer is formed are not clear, although some similarity with the formation of 3.8a in the reaction of 2.2a with P(OEt)₃ may exist.

3.5 Summary

During this chapter it has been shown that the dithiocarbamate ligands

are not behaving as the innocent spectator ligands we expected. Instead they become actively involved in the reaction, and are responsible for the formation of the disulfur ligand in **2.2**. The formation of **2.2** is independent of the isocyanate used in the reaction. However, if the substituent on the imido ligand contains an α -hydrogen atom the complex becomes air and water sensitive and difficult to isolate from the other complexes present. The substituent on the dithiocarbamate ligand does not influence the course of the reaction with the **closely** complexes obtained in slightly lower yield when the dimethyldithiocarbamate is used instead of the diethyldithiocarbamate.

Dimeric Molybdenum(V) Complexes

4.1 Introduction

Dimeric molybdenum complexes show great diversity in their structure and reactivity. They are found in a number of oxidation states, including mixed valence systems²⁰⁰. Many complexes contain metal-metal interactions, varying in bond order between one and four. Here only dimeric molybdenum(V) complexes will be considered, with greater emphasis placed on those containing imido ligands.

Molybdenum(V) dimers that contain π -donor groups such as oxo, imido and sulfido ligands can be split into two broad groups. In the first, the two metal atoms are linked by one π -donor ligand in a bridging mode, and the complex contains no metal-metal interaction. These types of complexes are typically observed in oxygen atom transfer reactions of monomeric bis(oxo) complexes.



Figure 4.1 Formation of Mo(V) Dimers in Oxygen Atom Transfer Reactions

As the reaction proceeds, the monomeric molybdenum(IV) complex $[MoO(L)_2]$ is generated. This can then undergo a conproportionation reaction with the molybdenum(VI) starting material to generate the molybdenum(V) dimer $[Mo_2(O)_2(L)_4(\mu-O)]^{201}$. The latter are not very stable, and exist in equilibrium with the two monomeric complexes. Maatta and co-workers^{202,203} synthesised the corresponding oxo/imido monomeric molybdenum(VI) complex $[MoO(NPh)(S_2CNEt_2)_2]$ **2.3a**. Here the possibility exists for the imido ligand to

be involved in the reaction, either in the transfer process, or to form the bridge between the two monomeric centres during dimer formation. Again transfer of the oxygen atom is observed upon reaction with triphenylphosphine, and although no crystallographic data is reported, assignment of the oxo ligand from the molybdenum(VI) species as the bridging group is made on the basis of ir spectroscopy.





The formation of these dimeric complexes has hindered the study of the kinetics of this oxygen atom transfer system. A number of groups have overcome this problem by using sterically demanding ligands to prevent the close approach of the two monomeric units^{23,24}.

The second type of dimeric molybdenum(V) system is based around the $[Mo_2(X)_2(\mu-X)_2]^{2+}$ (X=O, S, NR) core, and unlike the first, contains a metalmetal single bond. The remaining ligands are typically monoanionic chelates such as dithiocarbamate (S₂CNR₂), dithiophosphinate (S₂P(OR)₂) and cyclopentadienyl (C₅R₅). Discussion of these complexes will be divided into the those of the five-electron donor cyclopentadienyl ligand, and those of the three-electron donor sulfur bound chelating ligands such as dithiocarbamate and dithiophosphinate.

4.1.1 Cyclopentadienyl Complexes: The first cyclopentadienyl complex of

this type, namely $[Mo_2Cp_2(O)_2(\mu-O)_2]$, was reported by Cousins and Green in 1969²⁰⁴. It was obtained in good yield upon hydrolysis of $[MoCpCl_4]$ and other similar monomeric complexes. An X-ray structure performed in 1978²⁰⁵ revealed a puckered core geometry, with the two terminally bound oxo ligands being *cis* with respect to each other. The metal-metal bond length of 2.602(1) Å is typical for a single bond between two molybdenum atoms.



Figure 4.3 Preparation of $[Mo_2Cp_2O_2(\mu-O)_2]$

The complexes containing sulfido ligands in the coordination sphere are also known, being synthesised via the treatment of low valent complex $[MoCp^*(CO)_2]_2$ with elemental sulfur²⁰⁶. This reaction is complicated by the presence of three isomers of the empirical formula $[Mo_2Cp^*_2S_4]$, with conversion between the isomers being achieved by either UV photolysis or thermolysis of the reaction mixture²⁰⁷.



Figure 4.4 Conversion Between the Isomers of the Formula $[Mo_2 Cp*_2S_4]$

Interest in this system was revived in 1983 when Alper and co-workers reported the synthesis of the imido complex $[Mo_2Cp_2O_2(\mu-O)(\mu-4-MeC_6H_4)]^{208}$, the preparation involving the treatment of the molybdenum(I) dimer $[Mo_2Cp_2(CO)_6]$ with ArNO₂ in refluxing toluene.



Figure 4.5 Preparation of $[Mo_2Cp_2O_2(\mu-O)(\mu-4+MeC_6H_1N)]$

This was soon followed by the preparation of the fully substituted complex $[Mo_2Cp_2(NPh)_2(\mu-NPh)_2]^{209}$ via the treatment of tetraoxo species with four equivalents of phenylisocyanate in THF at 70°C. However, the study of the reactivity of this complex was hampered by its insolubility in common organic solvents, and thus in order to overcome this problem, analogous complexes with one substituent on the cyclopentadienyl rings were synthesised by similar means^{133,210}.



Figure 4.6 Synthesis of $[Mo_2(C_5H_4R)_2(NPh)_2(\mu-NPh)_2]$ (R=Me, ⁱPr)

The X-ray crystal structure of the tetraimido complex shows a significant change in the dimetallic core. Where as in the tetraoxo complex the terminal oxo ligands are in a *cis* arrangement, in the tetraimido complex the terminal imido groups now adopt a *trans* arrangement with respect to each other.

Accompanying this change, the $Mo_2(\mu-N)_2$ core becomes planar (maximum deviation from planarity 0.02 Å). This planar structure is also seen in the mixed ligand complexes $[Mo_2(C_5H_4Me)_2(O)_n(NPh)_{4-n}]$ (n=1-3)²¹¹.

Two theories have been proposed to explain this change in structure, based on the steric and electronic properties of the ligands present. Steric arguments, propose that introducing imido ligands into the bridging positions of a puckered core, will cause unfavourable repulsive forces between the substituents on the imido ligands. Which would be minimised if the core of the molecule is planar. The electronic argument for the change in structure is based upon the greater π -donor ability of the imido as compared to the oxo ligand. As more of the former are introduced into the coordination sphere, the metal atoms require less electron density from other bonds. Consequently the metal-metal interaction becomes less important than if oxo ligands are present, and the metal-metal bond elongates. In order to allow for this change in the metal-metal bond length, the core of the molecule becomes planar.

A number of examples have been reported of complexes that adopt the planar core geometry but do not contain imido ligands. However, many of them fit well into both arguments. For example $[Mo(Cp^*)(\mu-O)(O)]_2$ has a planar core, which may be a consequence of the more sterically demanding nature of the pentamethylcyclopentadienyl ligands, or their better electron donor properties.

One example which seems to support the electronic nature of this effect has recently been reported by Saunders and co-workers²¹², who synthesised the perfluoroimido complex $[Mo_2(MeC_5H_4)_2(O)_2(\mu-NC_6F_5)_2]$. An X-ray crystallographic analysis of this complex showed it to contain a puckered core with a *cis* configuration of the terminal oxo groups. As the perfluoro imido group is a poorer π -donor ligand than its hydrogen analogue, electronically the molybdenum atoms still require a significant amount of electron density from the metal-metal bond, which as a consequence is short [2.686(1) Å]. However the perfluoro imido group is much larger than a phenyl group, and as such should prohibit the formation of a puckered core if steric effects dominate.

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Figure 4.7 Formation of a Perfluorolmido Complex

4.1.2 Dithiocarbamate and Dithiophosphinate Complexes: Unlike the cyclopentadienyl complexes, the bidentate chelating ligands bound via sulfur atoms such as dithiocarbamate and dithiophosphinate, show exclusively a *cis* arrangement of the terminal π -donor ligands and a puckered core geometry. These complexes also show a more diverse range of reactions.

The complexes $[Mo_2(O)_{4\cdot n}(S)_n(S_2CNR_2)_2]$ (n=0²¹³ **4.1**, 1²¹⁴ **4.2**, 2²¹⁵ **3.2**, 3²¹⁶ **4.3**, 4¹⁹⁹ **4.4**) are all well known, their crystal structures having been reported. The preparation of the tetraoxo complex **4.1** is typically achieved by either hydrolysis of $[MoCl_5]$, followed by addition of NaS₂CNEt₂, or by reductive dimerisation of $[Mo(O)_2(S_2CNEt_2)_2]$ **1.2** with zinc dust and a catalytic amount of thiophenol²¹⁷.



Figure 4.8 Preparation of [Mo(O)(µ-O)(S₂CNEt₂)]₂ 4.1

The synthesis of the sulfido containing species is achieved via the replacement of oxo by sulfido ligands. This is accomplished by treatment of the oxo complex with hydrogen sulfide.



Figure 4.9 Replacement of Oxo Ligands by Sulfido Ligands Molybdenum(V) dimers with dithiophosphinate ligands to a large extent parallel those of the dithiocarbamate ligands, although the former have been more widely studied, possibly due to the extra diagnostic tool of ³¹P nmr spectroscopy available to aid with structure elucidation.

As with the dithiocarbamate ligand, the dimeric species containing mixtures of oxo and sulfido ligands are known for dithiophosphinate complexes, and display analogous structures to the latter^{218,219}. The first imido containing complex with dithiophosphinate ligands namely [Mo(μ -S)(4-MeC₆H₄N)(S₂P(OEt)₂)]₄ was reported by Wentworth and co-workers in 1980²²⁰. The synthesis from [Mo(NTol)(S₂P(OEt)₂)₃] and hydrogen sulfide proceeds in moderate yield, with the tetrameric nature of the complex being confirmed by osmometry.





The cubic nature of alternating molybdenum and sulfur atoms, was established by crystallography²²¹, and its was also noted that the cubane exists in a equilibrium with the dimeric subunits. The equilibrium between the cubane and the dimeric structures is not limited to the dithiophosphinate complexes, as substitution by dithiocarbamate ligands gives rise to similar mixtures of products²²². The formation of cubane structures however is restricted to complexes that contain terminal imido groups, as there have been no reports of this type of behaviour in the corresponding oxo complexes [Mo(μ -S)(O)(L)]₂ (L= S₂CNR₂, S₂P(OR)₂).



Figure 4.11 Equilibrium of the Dimer and the Tetramer (Imido and Dithiophosphinate Ligands Omitted for Clarity From Cubane Structure)

To investigate this difference further, one of the terminal imido groups was replaced by an oxo moiety via hydrolysis with HCl²²³. This complex also forms a cubane type structure, indicating that the effect of a single imido ligand on the equilibrium is enough to allow the formation of the cubane. The reason that imido ligands promote the formation of the cubane structure is not clear. The added steric requirements of the substituent on the imido ligand plays little part, facing away from the second molecule during formation of the cubane. The cubane. Thus, the greater π -donor properties of an imido ligand compared to an oxo ligand must be effecting the properties of the complex. One of the properties changed by the introduction of imido ligands is the basicity of the bridging sulfido ligands, which can be protonated upon treatment with trifluoroacetic acid²²⁴.



Figure 4.12 Protonation of $[{Mo(\mu-S)(4-MeC_6H_4N)(S_2P(OEt)_2)}_2]$ with CF₃COOH

As can be seen from the examples given above, although many molybdenum(V) dimers containing terminal imido ligands are known, reactions of these complexes occur mainly at the bridging ligands. Only one complex has been reported containing dithiophosphinate, while none with dithiocarbamate ligands having imido ligands in the bridge sites are known. During the thermolysis reactions discussed in Chapters 2 and 3, a range of dimeric molybdenum(V) complexes were obtained, a number of which contain bridging imido ligands. The nature of these dimers depend upon the substituent on the isocyanate, and will be discussed in three sections detailing differing types of substituent. The first of these details complexes containing the none sterically demanding phenyl and p-tolyl imido ligands.

4.2 Complexes Containing Phenyl or p-Tolyl Imido Ligands

4.2.1 Synthesis: Thermolysis of a toluene solution of $[Mo(O)_2(S_2CNEt_2)_2]$ **1.2** with RNCO (R=Ph, 4-MeC₆H₄) leads to formation of the yellow dimeric complexes $[Mo(\mu-NR')(O)(S_2CNR_2)]_2$ **4.5**, obtained in good yield after purification by column chromatography. They are identified by the presence of strong bands in the ir spectra at 948 and 932 cm⁻¹ assignable to Mo=O stretches, 1278 cm⁻¹ assignable to Mo=NR stretches, and 1585 cm⁻¹ assignable to C=N stretches. The ¹H nmr spectra contain only one set of signals for both the phenyl rings and the dithiocarbamate ligands, indicating that the molecule is symmetrical possessing either a mirror plane or a two fold

rotation axis. The third possible symmetry element, an inversion centre, is unlikely as they are believed to adopt the expected *cis* configuration of the terminal groups. The two terminal sites are believed to be occupied by oxo ligands, with the two imido ligands occupying the bridging sites. The presence of two strong Mo=O bands in the ir spectra confirms both the terminal nature of the oxo ligands and their *cis* disposition. This is because bands due to bridging oxo moieties in molecules of this type come at lower wavenumbers, and are not as strong as their terminal counterparts²²⁵, and that a *trans* disposition of ligands about the metal-metal bond would require only one ir band.



Figure 4.13 Thermolysis of $[Mo(O)_2(S_2CNEt_2)_2]$ **1.2** with RNCO (R=Ph, 4-MeC₆H₄)

These complexes could be formed in this reaction in two ways. Either by initial dimerisation of **1.2** giving $[Mo(\mu-O)(O)(S_2CNEt_2)]_2$ **4.1**, followed by substitution of both the bridging oxo ligands for imido groups (route a), or via substitution of one oxo ligand in the monomer to give $[MoO(NR)(S_2CNEt_2)_2]$ **2.3**, which then undergoes dimerisation (route b).



Figure 4.14 Possible Routes to $[{Mo(\mu-NR')(O)(S_2CNR_2)}_2]$ 4.5

Thermolysis of **1.2** without any isocyanate was carried out in order to ascertain whether route (a) is possible. This however did not lead to the recovery of any **4.1**, as would be expect if route (a) were possible. This implies the latter is unlikely to occur, and that **4.5** is formed by route (b). During this conversion the molybdenum atoms are reduced from the 6+ to the 5+ oxidation state. The species oxidised as a result of this transformation is the liberated dithiocarbamate ligand, which also dimerises to afford $(Et_2NCSS)_2$. This is recovered after chromatography as a yellow oil which elutes from the chromatography column in 25% dichloromethane in petrol, and was identified by comparison of its ir spectra with an authentic sample.

Treatment of **4.5a** with two further equivalents of phenylisocyanate in refluxing toluene was expected to lead to formation of $[Mo(\mu-NPh)(NPh)(S_2CNEt_2)]_2$ **4.6a**, as a result of replacement of the two terminal oxo ligands by imido moieties, this could then be compared to the known tetraoxo and tetrasulfido complexes with dithiocarbamate ligands, and the analogous cyclopentadienyl complexes. However, the only product obtained from this reaction after purification by column chromatography, was the red complex

 $[Mo_2(\mu-NPh){\mu-PhNC(O)NPh}(NPh)_2(S_2CNEt_2)_2]$ **4.7a**, identified by the presence of a strong band in the ir spectrum at 1710 cm⁻¹ due to the C=O moiety in the ureato ligand, and the ¹H nmr spectrum showing the ratio of imido to dithiocarbamate ligands as 5:2.



Figure 4.15 Reaction of $[{Mo(\mu-NR')(O)(S_2CNR_2)}_2]$ 4.5 with Phenylisocyanate

The structure of **4.7a** was confirmed by X-ray crystallography (important crystallographic parameters are summarised in Appendix 1.8). The ureato ligand bridges the dimetallic centre approximately symmetrically [Mo(1)-N(4) 2.147(13), Mo(2)-N(4) 2.169(13), Mo(1)-N(5) 2.386(14), Mo(2)-N(5) 2.338(14) Å], the other bridge site being occupied by a symmetrical imido ligand [Mo(1)-N(3) 1.973(15), Mo(2)-N(3) 1.991(15) Å]. The terminal sites are occupied by imido ligands [Mo(2)-N(6) 1.742(14), Mo(1)-N(7) 1.740(15) Å], the *trans* influence of which can be seen in the differences in the bond lengths from the metals to the ureato ligand, with those *trans* to the terminal imido ligands 0.24 Å longer than those *cis*. Consistent with this, there is a increase in the angle at N(5), which is 7.4° larger than that at N(4) [Mo(1)-N(5)-Mo(1) 74.9°, Mo(1)-N(4)-Mo(2) 67.5°]. A close metal-metal contact of 2.625(3) Å is indicative of a bond between the metal centres. However, electron counting the complex gives a total of 36-electrons.



Figure 4.16 Electron Counting 4.7a

Mo(1)-Mo(2)	2.625 (3)
Mo(1)-S(1)	2.466 (6)
Mo(1)-S(2)	2.533 (5)
Mo(2)-S(3)	2.546 (5)
Mo(2)-S(4)	2.483 (6)
Mo(1)-N(3)	1.973 (15)
Mo(2)-N(3)	1.991 (15)
Mo(1)-N(4)	2.147 (13)
Mo(2)-N(4)	2.169 (13)
Mo(1)-N(5)	2.386 (14)
Mo(2)-N(5)	2.338 (14)
Mo(2)-N(6)	1.742 (14)
Mo(1)-N(7)	1.740 (15)
O(1)-C(11)	1.211 (20)
N(4)-C(11)	1.420 (20)
N(5)-C(11)	1.386 (22)
S(1)-Mo(1)-S(2)	70.6 (2)
S(3)-Mo(2)-S(4)	70.2 (2)
Mo(1)-N(3)-Mo(2)	82.9 (6)
Mo(1)-N(4)-Mo(2)	74.9 (4)
Mo(1)-N(5)-Mo(2)	67.5 (4)
Mo(2)-N(6)-C(61)	168.4 (15)
Mo(1)-N(7)-C(71)	175.1 (13)
Mo(1)-Mo(2)-N(6)	105.8 (5)
Mo(2)-Mo(1)-N(7)	108.1 (5)



X-ray Crystal Structure of $[Mo_2(\mu-NPh)(\mu-PhNC(O)NPh)(NPh)_2(S_2CNEt_2)_2]$ 4.7a, with Selected Bond Lengths (Å) and Bond Angles (°)

This implies that there is no metal-metal bond and that the close contact of the metals is a result of the steric demands of the ureato ligand. Without a metal-metal interaction the complex would be expected to be paramagnetic. However, the ¹H nmr spectrum of this complex contains sharp peaks, indicating that it is diamagnetic. Thus, the two terminal imido ligands are believed to be three electron donors, allowing the metals to achieve a 34-electron count, with the metal-metal bond allowing spin pairing of the odd electron on each metal, making the complex diamagnetic.

The formation of **4.7a** can be explained in terms of an insertion of phenylisocyanate into one of the bridging imido ligands in the expected product from this reaction namely $[Mo(\mu-NPh)(NPh)(S_2CNEt_2)]_2$ **4.6a**. As noted earlier (1.5.3) this type of insertion reaction has been observed before for terminal imido ligands, although this is the first case of such a reaction at a bridging site. Ureato ligands have though been reported bridging dimetallic centres^{226,227,228,229}. The first such example being $[Fe_2\{\mu-PhNC(O)NPh\}(CO)_6]^{230}$, prepared via the treatment of $[Fe_3(CO)_{12}]$ with phenylisocyanate. It was initially formulated as the bis(isocyanate) complex $[Fe_2(PhNCO)_2(CO)_6]$ on the basis its ir spectrum, and it was not until 1967 that the true nature of the complex was shown by a X-ray crystallographic study²³¹.



Figure 4.17 Formation of [Fe₂{µ-PhNC(O)NPh}(CO)₆]

The occurrence of complexes containing ureato ligands formed via the insertion of an isocyanate molecule into an imido ligand, have increased along with the use of this method of imido ligand synthesis. It has recently been shown that a second insertion of an isocyanate into an ureato ligand is possible²³².



Figure 4.18 Insertion of an Isocyanate into an Ureato Ligand

The ureato ligand has been postulated as an intermediate in the exchange of terminal imido ligands in $[Mo(MeC_5H_4)(\mu-NPh)(NPh)]_2$, which upon treatment with p-tolylisocyanate exchanges its terminal phenylimido ligands for p-tolylimido ligands. However, it is interesting to note that in none of the reported examples of ureato ligands formed via the insertion of an isocyanate into an imido ligand, has the insertion process been reversible, which it would have to be in order to be implicated in the exchange of imido ligands²³³.



Figure 4.19 Imido Ligand Exchange Using Isocyanates

However, unlike in the previously reported examples^{74,90}, with $[Mo_2(\mu - NPh){\mu-PhNC(O)NPh}(NPh)_2(S_2CNEt_2)_2]$ **4.7a** the reverse reaction proceeds in good yield. Thus heating **4.7a** in toluene for 18 hours, leads upon cooling the solution to deposition of orange crystals of $[Mo(\mu-NPh)(NPh)(S_2CNEt_2)]_2$ **4.6a**. Identification was made by the absence of a band assignable to C=O in the ir spectrum, and the simplification of the ¹H nmr spectrum, which now shows two different imido environments and one dithiocarbamate environment. A result of the higher symmetry of the molecule, which as with $[Mo(\mu-NPh)(O)(S_2CNEt_2)]_2$ **4.5a** can now posses either a two fold rotation axis or a mirror plane. The intermediate nature of this complex and the reversibility of the reaction was confirmed by heating a toluene solution of **4.6a** with



phenylisocyanate, affording 4.7a in 50% yield after chromatography.

Figure 4.20 Reversibility of the Insertion Reaction

It was considered that the yield of **4.6a** from this reaction could be increased by the addition of an amine. This could then react with any liberated isocyanate molecules affording an urea molecule, which would prevent the reverse reaction. Attempts at this were carried out using 2-toluidine. The substituted amine being used in order to generate an asymmetrical urea molecule to establish that trapping had indeed occurred. This though led to a complex mixture of products as shown by ¹H nmr spectroscopy. The large number of products observed may be due to the amine substituting for the imido ligands in the complexes, a process that has been observed in a number of other systems¹²⁸. This problem could be overcome by the use of aniline instead of a substituted amine. However, proving that the amine had indeed trapped an isocyanate molecule would be more difficult.



Figure 4.21 Trapping of Liberated Isocyanate Using an Amine It was believed that [Mo₂(μ-NPh){μ-PhNC(O)NPh}(NPh)₂(S₂CNEt₂)₂] **4.7a** could be synthesised in a one pot preparation by the thermolysis of

 $[Mo(O)_2(S_2CNEt_2)_2]$ **1.2** with 2.5 equivalents of phenylisocyanate. However, when **1.2** was treated with 2.5 equivalents of phenylisocyanate in refluxing toluene, a third product was observed along with the expected products 4.7a and $[Mo(NPh)(S_2)(S_2CNEt_2)_2]$ **2.2a** upon purification by chromatography. The brick red coloured complex $[Mo_2(\mu-NPh)\{\mu-PhNC(NPh)NPh\}(NPh)_2(S_2CNEt_2)_2]$ **4.8a** was identified by the presence of an ir band at 1637 cm⁻¹ assignable to the C=N stretching frequency and the molecular ion peak in the mass spectrum at 1048. This complex is believed to be formed by the insertion of a diphenylcarbodiimide (PhN=C=NPh) molecule into the bridging imido of 4.6a. Full characterisation of this complex was hampered by its high water sensitivity, leading to the formation of diphenylurea which contaminated the ¹H nmr spectrum. The formation of diphenylurea is possibility the result of the diphenylcarbodiimide fragment in 4.8a being more labile than the phenylisocyanate fragment in **4.7a**. Any liberated carbodiimide would rapidly react with trace amounts of water forming diphenylurea. Some evidence for the lability of the diphenylcarbodiimide is gained from the mass spectrum which contains a peak at 852 corresponding to 4.6a, formed as a result of the loss of diphenylcarbodiimide from 4.8a.



Figure 4.22 Formation of $[Mo_2(\mu-NPh){\mu-PhNC(NPh)NPh}(NPh)_2(S_2CNEt_2)_2]$ 4.8a

Carbodiimides are known to be formed by the interaction of isocyanates with metal-oxo or imido complexes²³⁴. The mechanism via which this occurs is similar to that described for the exchange of imido ligands via treatment with an isocyanate (1.4.3). After the imido ligand is formed, a second molecule of isocyanate reacts with the imido ligand in a [2+2] cycloaddition to give a

metallacyclic complex, differing from the previously mentioned exchange process intermediate in that it is bound to the metal via an oxygen atom. This intermediate can now undergo a cleavage reaction to give a carbodiimide and an oxo ligand. The latter being transformed back to an imido ligand by interaction with more isocyanate.

$$M = O \xrightarrow{RNCO} M = NR \xrightarrow{RNCO} M \xrightarrow{R} C = NR \xrightarrow{RNCNR} M = O$$

Figure 4.23 Formation of Carbodiimide from Oxo or Imido Complexes

This system is further catalysed by traces of water, this hydrolyses the imido ligand to give an oxo ligand and an amine. The latter then reacts with a molecule of isocyanate to give a carbodiimide, regenerating the water molecule. The oxo ligand is then be converted back to an imido ligand via reaction with more isocyanate.

$$M = O \xrightarrow{RNCO} M = NR \xrightarrow{H_2O} M = O + RNH_2 \xrightarrow{RNCO} RNCNR$$

Figure 4.24 Catalytic Formation of Carbodiimide in the Presence of Water

As water was excluded from our reaction it is unlikely that latter mechanism is in operation here, and it is believed to be the former route that is responsible for the formation of the carbodiimide. However, the latter cannot be ruled out as only a small amount of water would be required for it to operate. The imido or oxo ligand containing complex responsible for the formation of the carbodiimide is unknown, however, it must be a monomeric species. Evidence for this is provided from the treatment of either [Mo(μ -NPh)(O)(S₂CNEt₂)]₂ **4.5a** or [Mo(μ -O)(O)(S₂CNEt₂)]₂ **4.1** with phenylisocyanate in refluxing toluene. Both reactions afford only **4.7a** upon chromatography, implying the absence of carbodiimide in this reaction.

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Figure 4.25 Reaction of Either $[Mo(\mu-NPh)(O)(S_2CNEt_2)]_2$ 4.5a or $[Mo(\mu-O)(O)(S_2CNEt_2)]_2$ 4.1 with Phenylisocyanate

The only monomeric complex isolated from this reaction is $[Mo(NPh)(S_2)(S_2CNEt_2)_2]$ **2.2a**. In order to ascertain whether this was the monomeric species responsible for the formation of the carbodiimide, **2.2a** was dissolved in toluene with **4.5a**, and thermolysis was carried out in the presence of 2.5 equivalents of phenylisocyanate. Upon after three days, the only complexes isolated after chromatography were **2.2a** (97% yield) and **4.7a** (95% yield). The absence of **4.8a** in this reaction indicates that **2.2a** is not responsible for the production of the carbodiimide in these reactions.

The corresponding ureato complex with a bridging sulfido ligand has also been prepared. Thus treatment of $[Mo_2(\mu-S)(\mu-NPh)(O)_2(S_2CNEt_2)_2]$ **3.8a** or $[Mo_2(\mu-S)(\mu-O)(O)_2(S_2CNEt_2)_2]$ **4.2** with the appropriate amounts of phenylisocyanate in refluxing toluene yields an orange crystalline solid $[Mo_2(\mu-S)(\mu-PhNC(O)NPh](NPh)_2(S_2CNEt_2)_2]$ **4.9a** after purification by chromatography (90% yield). The complex was identified by the presence of an ir band at 1714 cm⁻¹ assignable to the C=O of the ureato ligand, and a similar ¹H nmr spectrum to that of the corresponding bridging phenylimido complex **4.7a**. On the basis of this evidence alone it cannot be discounted that the isocyanate has inserted into the bridging sulfido moiety. Thus attempts were made to elucidate this problem by X-ray crystallography. Although this complex can be recrystallised from a wide range of solvents, attempts at X-ray crystallography on a number of crystals grown from different solvent mixtures all gave the same large unit cell upon indexing [U=24058(16)Å³] and so data collection was not feasible.



Figure 4.26 Reaction of Either $[Mo_2(\mu-S)(\mu-NPh)(O)_2(S_2CNEt_2)_2]$ 3.8a or $[Mo_2(\mu-S)(\mu-O)(O)_2(S_2CNEt_2)_2]$ 4.2 with Phenylisocyanate

4.2.2 Reactions:

Reaction of $[Mo_2(\mu-S){\mu-PhNC(O)(NPh}(NPh)_2(S_2CNEt_2)_2]$ 4.9a with 2,4-Dinitrophenylhydrazine: The bonding of the ureato ligand to the dimolybdenum centre allows for the possibility of reaction of the carbonyl group. This is due to the lone pairs on the nitrogen atoms becoming involved in bonding interactions with the dimetallic centre. Normally in the uncoordinated ligand these lone pairs become involved in bonding interactions with the carbon atom of the carbonyl (Fig 4.27). In this form the ligand would not be expected to undergo the condensation type reactions of organic carbonyl molecules and is the reason why amides and esters are unreactive towards these reagents.



Figure 4.27 Electronic Structure of Urea Thus, treatment of a dichloromethane solution of with 2,4dinitrophenylhydrazine gave the expected product $[Mo_2(\mu-S){\mu-PhNC(NNHC_6H_3(NO_2)_2)NPh}(NPh)_2(S_2CNEt_2)_2]$ **4.10a** as an orange oil. Initial characterisation was made on the basis of the loss of the ir stretch due to C=O which was monitored during the course of the reaction. Further attempts to obtain a crystalline solid failed leading to a oil in all cases. This is somewhat surprising considering the crystalline nature of the starting complex, and the use of 2,4-dinitrophenylhydrazine in organic chemistry to obtain crystalline adducts of ketones and aldehydes that can be identified by their melting point. However ¹H nmr studies on the oil showed no sign of any impurities, and was consistent with the formulation given. If it is now possible to liberate the coordinated organic fragment, this reaction could be extended further to the synthesis of nitrogen containing organic molecules.



Figure 4.28 Reaction of 4.9a with 2,4-Dinitrophenylhydrazine

Protonation of [{Mo(µ-NPh)(O)(S2CNEt2)}] 4.5a with HBF4: The protonation of 4.5a was of interest to see which of the π -donor ligands is more nucleophilic. Studies on the analogous cyclopentadienyl system $[Mo_2(C_5H_4Me)_2(\mu-NPh)(\mu-O)(O)_2]$ have shown that protonation occurs at the terminal oxo moiety upon treatment with trifluoroacetic acid²³⁵. Thus treatment of a dichloromethane of 4.5a with HBF4.Et2O gave an immediate colour change from yellow to red. The ¹H nmr spectrum of this sample was not as simple as expected for a protonated complex, and indicated that there was more that one complex present in solution. Crystals of a red complex were grown upon refrigeration of a dichloromethane solution to which a few drops of hexane had been added. The ¹H nmr spectra of these crystals showed there to be three inequivalent dithiocarbamate ligands and two inequivalent

imido ligands. The ir spectra showed the presence of oxo ligands due to bands at 964 cm⁻¹ as well as those due to the dithiocarbamate and imido ligands (1526 cm⁻¹ and 1280 cm⁻¹ respectively), the ir spectra also showed the presence of a $[BF_4]^-$ ion by the appearance of a broad band at 1052 cm⁻¹. An X-ray crystallographic study on these crystals (important crystallographic parameters summarised in Appendix 1.9) showed that the complex did indeed contain three dithiocarbamate ligands, having undergone replacement of one of the terminal oxo moieties by another dithiocarbamate.



Figure 4.29 Reaction of $[{Mo(\mu-NPh)(O)(S_2CNEt_2)}_2]$ 4.5a with HBF₄

As was noted earlier (2.1), this type of reaction is common in the monomeric bis(dithiocarbamate) molybdenum(VI) complexes, although we believe that it is the first time such a reaction has been observed at a dimeric molybdenum centre. The two metals in this complex are in differing environments. Thus Mo(1) displays a square based pyramidal geometry with the metal centre lying above that plane of the base of the pyramid, while Mo(2) has a distorted octahedral geometry. The two metal centres are bridged asymmetrically by two bridging imido ligands, being 0.1 Å closer to Mo(1) than Mo(2) [Mo(1)-N(4) 1.941(9), Mo(2)-N(5) 2.055, Mo(1)-N(5) 1.939(15), Mo(2)-N(5) 2.039(9) Å]. This asymmetrical bridging can be explained as a result of the imido ligands donating more electron density to Mo(1) than Mo(2). The former requires more electron density due to supporting a second dithiocarbamate ligand, which is a poorer electron-donor than the oxo ligand bound to Mo(2). Added to this, Mo(1) carries the complexes formal positive charge. The Mo-S bonds of the dithiocarbamate ligands on Mo(1) are affected



X-ray Crystal Structure of [Mo(µ-NPh)₂(O)(S₂CNEt₂)₃][BF₄] 4.11a, with Selected Bond Lengths (Å) and Bond Angles (°)

by the *trans* influence of the imido ligands in the bridge sites. Thus, those *trans* to imido ligands are ~0.1 Å longer than those that are *trans* to each other.

4.2.3 Summary: As was noted the introduction to this Chapter, complexes of the type $[Mo(\mu-X)(X)(L)]_2$ (were X is a π -donor ligand such as an oxo, and L is a sulfur bound chelate) show greater reactivity at the bridging ligands. This has now been carried into the chemistry of the complexes containing bridging imido ligand reported herein which show insertion reactions at these sites. However, as will be shown in the next section, this insertion reaction is extremely sensitive to the steric requirements of the ligand set.

4.3 Complexes Containing o-Tolyl Imido Ligands

4.3.1 Synthesis: When $[Mo(O)_2(S_2CNEt_2)_2]$ **1.2** is treated with otolylisocyanate in refluxing toluene, the only dimeric product observed with $[Mo(NR)(S_2)(S_2CNEt_2)_2]$ **2.2c** is $[\{Mo(\mu-NR)(NR)(S_2CNEt_2)\}_2]$ **4.6c** obtained as orange crystals (34% yield) after purification by chromatography.



Figure 4.30 Reaction of $[Mo(O)_2(S_2CNEt_2)_2]$ 1.2 with o-Tolylisocyanate

There is no evidence in this reaction for the presence of insertion products similar to those observed in the phenyl substituted complexes. The ¹H nmr spectrum of this complex at room temperature is complicated and indicates fluxional behaviour. On cooling the sample, the fluxionality was frozen out. However, a number of isomers remained indicated by the five resonances associated with the methyl on the phenyl ring which integrate for differing numbers of protons (δ 2.33 3.1H, 2.30 2.2H, 2.27 1.6H, 2.22 3.7H,
2.14 1.4H). These isomers are believed to be caused by different orientations of the phenyl rings and thus the methyl groups in the 2-position. This gives rise to a number of rotational isomers in solution, and the fluxionality of the molecule. On warming the sample to 323K the spectrum simplifies, now only two signals are seen for the methyls on the phenyl rings, that at δ 2.34 being much sharper than the one at δ 2.10. This may indicate that one of the sets of phenyl rings has a lower barrier to rotation than the other. Identifying which of the rings (either bridging or terminal) are responsible for these signals should be possible by comparing the spectra with that of [Mo(μ -NR)(O)(S₂CNEt₂)]₂ **4.5c** (discussed later in this section). The ¹H nmr spectrum of this complex shows a resonance at δ 2.53, which would appear to indicate that the sharper of the two signals is due to the bridging imido ligands. However, the large difference between the former and the latter precludes definite assignment.



Figure 4.31 Variable Temperature ¹H nmr Spectrum of 4.6c Between δ 1.9-2.7

Chapter IV: Dimeric Molybdenum(V) Complexes

The rotation of the phenyl rings was supported by the X-ray structure (important crystallographic parameters summarised in Appendix 1.10) which shows a disorder over the two possible sites for the methyls on both of the phenyl rings. The structure shows the expected geometry for complexes of this type, with a *cis* arrangement of terminal ligands. With only half of the molecule being unique, related to the second half by a C_2 rotation axis that passes through the molybdenum-molybdenum bond perpendicular to it. The bridging imido ligands approximately symmetrically bridge the dimetallic core [Mo(1)-N(3) 1.958(3), Mo(1)-N(3A) 1.978(4) Å]. The metal-metal bond at 2.633(1) Å is slightly longer than that of the tetraxoxo species 4.1²¹³ at 2.580(1) Å, with both of these being much shorter than that of the tetrasulfido species 4.4¹⁹⁹ at 2.801(2) Å. The increase on going to 4.4 is due to the increased size of the sulfido compared to that of either the oxo or imido ligands. In the case of going to imido from oxo ligands, the steric effect of the substituents on the former could play some role in the increase in bond length. However, it is more likely that the increase in this case arises from the ligands different π donor properties. As the imido ligand is a much stronger π -donor ligand, when this is coordinated to a metal centre, the metal would need less electron density from other sources, and as a result the metal-metal bond elongates.

The structure also explains why this complex does not react with a further molecule of o-tolylisocyanate to give an ureato ligand. The methyls on the phenyl rings block the approach of isocyanate molecules to the nitrogen atoms of the bridging imido ligands. While also making the molecule less susceptible to hydrolysis of the terminal imido groups, explaining why we do not see the formation of $[Mo(\mu-NR)(O)(S_2CNEt_2)]_2$ **4.5c** in this case.

The inability of these complexes to form products from the insertion of molecules into the bridging imido ligands was confirmed by thermolysis of $[Mo(\mu-O)(O)(S_2CNEt_2)]_2$ **4.1** with a five fold excess of o-tolylisocyanate, which afforded only **4.6c** upon purification by chromatography. This is in contrast with the earlier example, were treatment of **4.1** with a five fold excess of phenylisocyanate afforded the insertion product $[Mo_2(\mu-NPh)\{\mu-$

	Mo(1)-Mo(1A)	2.633 (1)
	Mo(1)-S(1)	2.481 (1)
	Mo(1)-S(2)	2.493 (1)
	Mo(1)-N(3)	1.958 (3)
	Mo(1)-N(3A)	1.978 (4)
	Mo(1)-N(2)	1.741 (3)
	S(1)-Mo(1)-S(2)	70.5 (1)
i	Mo(1)-N(3)-Mo(1A)	83.9 (1)
	N(2)-Mo(1)-Mo(1A)	108.7 (1)



X-ray Crystal Structure of $[Mo(\mu-2-MeC_6H_4N)(2-MeC_6H_4N)(S_2CNEt_2)]_2$ 4.6c, with Selected Bond Lengths (Å) and Bond Angles (°)

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PhNC(O)NPh}(NPh)₂(S_2CNEt_2)₂] **4.7a**. Further confirmation was achieved by the thermolysis of **4.6c** in toluene with o-tolylisocyanate. Again no reaction was observed even after prolonged thermolysis.



Figure 4.32 Thermolysis of $[Mo(\mu-O)(O)(S_2CNEt_2)]_2$ 4.1 with o-Tolylisocyanate

It is possible to synthesise **4.5c** by the acid hydrolysis of **4.6c**. Thus treatment of **4.6a** with an aqueous solution of trifluoroacetic acid lead to recovery of a yellow crystalline solid $[Mo(\mu-2-MeC_6H_4N)(O)(S_2CNEt_2)]_2$ **4.5c**, identified as such by the presence of two Mo=O stretches in the ir spectrum (948 and 932 cm⁻¹), and the simplification of the ¹H nmr spectrum, with only one of the possible rotamers being present in solution. The preference for one rotamer was confirmed by the X-ray structure of the complex (important crystallographic parameters are summarised in Appendix 1.11). This shows the expected *cis* configuration of dithiocarbamates, with the two imido ligands occupying the bridge sites in the puckered core of the dimer. Both of the imido ligands have only one of the two possible sites for the methyl group occupied, and bridge the dimetallic centre approximately symmetrically. The bond between the two metaks at 2.628(1) Å only slightly shorter than that in **4.6c**. Implying that the ligands in the terminal sites in complexes of this type have little effect on the length of the metal-metal interaction.

It is possible to convert this complex back into **4.6c**, thus thermolysis of a toluene solution with two equivalents of o-tolylisocyanate gives **4.6c** in 90% yield after purification by chromatography



X-ray Crystal Structure of $[Mo(\mu-2-MeC_6H_4N)(O)(S_2CNEt_2)]_2$ **4.5c**, with Selected Bond Lengths (Å) and Bond Angles (°)



Figure 4.33 Conversion Between 4.6c and 4.5c

4.3.2 Summary: There is a marked change in the reactivity of the dimeric complex $[Mo(\mu-NR)(NR)(S_2CNEt_2)]_2$ **4.6** upon increasing the steric demands of the group in the 2- position of the aryl ring. Thus, when the substituent is changed from a hydrogen to a methyl group, the complex ceases to undergo insertion reactions at a bridging imido moiety. We shall now see that upon further increasing the steric demands of the imido ligand through the use of bulky alkyl isocyanates, further structural changes occur in the isolated dimer.

4.4 Complexes Containing Alkyl and Bulky Aryl Imido Ligands

4.4.1 Synthesis: Treatment of [Mo(O)₂(S₂CNR₂)₂] **1.2** with R'NCO (R'='Bu R=Me, Et, R'=Adm R=Et, R'=2,6-Me₃C₆H₃ R=Et) led to isolation of the yellow dimeric complex [Mo₂(µ-S)₂(O)(NR')(S₂CNR₂)₂] 4.12d,h,i,h' in moderate to low yields (4.12h,i 10% yield, 4.12d 4% yield). All show a single Mo=O stretch in their ir spectra at ~955 cm⁻¹, and in their ¹H nmr spectra show two environments for the dithiocarbamate ligands confirming their unsymmetrical nature. The complexes were recovered as yellow crystalline needles from the chromatographic band containing the imido disulfur product $[Mo(NR')(S_2)(S_2CNR_2)_2]$ **2.2** (discussed in Chapter 3). It was shown that they are not formed by decomposition of 2.2 by recrystallisation of a pure sample

of $[Mo({}^{1}BuN)(S_{2})(S_{2}CNMe_{2})_{2}]$ **2.2h**', which showed no signs of the dimer in the ${}^{1}H$ nmr spectrum.



Figure 4.34 Thermolysis of 1.2 with RNCO (R=Adm, 'Bu, 2,6-Me₂C₆H₃)

X-ray structure determinations were performed on **4.12d** and **4.12h** (Important crystallographic parameters are summarised in Appendices 1.12 and 1.13). They showed the expected *cis* configuration of the dithiocarbamate ligands, with the metal centre being symmetrically bridged by two sulfido ligands. One of the metals supports a terminal imido moiety, and the other a terminal oxo. The metal-metal bond in these complexes is typical of complexes containing two sulfido bridges [**4.12h** 2.822(1), **4.12d** 2.806(1), [Mo₂(μ -S)₂(O)₂(S₂CNEt₂)₂]**3.2** 2.820(1)²¹⁵, [Mo₂(μ -S)₂(O)(S)(S₂CNPr₂)₂]**4.3** 2.826(3)²¹⁶, [Mo₂(μ -S)₂(S)₂(S)₂(S₂CNEt₂)₂] **4.4** 2.801(2)¹⁹⁹ Å], and as with the imido ligand bridged systems seem unaffected by the presence of different terminal ligands. In contrast to those complexes already reported that contain two bridging sulfido ligands and either one or two terminal imido ligands, these complex show no sign of forming cubane type structures.



Figure 4.35 Formation of Cubane Structure in Related Systems However one complex, **4.12d**, does form dimers via a none bonding contact in the solid state between O(1) and N(1)A of 2.950 Å. This can be



X-ray Crystal Structure of [Mo₂(µ-S)₂(^tBuN)(O)(S₂CNEt₂)₂] **4.12h**, with Selected Bond Lengths (Å) and Bond Angles (°)



X-ray Crystal Structure of $[Mo(\mu-S)_2(2,6-Me_2C_6H_3N)(O)(S_2CNEt_2)_2]$ **4.12d**, with Selected Bond Lengths (Å) and Bond Angles (°)

rationalised as a electronic attraction between the negatively charged oxo group and the nitrogen on the dithiocarbamate, which carries a positive charge. This positive charge arises from the second of the canonical forms of the dithiocarbamate ligand shown below.



Figure 4.36 Canonical Forms of the Dithiocarbamate Ligand

In this form the ligand contains a planar backbone and has some C=N character This form is assumed to be a major contributor to the overall bonding of the ligand as most dithiocarbamate complex have an IR band at ~1530 cm⁻¹ assignable to the C=N stretching frequency, and show planar backbones.

This interaction also forces the two methyls on the dithiocarbamate to point in the same direction, this avoids the unfavourable steric interactions with other molecules. This as noted previously, is not the lowest energy configuration of these ligands. The interaction is however not seen in the *t*-butyl complex. This is believed to be because of the steric bulk of the alkyl group preventing close enough approach of the two molecules.

The reason why these molecules do not form cubane type structures is not clear. The presence of imido ligands in the terminal sites is important as this behaviour has not been observed in complex that do not contain any, however the corresponding dithiophosphinate complexes are known and exist in equilibrium with their cubane analogues.

The route via which these complexes are formed is also unclear. No reaction was observed between $[Mo(\mu-S)(O)(S_2CNEt_2)]_2$ **3.2** and a number of isocyanates (R=Ph, 2,6-Me₂C₆H₃, ^tBu). This discounts that the dimer is formed before the introduction of the imido ligand, and implies that they are formed

from a monomeric complex. However, there has been no evidence for the formation of these complexes from the thermolysis reactions of the monomeric complexes ($[Mo(NR')_2(S_2CNR_2)_2]$ **1.1**, $[Mo(NR')(S_2)(S_2CNR_2)_2]$ **2.2**) isolated from the thermolysis reactions of $[Mo(O)_2(S_2CNEt_2)_2]$ **1.2**.

4.4.2 Summary: When alkyl isocyanates are used in the thermolysis reaction, the dimeric compounds recovered do not contain bridging imido ligands. Instead they contain sulfido ligands in the bridging sites, with terminal imido and oxo moieties. These complexes do not exist in solution as an equilibrium mixture of dimeric and tetrameric complexes, a phenomena seen earlier in similar complexes. The reason for this change in behaviour is not fully understood, but may be attributed to the electronic changes between imido and oxo ligands, and dithiocarbamate and dithiophosphinate ligands.

4.5 Comparison of the X-Ray Structures of Molybdenum(V) Dimers with Dithiocarbamate Ligands

Table 4.1 shows a comparison of bond lengths and bond angles from complexes of the type $[Mo(\mu-X)(X)(S_2CNR_2)]_2$ where X is any combination of oxo, sulfido or imido ligands. The table also includes two complexes (4.7a, 4.11a) reported herein that are not members of this class of compounds in that they do not contain four π -donor ligands. However, they are similar enough to these complexes to warrant discussion. All except for 4.11a show a *cis* configuration of the dithiocarbamate ligands with a puckered core geometry, The two molybdenum atoms have distorted square based pyramidal geometry with the metal lying above the plane defined by the two bridging ligands and the two sulfur atoms of the dithiocarbamate.

The length of the molybdenum-molybdenum bond appears to depend upon the size of the bridging ligands. Thus, when two oxo ligands are in the bridge site (4.1) the shortest bond is observed. Replacing both of the oxo

	Mo-Mo	Mo-O-Mo	Mo-N-Mo	Mo-S-Mo	Mo-O _b	Mo-N _b	Mo-S _b	Mo-O,	Mo-N,	Ref
[Mo(μ-O)(O)(S₂CNEt₂)]₂	2.580(1)	83.3(1)			1.940(2)			1.677(2) 1.680(2)		213
[Mo ₂ (μ-S)(μ-O)(O) ₂ (S ₂ CNPr ₂) ₂]	2.673(3)	87.8(4)	······································	70.9(2)	1.927(11)		2.305(5)			214
[Mo(μ-S)(O)(S ₂ CNH ₂)] ₂	2.820(1)			74.7 74.7			2.324(1) 2.325(1)	1.677(3)		215
[Mo ₂ (μ-S) ₂ (S)(O)(S ₂ CNEt ₂) ₂]	2.826(3)			75.1(3) 75.2(3)			2.317(8) 2.309(8) 2.322(7) 2.320(8)	*		216
[Mo(µ-S)(S)(S₂CNBu₂)]₂	2.801(2)			74.7(1)			2.307(4)			199
[Mo(μ-S)(4-MeC _e H₄N)(S₂CNEt₂)]₂	2.807(2)	l		74.2(1) 73.9(1)			2.343(3) 2.321(3) 2.313(3) 2.345(3)		1.722(8) 1.717(8)	222
[Mo ₂ (µ-S)(µ-NPh)(O) ₂ (S ₂ CNEt ₂) ₂]	2.732(1)		87.4(2)	72.0(1)		1.974(4) 1.979(5)	2.315(2) 2.334(2)	1.681(4) 1.681(5)		3.8a
$[Mo_2(NPh)_2(\mu-NPh)\{\mu-PhNC(O)NPh\}(S_2CNEt_2)_2]$	2.625(3)		82.9(6)			1.973(15) 1.991(13)			1.742(14) 1.740(15)	4.7a
[Mo ₂ (μ-NPh) ₂ (O)(S ₂ CNEt ₂) ₃][BF ₄]	2.654(2)		83.2(4) 83.7(4)			1.941(9) 2.055(15) 1.939(9) 2.039(9)		1.650(10)		4.11a
[Mo(μ-NR)(NR)(S₂CNEt₂)]₂ R=2-MeC₅H₄	2.633(1)		83.9(1)			1.958(3) 1.978(4)			1.741(3)	4.6c
[Mo(µ-NR)(O)(S2CNEt2)]2	2.628(1)		83.6(1) 83.8(1)			1.962(3) 1.980(3) 1.974(3) 1.960(3)		1.688(3) 1.689(3)		4.5c
[Mo ₂ (μ-S) ₂ (S)(N'Bu)(S ₂ CNEt ₂) ₂]	2.822(1)			74.5(1) 74.5(1)			2.326(2) 2.336(2) 2.334(2) 2.326(2)	1.670(4)	1.705(4)	4.12h
[Mo ₂ (μ-S) ₂ (S)(2,6-Me ₂ C _e H ₃ N)(S ₂ CNEt ₂) ₂]	2.806(1)			74.4(1) 74.4(1)			2.328(1) 2.313(1) 2.322(1) 2.320(1)	1.663(3)	1.713(3)	4.12d

* not reported due to disorder over the two terminal sites

Table 4.1 Comparison of Bond Lengths (Å) and Bond Angles (°) in Complexes of the Type $[Mo_2(\mu-X^1)(\mu-X^2)(X^3)(X^4)(S_2CNR_2)_2]$

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ligands by imido moieties (**4.5c**) leads to a small increase in the bond length, however if two sulfido ligands are placed into the bridge sites a large increase in length is observed (**3.2**). These changes in metal-metal bond length seem to be independent of the nature of the terminal ligands. Thus in the complexes were two sulfido ligands are in the bridge sites the metal-metal bond varies by only 0.025 Å. The two complexes which contain only one sulfido in a bridge site along with either an oxo or an imido ligand, both display metal-metal bond lengths intermediate between that of the complexes containing two of the same ligand in the bridge sites, indicating that lengthening of the bond upon substitution of bridging ligands for sulfido ligands is stepwise.

The bond lengths from the molybdenum atoms to the bridging ligands for any of the ligands does not vary as the other ligands are changed. Because of the consistency in the Mo- X_b bond lengths, the Mo- X_b -Mo angle does change with variations in the metal-metal bond length. Thus, when a mixed bridging system of one sulfido and either an oxo or an imido ligand is present, the sulfido ligand exhibits a smaller angle than is normally observed in the more prevalent bis(sulfido) complexes, and the oxo or imido ligand shows a similar change in its angle becoming larger.

As with the bridging ligands no changes are observed in the $Mo-X_t$ bond lengths throughout the complexes

4.6 Summary

During this Chapter it has been shown that via the thermolysis of $[Mo(O)_2(S_2CNR_2)_2]$ **1.2**, **1.2**' with organic isocyanates it is possible to synthesise a range of molybdenum(V) dimers. A number of these contain bridging imido ligands, a mode of imido ligation not previously reported in dithiocarbamate stabilised complexes of this type ligands. As with the corresponding bridging sulfido complexes, these imido ligands display a number of unusual reactions, including the first example of a reversible insertion of an isocyanate molecule into a bridging imido moiety. Not all the

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dimers obtained in this manner contain bridging imido ligands. A number contained two bridging sulfido ligands, as well as one terminal oxo ligand and one terminal imido ligand. Unlike the previously reported complexes of this type with dithiophosphinate ligands, the former do not undergo dimerisation to cubane structures.

Summary of Thermolysis of [Mo(O)₂(S_2CNEt_2)₂] in the Presence of RNCO

In the previous chapters the variety of products obtained from the thermolysis of $[Mo(O)_2(S_2CNEt_2)_2]$ **1.2** in the presence of organic isocyanates have been described. Here the pathways by which these complexes are formed will be considered in more detail

The simple explanation to the formation of these complexes, is that they result from the replacement of oxo for imido ligands in the products of the thermolysis of **1.2** alone in toluene. Thermolysis of **1.2** in toluene without any isocyanate gave two products after purification by column chromatography. These are the dimeric complex $[Mo_2(\mu-S)(\mu-O)(O)_2(S_2CNEt_2)_2]$ **4.2** and a brown complex **5.1**. The nature of **5.1** is uncertain, however, its ir spectra shows it to contain no oxo ligands, and its ¹H nmr spectrum contains broad peaks, either as a consequence of fluxional or paramagnetic behaviour in the molecule. Further characterisation was precluded due to difficulty experienced in obtaining a crystalline sample, and based on the available data it is believed to be a molybdenum sulfide complex containing dithiocarbamate ligands.



Figure 5.1 Thermolysis of $[Mo(O)_2(S_2CNEt_2)_2]$ 1.2 in Toluene

If these two complexes are the precursors to the observed products from the thermolysis **1.2** in the presence of isocyanate, then thermolysis of the former in the presence of isocyanates should lead to recovery of the latter. Thermolysis of **4.2** with excess phenylisocyanate afforded only the dimeric

complex $[Mo_2(\mu-S){\mu-PhNC(O)(NPh}(NPh)_2(S_2CNEt_2)_2]$ **4.9a**, a product not observed in the thermolysis of **1.2** with phenylisocyanate. This implies that the complexes isolated from the thermolysis of **1.2** without isocyanate being present are not simply precursors to the product obtained in the presence of isocyanates. As **5.1** contains no oxo ligands it is unlikely that it will yield any of the observed products and its reaction with isocyanates was not investigated.



Figure 5.2 Thermolysis of 4.2 with Excess Phenylisocyanate

It is thus believed that when isocyanates are added to the thermolysis reaction, **1.2** undergoes a substitution of one oxo ligand for an imido ligand affording [MoO(NR)(S₂CNEt₂)₂] **2.3** before they have the chance proceed down their normal thermolysis pathway. The occurrence of this initial substitution process also reinforces the earlier observation that [MoO(S₂)(S₂CNEt₂)₂] **3.1** is not a general intermediate in these reactions, as its formation would almost certainly occur before that of **2.3**. It is more likely that **3.1** plays no part in these reactions, as neither **3.1** or its thermal decomposition product [Mo(O)(μ -S)(S₂CNEt₂)]₂ **3.2**, are observed in the thermolysis of **1.2** without isocyanate, indicating its absence from that reaction.





The mixed oxo-imido complex **2.3** formed by this initial substitution reaction, is now believed to have a number of possible reactions which could take place. The first of these is the substitution of the remaining oxo for an imido ligand to give the target complex $[Mo(NR)_2(S_2CNEt_2)_2]$ **1.1**. Alternatively it could dimerise to give $[Mo(\mu-NR)(O)(S_2CNEt_2)]_2$ **4.5** losing two dithiocarbamate ligands in the process. The latter plays a part in the third possibility, which involves the loss of the oxo ligand, which is replaced in the coordination sphere by a dithiocarbamate ligand. This then cleaves both of its sulfur-carbon bonds to give the disulfur complex $[Mo(NR)(S_2)(S_2CNEt_2)_2]$ **2.2**.



When aryl isocyanates with substituents in the 2- and/or 6- position of the ring are used in the thermolysis reaction, the expected product **1.1** is recovered. In the case of the most bulky substituent (R=2,6-ⁱPr₂C₆H₃) the complex is stable in refluxing toluene for extended periods and takes no further part in the reaction. However, with less bulky substituents the bis(imido) complexes **1.1** can undergo further reaction. Thus, as was noted earlier (2.**5**.**i**) thermolysis of [Mo(2,6-Me₂C₆H₃N)₂(S₂CNEt₂)₂] **1.1d** leads to the formation of [Mo(2,6-Me₂C₆H₃N)(S₂)(S₂CNEt₂)₂] **2.2d** in moderate yield. This, and the thermal decomposition of **2.3**, give two possible routes to **2.2**. The former though only occurs for less bulky imido substituents, and thus cannot be considered a general route. The latter still remains speculative, and attempts

to synthesise **2.3** via literature methods²⁰³ have met with failure, thus preventing an independent study of the thermolysis reaction.



Figure 5.5 Thermolysis of $[Mo(NR)_2(S_2CNEt_2)_2]$ 1.1

The formation of the dimer $[Mo(\mu-NR)(O)(S_2CNEt_2)]_2$ **4.5** is the starting point for a range of dinuclear complexes obtained from these reactions. In the presence of further isocyanate, **4.5** can substitute both of its terminal oxo moieties for imido ligands, affording the complex $[{Mo(\mu-NR)(NR)(S_2CNEt_2)}_2]$ **4.6**. In the case of o-tolyl substituents, this complex is resistant to further attack from either water or isocyanate, and is the recovered product in this case. However, if phenyl imido ligands are present **4.6** is susceptible to attack at one of the bridging imido ligands from a further molecule of isocyanate. This leads to the formation of $[Mo_2(\mu-NPh)\{\mu-PhNC(O)NPh\}(NPh)_2(S_2CNEt_2)_2]$ **4.7a** which contains a bridging ureato ligand.



Figure 5.6 Formation of 4.7a

A second insertion product is also observed in the reaction with phenylisocyanate. Here a molecule of diphenylcarbodiimide inserts into the bridging imido moiety affording **4.8a**.



Figure 5.7 Insertion of Diphenylcarbodiimide into 4.6a

The formation of the carbodiimide molecule involved in this reaction, is produced as a result of the interaction of an isocyanate with an imido ligand which affords an oxo ligand and a carbodiimide molecule²³⁴.



Figure 5.8 Formation of Carbodiimides From the Interaction of Isocyanates with Imido Ligands

The process via which a third type of dimer [Mo₂(μ- $S_{2}(O)(NR)(S_{2}CNEt_{2})_{2}$] **4.12** are formed is uncertain. A few possible routes to these complexes have been proposed but have been shown by independent be possible. It has been reported¹⁶⁰ that the thermolysis of reactions to not $[MoO(S_2)(S_2CNEt_2)_2]$ 3.1 leads to the formation of $[Mo(\mu-S)(O)(S_2CNEt_2)]_2$ 3.2 in good yield. The latter could then be envisaged to undergo a reaction with an isocyanate affording 4.12. As was noted earlier, the presence of 3.1 in these reactions is unlikely, and further evidence against this route was supplied by the thermolysis of 3.2 in toluene with a number of isocyanates (R=Ph, 2,6-Me₂C₆H₃, ^tBu), none of which afforded the corresponding imido substituted complex upon workup.



Figure 5.9 Possible Routes to 4.12

А second route proposed was that thermolysis of [Mo(NR)(S₂)(S₂CNEt_s)₂] **2.2** could lead to formation of **4.12** in an analogous reaction to that undergone by 3.1. Prolonged thermolysis of 2.2 (R=Ph R'=Et **2.2a**, R=^tBu R'=Me **2.2h**') in toluene did not lead to any decomposition again discounting this as a possible route. A number of complexes have still to be investigated as possible precursors to 4.12. These are the bis(alkylimido) complexes 1.1, which although characterised could not be produced in sufficiently pure quantities to undergo thermolysis, and the complexes [MoO(NR)(S₂CNEt₂)₂] 2.3 which although are known (R=Ph, p-Tol R'=Et), eluded synthesis via the literature methods²⁰³. Both of these complexes could be envisaged to undergo dimerisation to give 4.12.

Experimental

6.1 General Experimental

All preparations were carried out under an atmosphere of dinitrogen using standard Schlenk line techniques unless otherwise stated. Nmr spectra were obtained using a Varian VXR400 and referenced to residual solvent peaks. ir spectra were obtained from KBr discs using a Nicolet 205 FT-IR. Microanalysis and Mass Spectra were performed in the Department of Chemistry UCL.

Solvents were freshly distilled from the following drying agents and degassed prior to use, dichloromethane (calcium hydride), petrols (Na/K alloy), tetrahydrofuran (potassium), toluene (sodium), diethyl ether (Na/K alloy), 1,2-dimethoxyethane (potassium), 1,2-dichloroethane (P_2O_5). column chromatography was performed using deactivated alumina (6% w/w water) and petrols (40:60).

The following compounds were bought from Aldrich and used as acquired, dimethylacetylenedicarboxylate, propylene sulphide. phenylisocyanate, phenylisothiocyanate, p-tolylisocyanate, o-tolylisocyanate, 2,6-dimethylphenylisocyanate, 2,6-dichlorophenylisocyanate 2,6diisopropylphenylisocyanate, allylisocyanate, *t*-butylisocyanate, adamantylisocyanate, isopropylisocyanate, dimethyldithiocarbamate sodium salt dihydrate, diethyldithiocarbamate sodium salt trihydrate, diethyldithiocarbamate ammonium salt, sodium molybdate(VI) dihydrate, sodium molybdate(VI), triphenylphosphine, trimethylsilylchloride, triethylamine, 2,6-dimethylaniline, 2,6-diisopropylaniline, 2,6-dichloroaniline, aniline, tbutylamine, tetrafluoroboric acid, trifluoroacetic acid, zinc dust, thiophenol, 3chloroperoxybenzoic acid.

Tables 6.1 and 6.2 contain analytical data for complexes for the complexes obtained from the thermolysis of **1.2** or **1.2**' with organic isocyantes.

6.2 Experimental for Chapter 2

$[Mo(O)_2(S_2CNEt_2)_2] 1.2^2$

 $NaS_2CNEt_2.3H_2O$ (15.93 g, 74.8 mmol) and $Na_2MoO_4.2H_2O$ (14.46 g, 66.0 mmol) were dissolved in water (300 ml). To this stirred solution was slowly added hydrochloric acid (315 ml, 0.6 M) causing precipitation of a brown solid. The precipitate was filtered and washed with water (2x100 ml). Recrystallization was achieved from benzene and petroleum spirit (30 g, 97%).

[Mo(O)₂(S₂CNMe₂)₂] 1.2²

A solution of $Na_2MoO_4.2H_2O$ (24.2 g, 0.10 mol) and $NaS_2CNMe_2.2H_2O$ (35.8 g, 0.20 mol) in water (300 ml) was prepared. On slow acidification of this solution with hydrochloric acid (315 ml, 1.2 M) a yellow precipitate formed. The precipitate was filtered and washed with water, and dried (36.4 g, 99%).

Reaction of [Mo(O)₂(S₂CNEt₂)₂] 1.2 with 2,6-Me₂C₆H₃NCO

 $[Mo(O)_2(S_2CNEt_2)_2]$ **1.2** (1.34 g, 3.16 mmol) was dissolved in toluene (100 ml). 2,6-Dimethylphenylisocyanate (0.50 ml, 3.42 mmol) was added via a degassed syringe. The resulting solution was refluxed for 1 day, after which time the volatiles were removed under reduced pressure. The resulting solid was absorbed onto alumina and passed down a chromatography column. A brown band $[Mo(2,6-Me_2C_6H_3N)_2(S_2CNEt_2)_2]$ **1.1d** (0.60 g, 26%) was obtained upon elution with 20% dichloromethane in petrols, and an orange band $[Mo_2(\mu-S)_2(O)(2,6-Me_2C_6H_3N)(S_2CNEt_2)_2]$ **4.12d** (0.10 g, 4%) was obtained upon elution with 25% dichloromethane in petrol. A further brown band $[Mo(2,6-Me_2C_6H_3N)(S_2CNEt_2)_2]$ **2.2d** (0.40 g, 22% (33% based on S)) was obtained after further elution with 40% dichloromethane in petrol. Crystals of **1.1d**, and **2.2d** were obtained by slow diffusion of methanol into a dichloromethane

solutions.

- **1.1d** ¹H nmr (CDCl₃, 313K); δ 6.90 (d, 4H, J 7.2, **m**-C₆H₃), 6.73 (t, 2H, J 7.2, p-C₆H₃), 3.83 (br, 8H, CH₂) 2.35 (s, 12H, CH₃C₆H₃), 1.28 (s, 12H, CH₂CH₃): ¹H nmr (CDCl₃, 213K); δ 6.90 (d, 4H, J 7.2, **m**-C₆H₃), 6.73 (t, 2H, J 7.2, p-C₆H₃), 3.96-4.05 (m, 2H, CH₂), 3.78-3.82 (m, 4H, CH₂), 3.60-3.69 (m, 2H, CH₂), 1.34 (s, 12H, CH₃C₆H₃), 1.26 (t, 6H, J 7.2, CH₂CH₃), 1.23 (t, 6H, J 7.2, CH₂CH₃): ir v/cm⁻¹; 1504s, 1457w, 1440w, 1426m, 1352m, 1274s, 1245w, 1149w, 1092w, 957w, 846w, 778w, 572w.
- 4.12d ¹H nmr (CDCl₃); δ 7.07 (t, 1H, J 7.3, p-C₆H₃), 6.96 (d, 2H, J 7.4, m--C₆H₃), 4.04-3,65 (m, 8H, CH₂), 2.51 (s, 6H, CH₃C₆H₃), 1.35 (t, 6H, J 7.2, CH₃CH₂), 1.23 (t, 6H, J 7.2, CH₃CH₂): ir υ/cm⁻¹ 1533m, 1516s, 1457m, 1438m, 1378w, 1335m, 1309m, 1278s, 1203m, 1148m, 972m, 764s, 756m, 668m.
- **2.2d** ¹H nmr (CDCl₃); δ 6.89 (t, 1H, J 7.8, p-C₆H₃), 6.81 (d, 2H, J 7.8, m-C₆H₃), 4.03-3.50 (m, 8H, CH₂), 2.49 (s, 6H, Me₂C₆H₃), 1.37 (t, 3H, J 7.2, CH₂*Me*), 1.37 (t, 3H, J 7.2, CH₂*Me*), 1.31 (t, 3H, J 7.2, CH₂*Me*), 1.15 (t, 3H, J 7.2, CH₂*Me*): ¹³C{¹H} (CDCl₃); δ 204.9 (S₂CN), 203.8 (S₂CN), 141.3, 127.7, 127.5 (C₆H₃), 45.5, 45.0, 44.6, 44.0 (CH₂), 19.4 (*C*H₃C₆H₃), 12.9, 12.7, 12.5, 12.1 (CH₂*C*H₃): ir v/cm⁻¹; 1504s, 1459m, 1434s, 1378w, 1355w, 1275s, 1209m, 1150m, 1094w, 1074w, 849w, 772w, 549w.

Reaction of [Mo(O)₂(S₂CNEt₂)₂] 1.2 with 2,6-Cl₂C₆H₃NCO

 $[Mo(O)_2(S_2CNEt_2)_2]$ **1.2** (0.90 g, 2.12 mmol) and 2,6dichlorophenylisocyanate (0.40 g, 2.14 mmol) were placed into a schlenk and degassed. Toluene (100 ml) was added and resulting solution was refluxed for 1 day, after which time volatiles were removed under reduced pressure. The resulting solid was absorbed onto alumina and passed down a chromatography column. A brown band $[Mo(2,6-Cl_2C_6H_3N)_2(S_2CNEt_2)_2]$ **1.1e** (0.22 g, 14%) was obtained after eluting with 20% dichloromethane in petrol. A further brown band $[Mo(2,6-Cl_2C_6H_3N)(S_2)(S_2CNEt_2)_2]$ **2.2e** (0.12 g, 9% (14% based on S)) was obtained upon elution with 40% dichloromethane in petrols. Crystals of **1.1e** and **2.2e** were obtained by slow diffusion of methanol into a dichloromethane solution.

- 1.1e ¹H nmr (CDCl₃); δ 7.12 (d, 4H, J 7.5, m-C₆H₃), 6.68 (t, 2H, J 7.2, p-C₆H₃), 3.82 (br, 8H, CH₂), 1.46 (br, 12H, CH₃): ir υ/cm⁻¹; 1508s, 1432s, 1311m, 1275m, 1205w, 1070w, 960m, 790m. Analysis Calculated for MoC₂₂H₂₆N₄S₄Cl₄ %Cl=19.72, Found %Cl=19.90.
- 2.2e ¹H nmr (CDCl₃); δ 7.09 (d, 2H, J 7.5, m-C₆H₃), 6.92 (t, 1H, J 7.5, p-C₆H₃), 4.02-3.47 (m, 8H, CH₂), 1.38 (t, 3H, J 7.3, CH₃), 1.36 (t, 3H, J 7.2, CH₃), 1.30 (t, 3H, J 7.2, CH₃), 1.13 (t, 3H, J 7.0, CH₃): ir υ/cm⁻¹; 1504s, 1458w, 1430s, 1411w, 1379w, 1351w, 1304w, 1273m, 1207m, 1195w, 1149m, 1072m, 969w, 850w, 794m, 775m, 723m, 548w. Analysis Calculated for MoC₁₆H₂₃N₃S₆Cl₂ %Cl=11.34, Found %Cl=11.91.

Reaction of $[Mo(O)_2(S_2CNEt_2)_2]$ 1.2 with 2,6-ⁱPr₂C₆H₃NCO (*)

 $[Mo(O)_2(S_2CNEt_2)_2]$ **1.2** (1.00 g, 2.36 mmol) was dissolved in toluene (100 ml). 2,6-diisopropylphenylisocyanate (1.00 ml, 4.92 mmol) was added via a degassed syringe. This solution was refluxed for 3 days, after which time volatiles were removed under reduced pressure. The resulting solid was absorbed onto alumina and passed down a chromatography column. A brown band was obtained upon elution with 20% dichloromethane in petrols, which was identified as $[Mo(2,6-{}^{i}Pr_2C_6H_3N)_2(S_2CNEt_2)_2]$ **1.1f** (0.53 g, 27% yield). A purple band $[Mo(2,6-{}^{i}Pr_2C_6H_3N)(S_2)(S_2CNEt_2)_2]$ **2.2f** (0.35 g, 24% (36% based on S)) was obtained after further elution with 40% dichloromethane in petrol. Crystals of **1.1f** and **2.2f** were obtained by slow diffusion of methanol into a dichloromethane solution.

1.1f ¹H nmr (C_7D_8 , 373K); δ 6.95 (d, 4H, J 7.6, m- C_6H_3), 6.80 (t, 2H, J 7.6, p- C_6H_3), 4.08 (septet, 4H, J 6.8, C*H*Me₂), 3.46 (q, 8H, J 7.0, C*H*Me₂),

1.19 (d, 24H, J 6.8, CH*Me*₂), 0.96 (t, 12H, J 7.0, CH₂*Me*): (C₇D₈, 253K); δ 6.96 (d, 4H, J 7.6, m-C₆H₃), 6.84 (t, 2H, J 7.6, p-C₆H₃), 4.17 (septet, 4H, J 6.8, C*H*Me₂), 3.47 (sextet, 2H, J 6.8, C*H*₂Me), 3.14 (m, 4H, C*H*₂Me), 2.93 (sextet, 2H, C*H*₂Me), 1.28 (d, 12H, J 6.8, CH*Me*₂), 1.16 (d, 12H, J 6.8, CH*Me*₂), 0.81 (t, 6H, J 6.8, CH₂*Me*), 0.74 (t, 6H, J 7.0, CH₂*Me*): ¹³C{¹H} nmr (CDCl₃, 253K); δ 201.4 (S₂CN), 153.8 (ipso-C₆H₃), 141.6 (o-C₆H₃), 124.0 (p-C₆H₃), 122.1 (m-C₆H₃), 46.0, 45.4 (CH₂), 28.1 (CH), 24.5, 23.6 ((*C*H₃)₂CH), 12.8, 12.1 (*C*H₃CH₂): ir v/cm⁻¹; 1267s, 1210m, 1149m, 1095w, 1075m, 962m, 847w, 755s.

2.2f ¹H nmr (CDCl₃); δ 7.06 (t, 1H , J 7.0, p-C₆H₃) 6.97 (d, 2H, J 7.3, o-C₆H₃), 3.49-4.01 (m, 10H ,CH₂,CH), 1.37 (t, 3H, J 7.2, CH₂CH₃), 1.36 (t, 3H, J 7.2, CH₂CH₃), 1.28 (t, 3H, J 7.1, CH₂CH₃), 1.20 (d, 12H, J 7.0, CH(CH₃)₂), 1.14 (t, 3H, J 7.2, CH₂CH₃): ir v/cm⁻¹; 1641s, 1553s, 1519m, 1248m, 744w, 669w, 419w.

Reaction of $[Mo(O)_2(S_2CNMe_2)_2]$ 1.2' with 2,6-ⁱPr₂C₆H₃NCO (*)

 $[Mo(O)_2(S_2CNMe_2)_2]$ **1.2'** (1.00 g, 2.72 mmol) was dissolved in toluene (100 ml). 2,6-Diisopropylphenylisocyanate (1.15 ml, 5.66 mmol) was added via a degassed syringe. This solution was refluxed for 3 days, after which time volatiles were removed at reduced pressure. The resulting solid was absorbed onto alumina and passed down a chromatography column. A brown band $[Mo(2,6-Pr_2C_6H_3N)_2(S_2CNMe_2)_2]$ **1.1f'** (0.62 g, 33% yield) was obtained by elution with 20% dichloromethane in petrols. A purple band $[Mo(2,6-Pr_2C_6H_3N)(S_2)(S_2CNMe_2)_2]$ **2.2f'** (0.18 g, 12% (17% based on S)) was obtained after further elution with 40% dichloromethane in petrol. Crystals of **1.1f'** and **2.2f'** were obtained by slow diffusion of methanol into a dichloromethane solution.

1.1f' ¹H nmr (C₇D₈, 253K); δ 6.94 (d, 4H, J 7.3, m-C₆H₃) 6.85 (t, 2H, J 7.3, p-C₆H₃), 4.20-4.11 (m, 4H, CH), 2.46 (s, 6H, NMe₂), 2.50 (s, 6H, NMe₂), 1.29 (d, 12H, J 7.0, CH*Me*₂), 1.25 (d, 12H, J 7.0, C*H*Me₂): ¹H nmr

 $(C_7D_8, 373K)$; δ 6.90 (d, 4H, J 7.3, m- C_6H_3), 6.85 (t, 2H, J 7.3, p- C_6H_3), 4.04 (sept, 4H, J 6.9, CH), 2.74 (s, 12H, NMe₂), 1.17 (d, 24H, J 6.9, CH*Me*₂): ir v/cm⁻¹; 1519s, 1511s, 1455m, 1389s, 1261s, 1146br, 987m, 955m, 757m.

2.2f' ¹H nmr (CDCl₃); δ 7.06 (t, 1H, J 7.1, p-C₆H₃), 6.97 (d, 2H, J 7.3, m-C₆H₃), 3.74 (sept, 2H, J 7.0, CH), 3.46 (s, 3H, CH₃N), 3.44 (s, 3H, CH₃N), 3.33 (s, 3H, CH₃N), 3.19 (s, 3H, CH₃N), 1.20 (d, 12H, J 6.9, (CH₃)₂CH): ir υ/cm⁻¹; 1542s, 1509s, 1457m, 1395s, 1254m, 1145m, 756m.

Reaction of [Mo(O)₂(S₂CNEt₂)₂] 1.2 with 2-MeC₆H₄NCO

[Mo(O)₂(S₂CNEt₂)₂] **1.2** (1.18 g, 2.78 mmol) was dissolved in toluene (100 ml). o-Tolylisocyanate (0.40 ml, 3.01 mmol) was added via a degassed syringe. The resulting solution was refluxed for 1 day, after which time volatiles were removed under reduced pressure. The resulting solid was absorbed onto alumina and passed down a chromatography column. A brown band began to move down the column upon elution with 20% dichloromethane in petrols. However rapidly quickly decomposed to give yellow and orange compounds. Elution with 40% dichloromethane in petrols gave a purple band identified as [Mo(2-MeC₆H₄N)(S₂)(S₂CNEt₂)₂] **2.2c** (0.32 g, 20% (30% based on S). Crystals of 2.2c were grown by slow diffusion of methanol into a dichloromethane solution. A similar reaction was carried out for 3 days using 1.2 (1.02 g, 2.40 mmol), o-tolylisocyanate (0.32 ml, 2.41 mmol) and toluene (100 ml). The products from this reaction were also purified by column chromatography. Elution with 25% dichloromethane in petrols afforded an orange band [Mo(μ -2- MeC_6H_4N)(2- MeC_6H_4N)(S₂CNEt₂)]₂ **4.6c** (0.38 g, 34%). Crystal were obtained by slow diffusion of methanol into a dichloromethane solution. Elution with 40% dichloromethane in petrols gave a purple band identified as [Mo(2- $MeC_{6}H_{4}N(S_{2})(S_{2}CNEt_{2})_{2}$] **2.2c** (0.32 g, 24%).

2.2c ¹H nmr (CDCl₃); δ 7.35-7.33 (m, 1H, C₆H₄), 7.03-6.98 (m, 3H, C₆H₄),

3.97-3.51 (m, 8H, CH_2), 1.37 (t, 3H, J 7.2, CH_3), 1.35 (t, 3H, J 7.2, CH_3), 1.32 (t, 3H, J 7.2, CH_3), 1.15 (t, 3H, J 7.0, CH_3): ir υ/cm^{-1} ; 1527s, 1505s, 1433s, 1380w, 1354m, 1298m, 1273s, 1207m, 1149m, 1115w, 1096w, 1078m, 1001w, 849m, 763m, 548m.

4.6c ¹H nmr (CDCl₃, 233K); δ 7.26 (br, 4H, C₆H₄), 7.00 (br, 2H, C₆H₄), 6.90 (br, 2H, C₆H₄), 6.82 (br, 2H, C₆H₄), 6.71, br, 2H, C₆H₄), 6.55 (br, 4H, C₆H₄), 3.80 (br, 8H, CH₂), 2.34 (br, s, 6H, CH₃C₆H₄), 2.10 (br, 6H, CH₃C₆H₄), 1.29, (br, t, 12H, CH₂CH₃): ¹H nmr (CDCl₃, 313K); δ 6.41-6.46 (m, 2H, C₆H₄), 6.52-6.77 (m, 8H, C₆H₄), 6.92, (t, 2H, J 7.5, C₆H₄), 7.07 (t, 2H, J 7.5, C₆H₄), 7.22 (t, 2H, J 7.4, C₆H₄), 3.56-3.85 (m, 8H, CH₂), 2.33 (s, 3.1H, CH₃C₆H₄), 2.30 (s, 2.2H, CH₃C₆H₄), 2.27 (s, 1.6H, CH₃C₆H₄), 2.22 (s, 3.7H, CH₃C₆H₄), 2.14 (s, 1.4H, CH₃C₆H₄), 1.21 (t, 12H, J 7.3, CH₂CH₃): ir v/cm⁻¹; 1515s, 1472m, 1455m, 1437m, 1321m, 1272s, 1263s, 1204w, 1150w, 1113w, 1076w, 992w, 756s, 718w. Analysis calculated for Mo₂C₃₈H₄₈S₄N₆ %C=50.21, %H=5.32, %N=9.12, %S=14.11. Found %C=49.74, %H=5.23, %N=9.12, %S=14.22.

[MoCl₂(NPh)₂(DME)] 2.1a⁶⁵

To a stirred slurry of 1,2-dimethoxyethane (100 ml) and Na_2MoO_4 (5.00 added triethylamine (14.0 ml, 147 g, 24 mmol) was mmol), trimethylsilylchloride (35.0 ml, 322 mmol) and aniline (5.0 ml, 58 mmol). The resulting slurry was heated overnight at 70°C during which time a colour change from white to yellow to red was observed. The slurry was allowed to cool and filtered, the residue was washed with diethylether (3x100 ml) and the washings combined with the original filtrate. The volatiles were removed at reduced pressure to yield pure red [MoCl₂(NPh)₂(DME)] 2.1a (5.00 g, 47% yield).

$[Mo(NPh)_2(S_2CNEt_2)_2]$ 1.1a

 $[MoCl_2(NPh)_2(DME)]$ **2.1a** (0.51 g, 1.16 mmol) and $[NH_4][S_2CNEt_2]$ (0.40 g, 2.41 mmol) were placed in a schlenk. To this was added diethylether (100 ml) and the resultant solution stirred for 12 hours, during which time a colour change from red to brown was observed along with deposition of a brown solid. The solution was filtered leaving a brown solid, the ¹H nmr spectra of this solid showed the presence of signals assignable to phenyl rings and diethyldithiocarbamate ligands. Attempts to recrystallise this solid from dichloromethane or toluene met with failure.

¹H nmr (CDCl₃, 233K); δ 7.69 (d, 4H, J 7.3, o-C₆H₅), 7.16 (t, 4H, J 7.5, m-C₆H₅), 6.76 (t, 2H, J 7.3, p-C₆H₅), 3.05-3.89 (m, 8H, CH₂), 1.20-1.43 (m, 12H, CH₃), impurities 7.41 (m, 1H), 7.35 (m, 0.8H), 4.18 (m, 1.2H), 1.15 (t, 0.5H), 1.11 (t, 0.6H)

[MoCl₂(2,6-Me₂C₆H₃N)₂(DME)] 2.1d⁶⁵

To a stirred slurry of 1,2-dimethoxyethane (100 ml) and Na₂MoO₄ (5.00 added triethylamine (14.0 ml, 147 g, 24 mmol) was mmol), trimethylsilylchloride (35.0 ml, 322 mmol) and 2,6-dimethylaniline (0.50 ml, 53 mmol). The resulting slurry was heated overnight at 70°C during which time a colour change from white to yellow to red was observed. The slurry was allowed to cool and filtered, the residue was washed with diethylether (3x100 ml) and the washings combined with the original filtrate. The volatiles were removed at reduced pressure to yield a highly pure red solid [MoCl₂(2,6-Me₂C₆H₃N)₂(DME)] **2.1d** (5.50 g, 46% yield).

$[Mo(2,6-Me_2C_6H_3N)_2(S_2CNEt_2)_2]$ 1.1d

 $[MoCl_2(2,6-Me_2C_6H_3N)_2(DME)] \ \textbf{2.1d} (0.55 \ \text{g}, \ 1.11 \ \text{mmol}) \text{ and} \\ [NH_4][S_2CNEt_2] (0.50 \ \text{g}, \ 2.40 \ \text{mmol}) \text{ were placed in a schlenk. To this was}$

added diethylether (100 ml) and the resultant solution stirred for 12 hours. Volatiles were removed at reduced pressure, and the resulting solid absorbed onto alumina and placed onto a column. Elution with 30% dichloromethane in petrols gave a brown band which was identified as [Mo(2,6-Me₂C₆H₃N)₂(S₂CNEt₂)₂] **1.1d**. Yield (0.60 g, 85%).

[MoCl₂(2,6-Cl₂C₆H₄N)₂(DME)] 2.1e⁶⁵

To a stirred slurry of 1,2-dimethoxyethane (100 ml) and Na₂MoO₄ (1.00 g, 4.8 mmol) was added triethylamine (2.7 ml, 28 mmol), trimethylsilylchloride (6.8 ml, 62.6 mmol). To this was added a 1,2-dimethoxyethane (20 ml) solution of 2,6-dichloroaniline (1.57 g, 9.7 mmol). The resulting slurry was heated overnight at 70°C during which time a colour change from white to yellow to red was observed. The slurry was allowed to cool and filtered, the residue was washed with diethylether (3x100 ml) and the washings combined with the original filtrate. The volatiles were removed at reduced pressure to yield pure red [MoCl₂(2,6-Cl₂C₆H₃N)₂(DME)] **2.1e** (2.4 g, 85% yield).

$[Mo(2,6-Cl_2C_6H_3N)_2(S_2CNEt_2)_2]$ 1.1e

 $[MoCl_2(2,6-Cl_2C_6H_3N)_2(DME)]$ **2.1e** (0.52 g, 0.90 mmol) and $[NH_4][S_2CNEt_2]$ (0.30 g, 1.8 mmol) were placed in a schlenk. To this was added diethylether (100 ml) and the resultant solution stirred for 12 hours. Volatiles were removed at reduced pressure, and the resulting solid absorbed onto alumina and placed onto a column. Elution with 30% dichloromethane in petrols gave a brown band which was identified as $[Mo(2,6-Cl_2C_6H_3N)_2(S_2CNEt_2)_2]$ **1.1e**. Yield (0.38 g, 59%).

[MoCl₂(2,6-ⁱPr₂C₆H₃N)₂(DME)] 2.1f⁶⁵

To a stirred slurry of 1,2-dimethoxyethane (100 ml) and Na_2MoO_4 (1.00

g, 4.8 mmol) was added triethylamine (2.7 ml, 28 mmol), trimethylsilylchloride (6.8 ml, 62.6 mmol) and 2,6-diisopropylaniline (1.8 ml, 10 mmol). The resulting slurry was heated overnight at 70°C during which time a colour change from white to yellow to red was observed. The slurry was allowed to cool and filtered. The residue was washed with diethylether (3x100 ml) and the washings combined with the original filtrate. The volatiles were removed at reduced pressure to yield pure red [MoCl₂(2,6-ⁱPr₂C₆H₃N)₂(DME)] **2.1f** (3.00 g, 95% yield).

$[Mo(2,6-{}^{i}Pr_{2}C_{6}H_{3}N)_{2}(S_{2}CNEt_{2})_{2}]$ 1.1f

 $[Mo(2,6-{}^{i}Pr_{2}C_{6}H_{3}N)_{2}CI_{2}(DME)]$ **2.1f** (0.60 g, 0.99 mmol) and $[NH_{4}][S_{2}CNEt_{2}]$ (0.55 g, 3.3 mmol) were placed in a schlenk. To this was added diethylether (100 ml) and the resultant solution stirred for 12 hours. Volatiles were removed and the resulting solid absorbed onto alumina and placed onto a column. Elution with 30% dichloromethane in petrols gave a brown band which was identified as $[Mo(2,6-{}^{i}Pr_{2}C_{6}H_{3}N)_{2}(S_{2}CNEt_{2})_{2}]$ **1.1f**. Yield (0.62 g, 85%).

[MoCl₂(N^tBu)₂(DME)] 2.1h⁶⁵

To a stirred slurry of 1,2-dimethoxyethane (100 ml) and Na₂MoO₄ (1.96 g, 1.96 mmol) was added triethylamine (6.0 ml, 63 mmol), trimethylsilylchloride (15.0 ml, 138 mmol) and *t*-butylamine (1.42 ml, 19 mmol). The resulting slurry was heated overnight at 70°C during which time a colour change from white to yellow was observed. The slurry was allowed to cool and filtered, the residue was washed with diethylether (3x100 ml) and the washings combined with the original filtrate. Volatiles were removed under reduced pressure to yield a viscous yellow liquid. This was washed with petrol (2x50 ml) yielding a yellow solid [MoCl₂(N^tBu)₂(DME)] **2.1h** (3.50 g, 92% yield).

.

$[Mo(^{t}BuN)_{2}(S_{2}CNEt_{2})_{2}]$ 1.1h

 $[MoCl_2(N^tBu)_2(DME)]$ **2.1h** (0.70 g, 1.94 mmol) and $[NH_4][S_2CNEt_2]$ (0.70 g, 4.22 mmol) were placed in a schlenk. To this was added diethylether (100 ml) and the resultant solution stirred for 12 hours, during which time a colour change from yellow to orange was observed. The solution was then filtered and reduced in volume to 30 ml. Upon refrigeration of this solution overnight a fine orange precipitate was deposited $[Mo(N^tBu)_2(S_2CNEt_2)_2]$ **1.1h**. (0.10 g, 11%). The precipitate was filtered and dried under vacuum.

1.1h ¹H nmr (CDCl₃); δ 3.80 (q, 8H, J 7.2, CH₂), 1.37 (s, 18H, C(CH₃)₃), 1.23 (t, 12H, J 7.2, CH₂CH₃): ir υ/cm⁻¹; 1496s, 1459m, 1449m, 1353m, 1263s, 1246m, 1201s, 1137m, 1094m, 1075m, 1066m, 1019m, 914w, 843w, 799m: Analysis calculated for MoC₁₈H₃₈S₄N₄ %C=40.43, %H=7.16, %N=10.48, %S=23.98. Found %C=41.22, %H=6.50, %N=9.98, %S=22.81.

Thermolysis of $[Mo(2,6-Me_2C_6H_3N)_2(S_2CNEt_2)_2]$ 1.1d

 $[Mo(2,6-Me_2C_6H_3N)_2(S_2CNEt_2)_2]$ **1.1d** (0.15 g, 0.24 mmol) was dissolved in toluene (100 ml) and refluxed for 18 hours. The resultant solution was cooled and the volatiles removed, leaving a black residue. This was absorbed onto alumina and passed down a chromatography column. Elution with 20% dichloromethane in petrols gave a brown band, identified as **1.1d** (0.07 g ,50%). Further elution with 40% dichloromethane in petrols gave a brown band identified as **2.2d** (0.04 g 29% (44% based on S)).

Thermolysis of $[Mo(2,6-Pr_2C_6H_3N)_2(S_2CNEt_2)_2]$ 1.1f (*)

 $[Mo(2,6-{}^{i}Pr_{2}C_{6}H_{3}N)_{2}(S_{2}CNEt_{2})_{2}]$ **1.1f** (0.10 g, 0.13 mmol) was dissolved in toluene (100 ml) and refluxed for 18 hours. The resultant solution was cooled and the volatiles removed, leaving a black residue. This was absorbed onto alumina and passed down a chromatography column. Elution with 20% dichloromethane in petrols gave a brown band, identified as **1.1f** (0.10 g, 100%).

Reaction of $[Mo(2,6-Pr_2C_6H_3N)_2(S_2CNEt_2)_2]$ 1.1f with Mel (*)

 $[Mo(2,6-{}^{i}Pr_{2}C_{6}H_{3}N)_{2}(S_{2}CNEt_{2})_{2}]$ **1.1f** (0.10 g, 0.13 mmol) was dissolved in toluene (100 ml). To this solution was added via a degassed syringe methyliodide (0.02 ml, 0.13 mmol). The resultant solution was cooled and the volatiles removed, leaving a black residue. This was absorbed onto alumina and passed down a chromatography column. Elution with 20% dichloromethane in petrols gave a brown band, identified as **1.1f**.

Reaction of $[Mo(2,6-Pr_2C_6H_3N)_2(S_2CNEt_2)_2]$ 1.1f with DMAD (*)

 $[Mo(2,6-{}^{i}Pr_{2}C_{6}H_{3}N)_{2}(S_{2}CNEt_{2})_{2}]$ **1.1f** (0.10 g, 0.13 mmol) was dissolved in toluene (100 ml). To this solution was added via a degassed syringe DMAD (0.02 g, 0.13 mmol). The resultant solution was cooled and the volatiles removed, leaving a black residue. This was absorbed onto alumina and passed down a chromatography column. Elution with 20% dichloromethane in petrols gave a brown band, identified as **1.1f**.

6.3 Experimental for Chapter 3

Reaction of [Mo(O)₂(S₂CNEt₂)₂] 1.2 with 1 Equivalent of PhNCO

 $[Mo(O)_2(S_2CNEt_2)_2]$ **1.2** (1.13 g, 2.66 mmol) was dissolved in toluene (100 ml). Phenylisocyanate (0.25 ml, 2.66 mmol) was added via a degassed syringe. The solution was refluxed for 3 days, after which time volatiles were removed under reduced pressure. The resulting solid was absorbed onto alumina and passed down a chromatography column. A yellow band, identified

as $(Et_2NCSS)_2$ by comparison of its ir with that of an authentic sample, was obtained after elution with 20% dichloromethane in petrols. A purple band $[Mo(NPh)(S_2)(S_2CNEt_2)_2]$ **2.2a** (0.33 g, 23% (34% based on S)) was obtained after eluting with 40% dichloromethane in petrol. Upon further elution with 90% dichloromethane in petrols a yellow complex $[Mo(\mu-NPh)(O)(S_2CNEt_2)_2]$ **4.5a** (0.74 g, 76%) was obtained. Crystals of **2.2a** and **4.5a** were obtained by slow diffusion of methanol into a dichloromethane solution.

- 2.2a ¹H nmr (CDCl₃); δ 7.44 (t, 2H, J 7.2, m-C₆H₅), 7.20 (d, 2H, J 7.1, o-C₆H₅), 7.15 (t, 1H, J 7.2, p-C₆H₅), 4.07-3.52 (m, 8H, CH₂), 1.37 (t, 3H, J 7.1, Me), 1.35 (t, 3H, J 7.1, Me), 1.31 (t, 3H, J 7.2, Me), 1.14 (t, 3H, J 7.2, Me): ¹³C{¹H} nmr (CDCl₃); δ 204.6 203.6 (S₂CN), 154.2 (ipso-C₆H₅), 128.3 (C₆H₅), 127.6 (p-C₆H₅), 126.9 (C₆H₅), 45.6, 45.1, 44.6, 44.0 (CH₂), 12.8, 12.6, 12.4, 12.1 (CH₃): ir υ/cm⁻¹; 1522s, 1497s, 1456m, 1435s, 1275s, 1206w, 1146m, 1092w, 1072m, 759m, 682m, 669m, 653m, 522w.
- 4.5a ¹H nmr (CDCl₃); δ 7.43 (t, 4H, J 7.1, m-C₆H₅), 7.31 (d, 4H, J 7.0, o-C₆H₅), 7.17 (t, 2H, J 7.1 p-C₆H₅), 3.86 (q, 8H, J 7.0, CH₂), 1.30 (t, 12H, J 7.0, Me): ir υ/cm⁻¹; 1585m, 1524vs, 1476s, 1457s, 1439s, 1381w, 1356w, 1278s, 1202m, 1151m, 1075m, 948s, 932s, 768m, 695m.

R	R'	%C	%Н	%N	%S
Ph	Et	34.61 (35.09)	4.58 (4.60)	7.53 (7.67)	33.93 (35.12)
p-tolyl	Et	36.47 (36.34)	5.11 (4.84)	7.26 (7.47)	32.67 (33.41)
o-tolyl	Et	36.23 (36.34)	4.64 (4.84)	7.30 (7.47)	32.29 (33.41)
2,6-Cl ₂ C ₆ H ₃	Et	31.27 (31.34)	3.42 (3.76)	6.70 (6.81)	30.71 (31.10)
2,6-Me ₂ C ₆ H ₃	Et	37.31 (37.55)	5.49 (5.07)	7.15 (7.29)	32.67 (33.41)
2,6- ⁱ Pr ₂ C ₆ H ₃	Et	41.80 (41.84)	6.14 (5.86)	6.50 (6.66)	30.32 (30.43)
'Ви	Et	31.44 (31.56)	5.17 (5.54)	7.75 (7.96)	35.52 (36.46)
Adamantyl	Et	39.49 (39.65)	5.72 (5.82)	6.72 (6.93)	31.36 (31.76)
Ph	Me	28.82 (29.31)	3.47 (3.49)	8.18 (8.54)	38.00 (39.14)
2,6- ⁱ Pr ₂ C ₆ H ₃	Me	37.43 (37.55)	4.90 (5.08)	7.07 (7.30)	32.85 (33.41)
'Bu	Me	25.26 (25.47)	4.28 (4.49)	8.51 (8.91)	40.61 (40.79)

Table 6.1 Analytical Data for Mo(S₂)(NR)(S₂CNR')₂: Calculated Figures in Parenthesis

Reaction of [Mo(O)₂(S₂CNEt₂)₂] 1.2 with 4-MeC₆H₄NCO

 $[Mo(O)_2(S_2CNEt_2)_2]$ **1.2** (0.58 g, 1.36 mmol) was dissolved in toluene (100 ml). p-Tolylisocyanate (0.19 ml, 1.42 mmol) was added via a degassed syringe. The resulting solution was refluxed for 3 days, after which time volatiles were removed under reduced pressure. The resulting solid was absorbed onto alumina and passed down a chromatography column. A purple band $[Mo(4-MeC_6H_4N)(S_2)(S_2CNEt_2)_2]$ **2.2b** (0.18 g, 24% (36% based on S)) was obtained after eluting with 40% dichloromethane in petrol. Further elution with 5% methanol in dichloromethane gave a yellow band identified as $[Mo(\mu-4-MeC_6H_4N)(O)(S_2CNEt_2)]_2$ **4.5b** (0.50 g, 50%). Crystals of **2.2b** and **4.5b** were obtained by slow diffusion of methanol into a dichloromethane solution.

2.2b ¹H nmr (CDCl₃); δ 7.14 (d, 2H, J 8.2, C₆H₄),6.98 (d, 2H, J 8.2, C₆H₄), 3.96-3.50 (m, 8H, CH₂), 2.30 (s, 3H, CH₃C₆H₄), 1.37 (t, 3H, J 7.3, CH₂CH₃), 1.35 (t, 3H, J 7.4, CH₂CH₃), 1.33 (t, 3H, J 7.1, CH₂CH₃), 1.15 (t, 3H, J 7.0, CH₂CH₃): ¹³C{¹H} nmr (CDCl₃); δ 204.7, 203.7 (S₂CN), 138.3, 128.9, 126.9 (C₆H₄), 45.6, 45.1, 44.6, 43.9 (CH₂), 21.64 (CH₃C₆H₄), 12.8, 12.6, 12.4, 12.1 (CH₂CH₃): ir v/cm⁻¹; 1522s, 1499s, 1456m, 1436m, 1355m, 1297w, 1276s, 1208m, 1148m, 1091w, 1070w, 818m, 552w.

4.5b ¹H nmr (CDCl₃); δ 7.37 (s, 4H, C₆H₄), 3.86 (q, 8H, J 7.3, CH₂), 2.43 (s, 6H, C₆H₄CH₃), 1.30 (t, 12H, J 7.3, CH₂CH₃): ir υ/cm⁻¹; 1522s, 1497s, 1458m, 1440m, 1380w, 1357w, 1277s, 1203m, 1151w, 1096w, 1077w, 946s, 930m, 826m.

Table 6.2 Analytical Data for Products from the Reaction of $[Mo(O)_2(S_2CNR'_2)_2]$ with RNCO. Calculated Figures in Parenthesis

	R	R'	Compound	%Н	%N	%S
[Mo(µ-NR)(O)(S₂CNR')]₂	Ph	Et	37.63 (37.61)	4.24 (4.30)	7.83 (7.97)	17.51 (18.25)
	Ph	Me	32.37 (33.44)	3.32 (3.43)	8.40 (8.67)	20.90 (19.84)
	pTolyl	Et	39.84 (39.45)	4.46 (4.69)	7.54 (7.67)	17.01 (17.55)
[Mo(NR) ₂ (S ₂ CNR') ₂]	2,6- ⁱ Pr ₂ C ₆ H ₃	Et	54.54 (54.96)	7.32 (7.32)	7.31 (7.54)	17.50 (17.26)
	2,6- ^I Pr ₂ C ₆ H ₃	Me	52.28 (52.46)	6.72 (6.75)	7.99 (8.16)	18.80 (18.67)
	2,6-Me ₂ C ₆ H ₃	Et	49.37 (49.36)	5.63 (6.06)	8.68 (8.86)	20.14 (20.23)
	2,6-Cl ₂ C ₆ H ₃	Et	37.48 (37.08)	3.94 (3.68)	7.63 (7.87)	18.07 (17.96)
$[Mo_2(\mu-S)_2(O)(NR)(S_2CNR')_2]$	^t Bu	Et	26.30 (26.29)	4.42 (4.57)	6.49 (6.57)	29.49 (30.07)
	'Bu	Me	20.34 (20.58)	3.68 (3.63)	6.96 (7.20)	31.97 (32.96)
	Adm	Et	32.92 (33.47)	4.80 (4.91)	5.76 (5.85)	26.75 (26.80)

Reaction of [Mo(O)₂(S₂CNEt₂)₂] 1.2 with ^tBuNCO

 $[Mo(O)_2(S_2CNEt_2)_2]$ **1.2** (4.01 g, 9.45 mmol) was dissolved in toluene (100 ml). *t*-Butylisocyanate (1.0 ml, 10.1 mmol) was added via a degassed syringe. The solution was refluxed for 3 days, after which time volatiles were removed at reduced pressure. The resulting solid was absorbed onto alumina and passed down a chromatography column. A red band was obtained after eluting with 40% dichloromethane in petrol. Crystals of a yellow compound $[Mo_2(\mu-S)_2(O)(N^tBu)(S_2CNEt_2)_2]$ **4.12h** (0.60 g, 10%) and a red compound $[Mo(N^tBu)(S_2)(S_2CNEt_2)_2]$ **2.2h** (0.90 g, 18% (27% based on S)) were obtained upon slow diffusion of methanol into a dichloromethane solution.

- 2.2h ¹H nmr (CDCl₃); δ 3.91-3.49 (m, 8H, CH₂), 1.34 (t, 3H, J 7.2, CH₃CH₂),
 1.20 (s, 9H, C(CH₃)₃), 1.31 (t, 6H, J 7.2, CH₃CH₂), 1.09 (t, 3H, J 7.2, CH₃CH₂): ir υ/cm⁻¹; 1509br, 1436m, 1355w, 1275m, 1227m, 1148w, 1072w.
- 4.12h ¹H nmr (CDCl₃); δ 4.00-3.94 (m, 8H, CH₂), 1.40 (t, 6H, J 7.2, CH₃CH₂), 1.37, (t, 6H, J 7.1, CH₃CH₂), 1.02 (s, 9H, C(CH₃)₃): ir υ/cm⁻¹; 1528br, 1457m, 1439s, 1379w, 1356m, 1301w, 1281s, 1222s, 1206s, 1154m, 1095w, 1076m, 957s, 848m.

Reaction of [Mo(O)₂(S₂CNEt₂)₂] 1.2 with AdmNCO

 $[Mo(O)_2(S_2CNEt_2)_2]$ **1.2** (0.56 g, 1.32 mmol) and adamantylisocyanate (0.22 g, 1.33 mmol) were dissolved in toluene (100 ml). The resulting solution was refluxed for 3 days, after which time volatiles were removed under reduced pressure The resulting solid was absorbed onto alumina and passed down a chromatography column. A red band was obtained after eluting with 40% dichloromethane in petrol. Crystals of a yellow compound $[Mo_2(\mu-S)_2(O)(NAdm)(S_2CNEt_2)_2]$ **4.12i** (0.15 g, 32%) and a red compound $[Mo(NAdm)(S_2)(S_2CNEt_2)_2]$ **2.2i** (0.24 g, 31% (46% based on S)) were obtained by slow diffusion of methanol into a dichloromethane solution of the band.
- ¹H nmr (CDCl₃); δ 3.95-3.49 (m, 8H, CH₂), 1.97 (br s, 3H, Adm), 1.90 (br s, 6H, Adm), 1.58 (br, 6H, Adm), 1.34 (t, 9H, J 7.2, CH₃), 1.12 (t, 3H, J 7.2 CH₃): ir υ/cm⁻¹; 1500s, 1457w, 1429m, 1378w, 1354w, 1301w, 1275m, 1230w, 1209m, 1149m, 1094w, 1075w, 999br, 848w, 552w.
- 4.12i ¹H nmr (CDCl₃); δ 4.06-3.86 (m, 8H, CH₂), 1.87 (br s, 3H, Adm), 1.61 (br s, 6H, Adm), 1.56 (s, 6H, Adm), 1.40 (t, 6H, J 7.2, CH₃), 1.36 (t, 6H, J 7.2, CH₃): ir υ/cm⁻¹; 1531s, 1502s, 1452m, 1438m, 1357m, 1298w, 1280s, 1229m, 1204m, 1148w, 1095w, 1087w, 1075w, 953s, 845w, 482w.

Reaction of [Mo(O)₂(S₂CNMe₂)₂] 1.2' with PhNCO (*)

 $[Mo(O)_2(S_2CNMe_2)_2]$ **1.2'** (1.00 g, 2.72 mmol) was dissolved in toluene (100 ml). Phenylisocyanate (0.33 ml, 2.77 mmol) was added via a degassed syringe. The solution was refluxed for 3 days, after which time volatiles were removed under reduced pressure. The resulting solid was absorbed onto alumina and passed down a chromatography column. A purple band $[Mo(NPh)(S_2)(S_2CNMe_2)_2]$ **2.2a'** (0.27 g, 21% (32% based on S)) was obtained after eluting with 40% dichloromethane in petrol. A yellow band $[Mo(\mu NPh)(O)(S_2CNMe_2)]_2$ **4.5a'** (0.43 g, 49%) was obtained upon elution with 1% methanol in dichloromethane. Crystals of **2.2a'** and **4.5a'** were obtained by slow diffusion of methanol into a dichloromethane solution.

- 2.2a' ¹H nmr (CDCl₃); δ 7.30-7.15 (m, 5H, Ph), 3.47 (s, 3H, Me), 3.44 (s, 3H, Me), 3.39 (s, 3H, Me), 3.18 (s, 3H, Me): ¹³C{¹H} nmr (CDCl₃); δ 205.0, 206.1 (S₂CN) 127.2, 127.9, 128.4, 154.5 (Ph) 40.8, 40.5, 39.2, 38.6 (Me): ir υ/cm⁻¹; 1536s, 1467m, 1392s, 1314m, 1252m, 1149s, 1060w, 934m, 754m.
- 4.5a' ¹H nmr (CDCl₃); δ 7.40 (t, 4H, J 7.5, o-C₆H₅), 7.31 (d, 4H, J 7.5, m-C₆H₅), 7.17 (t, 2H, J 7.3, p-C₆H₅), 3.46 (s, 12H, Me): ir υ/cm⁻¹; 1555s, 1478m, 1444w, 1401s, 1261m, 1158m, 945s, 766m, 694m.

Reaction of $[Mo(O)_2(S_2CNMe_2)_2]$ 1.2' with 'BuNCO (*)

 $[Mo(O)_2(S_2CNMe_2)_2]$ **1.2'** (1.00 g, 2.72 mmol) was dissolved in toluene (100 ml). *t*-Butylisocyanate (0.31 ml, 3.10 mmol) was added via a degassed syringe. The solution was refluxed for 3 days, after which time volatiles were removed at reduced pressure. The resulting solid was absorbed onto alumina and passed down a chromatography column. A red band was obtained after eluting with 40% dichloromethane in petrol. Crystals of a red complex $[Mo({}^{t}BuN)(S_2)(S_2CNMe_2)_2]$ **2.2h'** (0.18 g, 15% (23% based on S)) and a yellow complex $[Mo_2(\mu-S)_2(O)(N{}^{t}Bu)(S_2CNMe_2)_2]$ **4.12h'** (0.41 g, 50%) were obtained by slow diffusion of methanol into a dichloromethane solution.

- 2.2h' ¹H nmr (CDCl₃); δ 3.46 (s, 3H, NMe), 3.42 (s, 3H, NMe), 3.40 (s, 3H, NMe), 3.16 (s, 3H, NMe), 1.27 (s, 9H, CMe₃): ir υ/cm⁻¹; 1539s, 1523s, 1469m, 1445m, 1390s, 1250m, 1221s, 1147s, 1048m, 987m, 577w, 569w, 550m, 445w.
- **4.12h**^{'1}H nmr (CDCl₃); δ 3.58 (s, 6H, NMe₂), 3.53 (s, 6H, NMe₂), 1.02 (s, 9H, CMe₃): ir υ/cm⁻¹; 1550s, 1540s, 1396s, 1358w, 1219s, 1146m, 949s.

Reaction of [Mo(O)₂(S₂CNEt₂)₂] 1.2 with AllyINCO (*)

 $[Mo(O)_2(S_2CNEt_2)_2]$ **1.2** (1.00 g, 2.4 mmol) was dissolved in toluene (100 ml). Allylisocyanate (0.21 ml, 2.4 mmol) was added via a degassed syringe. The solution was refluxed for 3 days, after which time volatiles were removed under reduced pressure. The resulting solid was absorbed onto alumina and passed down a chromatography column. A red band began to elute down the column with 40% dichloromethane in petrol. However extensive decomposition was observed for this and the other products of this reaction. Attempts at obtaining crystalline samples of the products of this reaction were unsuccessful.

Reaction of [Mo(O)₂(S₂CNEt₂)₂] 1.2 with ⁱPrNCO (*)

 $[Mo(O)_2(S_2CNEt_2)_2]$ **1.2** (1.00 g, 2.4 mmol) was dissolved in toluene (100 ml). *i*-Propylisocyanate (0.20 ml, 2.4 mmol) was added vis a degassed syringe. The solution was refluxed for 3 days, after which time volatiles were removed under reduced pressure, The resulting solid was absorbed onto alumina and passed down a chromatography column. A red band began to elute down the column with 40% dichloromethane in petrol. However, extensive decomposition was observed for this and the other products from this reaction.

[MoO(S₂)(S₂CNEt₂)₂] 3.1¹⁶⁰

 $[Mo(O)_2(S_2CNEt_2)_2]$ **1.2** (2.22 g, 5.23 mmol) was dissolved in dichloromethane (50 ml). To this stirred solution was added triphenylphosphine (1.37 g, 5.23 mmol), the resulting solution, was then refluxed for 3 hours to give a red solution of $[MoO(S_2CNEt_2)_2]$. After cooling propylene sulphide (1.27 ml, 17 mmol) was added and the solution stirred for a further hour to give a blue/green solution. Volatiles were removed under reduced pressure to yield a blue solid $[MoO(S_2)(S_2CNEt_2)_2]$ **3.1** (2.07 g, 90%), which was recrystallized from a solution of dichloromethane and methanol.

Reaction of [MoO(S₂)(S₂CNEt₂)₂] 3.1 and PhNCO

To a solution of $[MoO(S_2)(S_2CNEt_2)_2]$ **3.1** (0.19 g, 0.41 mol) in toluene (50 ml) was added via a degassed syringe phenylisocyanate (0.05 ml, 0.42 mmol). The resulting solution was refluxed for 20 hours. Volatiles were removed at reduced pressure and the products purified by chromatography. Elution with 40% dichloromethane in petrols yielded $[Mo(NPh)(S_2)(S_2CNEt_2)_2]$ **2.2a** (0.20 g, 90%) identified by comparison of ir and nmr spectra with an authentic sample. Upon further elution with 90% dichloromethane in petrols afforded a yellow band identified as $[Mo(\mu-S)(O)(S_2CNEt_2)]_2$ **3.2** (0.01 g, 9%) by comparison of ir and nmr spectra with the literature²¹⁷.

Reaction of [MoO(S₂)(S₂CNEt₂)₂] 3.1 and ^tBuNCO

To a solution of $[MoO(S_2)(S_2CNEt_2)_2]$ **3.1** (0.52 g, 1.10 mol) in toluene (100 ml) was added via a degassed syringe *t*-butylisocyanate (0.11 ml, 1.11 mmol). The resulting solution was refluxed for 20 hours, after which time volatiles were removed at reduced pressure, The remaining solid purified by chromatography. Elution with 90% dichloromethane in petrols afforded a yellow band identified as $[Mo(\mu-S)(O)(S_2CNEt_2)]_2$ **3.2** by comparison of ir and nmr spectra with the literature²¹⁷.

Thermolysis of [Mo(NPh)(S₂)(S₂CNEt₂)₂] 2.2a

A toluene (50 ml) solution of $[Mo(NPh)(S_2)(S_2CNMe_2)_2]$ **2.2a** (0.20 g, 0.36 mmol) was refluxed for 18 hours. After which time volatiles were removed under reduced pressure affording a purple solid. ¹H nmr spectroscopy showed only **2.2a** to be present.

Thermolysis of [Mo('BuN)(S₂)(S₂CNMe₂)₂] 2.2h'

A toluene (50 ml) solution of $[Mo({}^{t}BuN)(S_{2})(S_{2}CNEt_{2})_{2}]$ **2.2h**' (0.10 g, 0.21 mmol) was refluxed for 18 hours. After which time volatiles were removed under reduced pressure affording a red solid. ¹H nmr spectroscopy showed only **2.2h**' to be present.

Reaction of [Mo(NPh)(S₂)(S₂CNEt₂)₂] 2.2a with DMAD

 $[Mo(NPh)(S_2)(S_2CNEt_2)_2]$ **2.2a** (0.25 g, 0.46 mmol) was dissolved in toluene (50 ml). To this solution was added via a degassed syringe DMAD (0.08 ml, 0.56 mmol). The resulting solution was refluxed for 20 hours after

which time the solution had changed colour going from blue to green. Volatiles were removed under reduced pressure, and the resulting green solid was absorbed onto alumina and passed down a chromatography column. Elution with 20% dichloromethane in petrol afforded an orange complex [Mo{SNC(R)C(R)S}{SC(R)C(R)S(NEt_2)C}(S_2CNEt_2)] (R=CO_2Me) **3.3a**. Further elution with 40% dichloromethane in petrol afforded a blue complex identified as [Mo{PhNC(R)C(R)S}{SC(R)C(R)C(R)C(NEt_2)S}(S_2CNEt_2)] (R=CO_2Me) **3.4a** (0.10 g, 27%). Finally elution with 80% dichloromethane afforded a green complex [Mo{SNC(R)C(R)S}{SC(R)C(R)C(NEt_2)S}(S_2CNEt_2)] (R=CO_2Me) **3.5a**. Crystals of **3.4a** were obtained by the slow diffusion of petrol into a dichloromethane solution, attempts to recrystallise **3.3a** and **3.5a** by various methods met with failure.

- 3.3a ¹H nmr (CDCl₃); δ 7.51-7.12 (m, 26), 7.05 (d, 3, J 7.1), 3.96 (s, 15), 3.90 (s, 14), 3.84 (s, 14), 3.80 (s, 15), 3.74 (s, 16), 3.66 (s, 15), 3.51 (s, 14), 4.09-3.33 (m, 40), 1.15-1.13 (m, 81): ir υ/cm⁻¹; 1721br, 1510br, 1340br, 1265m, 1220br, 1101br, 750m, 700m.
- 3.4a ¹H nmr (CDCl₃); δ 7.36-7.06 (m, 5H, Ph), 3.94-3.39 (m, 8H, CH₂), 3.82 (s, 3H, OCH₃), 3.71 (s, 3H, OCH₃), 3.69 (s, 3H, OCH₃), 3.47 (s, 3H, OCH₃), 1.42 (t, 3H, J 7.2, CH₃), 1.41 (t, 3H, J 7.2, CH₃), 1.26 (t, 3H, J 7.2, CH₃), 1.24 (t, 3H, J 7.2, CH₃): ir υ/cm⁻¹; 1731m, 1718s, 1701m, 1685s, 1559m, 1510m, 1473w, 1457w, 1433m, 1357w, 1337m, 1264s, 1246m, 1223s, 1198m, 1153m, 1079m, 850w, 753w, 748w, 700w; Analysis calculated for MoC₃₈H₃₇S₅N₃O₈ %C=42.03, %H=4.66, %N=5.25, %S=20.04. Found %C=41.44, %H=4.59, %N=4.85, %S=19.12.
- 3.5a ¹H nmr (CDCl₃); δ 7.26-7.20 (m, 5), 7.15 (m, 15), 7.06 (m, 5), 3.92 (s, 18), 3.84 (s, 18), 3.77 (s, 19), 3.67 (s, 18), 3.65 (s, 17), 3.43 (s, 18), 3.95-3.30 (m, 60), 1.42-1.38 (m, 51), 1.24-1.21 (m, 32), 1.13 (t, 13, J 7.3), 1.05, (t, 12 J 7.3): ir υ/cm⁻¹; 1725br, 1430br, 1360br, 1300m, 1270m, 1200br, 1070br, 755m, 701m.

Reaction of [Mo(O)₂(S₂CNEt₂)₂] 1.2 with PhNCS

 $[Mo(O)_2(S_2CNEt_2)_2]$ **1.2** (0.68 g, 1.6 mmol) was dissolved in toluene (100 ml), to this solution was added phenylisothiocyanate (0.15 ml, 1.6 mmol) via a degassed syringe. The resulting solution was refluxed for 3 days after which time volatiles were removed under reduced pressure, and the products purified by chromatography. Eluting with 40% dichloromethane in petrols gave $[Mo(NPh)(S_2)(S_2CNEt_2)_2]$ **2.2a** (0.17 g, 15%). Elution with 1% methanol in dichloromethane gave a yellow band identified as $[Mo(\mu-NPh)(O)(S_2CNEt_2)]_2$ **4.5a** (0.31 g, 55%).

Reaction of [Mo(NPh)(S₂)(S₂CNEt₂)₂] 2.2a with P(OEt)₃ and Air

 $[Mo(NPh)(S_2)(S_2CNEt_2)_2]$ 2.2a (0.36 g, 0.58 mmol) was dissolved in dichloromethane (50 ml). To this was added via a degassed syringe P(OEt), (0.30 ml, 1.8 mmol). This solution was stirred for 5 hours after which time the blue solution had turned brown. This solution was then exposed to the atmosphere and stirred for a further 24 hours. During this period the colour changed from brown to red and finally to yellow. Volatiles were removed at reduced yield brown/yellow pressure to а solid [Mo₂(μ-S)(μ-NPh)(O)₂(S₂CNEt₂)₂] **3.8a** (0.35 g, 60%). Crystals were obtained by diffusion of methanol into a dichloromethane solution. The reaction was repeated using similar amount of material. Changing the procedure by adding a dichloromethane solution of 2.2a to a dichloromethane solution of $P(OEt)_3$ in the initial steps. However, this method also afforded a similar yield of 3.8a.

3.8a ¹H nmr (CDCl₃); δ 7.42 (t, 2H, J 7.4, m-C₆H₅), 7.20 (t, 1H, J 7.3, p-C₆H₅), 7.14 (d, 2H, J 7.2, o-C₆H₅), 4.07-3.76 (m, 8H, CH₂), 1.38 (t, 6H, J 7.2, Me), 1.31 (t, 6H, J 7.2, Me): ¹³C{¹H} nmr (CDCl₃); δ 204.5 (S₂CN), 164.5 (ipso-C₆H₅), 128.0, 125.0 (C₆H₅), 124.7 (p-C₆H₅), 46.4, 46.1 (CH₂), 12.6, 12.5 (CH₃): ir v/cm⁻¹; 1530s, 1479m, 1457m, 1440m, 1380m, 1353m, 1279s, 1201m, 1151m, 1084m, 953s, 941s, 843w,

772m, 691m. Analysis calculated for $Mo_2C_{16}H_{25}N_3O_2S_5$ %C=29.86, %H=3.91, %N=6.52, %S=24.91. Found %C=29.65, %H=3.83, %N=6.37, %S=24.65.

Protonation of [Mo(NPh)(S₂)(S₂CNEt₂)₂] 2.2a with HBF₄

To a dichloromethane (20 ml) solution of $[Mo(NPh)(S_2)(S_2CNEt_2)_2]$ **2.2a** (0.20 g, 0.36 mmol) was added a few drops of HBF₄. An immediate colour change from blue to brown was observed. The solvent was removed using a rotary evaporator and the resulting brown oil washed with ether (3x20 ml). The ¹H nmr spectra of this oil indicated the presence of more than one complex. attempts to separate these complexes by a number of methods met with failure.

¹H nmr (CDCl₃); δ 7.65 (m, 11), 7.41 (m, 20), 7.30 (d, 8), 3.80-4.05 (m, 50), 3.72 (q, 5, J 7.1), 3.65 (q, 4, J 7.1), 1.16-1.52 (m, 154), 0.87 (t, 20, J 7.0)

Oxidation of $[Mo(NPh)(S_2)(S_2CNEt_2)_2]$ 2.2a with 3-Chloroperoxybenzoic Acid

To a dichloromethane (50 ml) solution of $[Mo(NPh)(S_2)(S_2CNEt_2)_2]$ **2.2a** (0.25 g, 0.45 mmol) was added a dichloromethane solution of 2-chloroperoxybenzoic acid (acquired as a 50% mixture with 3-chlorobenzoic acid 0.16 g, 0.46 mmol). An immediate colour change from blue to green was observed, and the solution stirred for a further 30 minutes. Volatiles were then removed at reduced pressure, affording a green solid which was washed with ether (3x70 ml). The ¹H nmr spectrum of this solid indicated the presence of more than one complex. Attempts to purify this mixture by recrystallisation of a refrigerated solution, prepared by dissolving the solid in the minimum amount of dichloromethane (10 ml), and adding to this petrol (3 ml), met with failure. Purification was then attempted via the use of column chromatography.

However the green solid quickly decomposed on the column affording a yellow complex that became stuck on the column. A small amount of a yellow complex was obtained after elution with 90% dichloromethane in petrol, and was identified as $[Mo_2(\mu-S)(\mu-NPh)(O)_2(S_2CNEt_2)_2]$ **3.8a** (0.01 g, 7%)

¹H nmr (CDCl₃); δ 7.41 (t, 10), 7.21-7.11 (m, 13), 4.11-3.70 (m, 53), 1.40-1.20 (m, 66)

6.4 Experimental for Chapter 4

Reaction of [Mo(µ-NPh)(O)(S₂CNEt₂)]₂ 4.5a with PhNCO

To a toluene (100 ml) solution of $[Mo(\mu-NPh)(O)(S_2CNEt_2)]_2$ **4.5a** (1.08 g, 1.59 mmol) was added via a degassed syringe phenylisocyanate (0.38 ml, 3.18 mmol). The solution was refluxed for one day, after which time volatiles were removed under reduced pressure, and the products purified by chromatography. Eluting with 90% dichloromethane gave a red band identified as $[Mo_2(NPh)_2(\mu-NPh)\{\mu-PhNC(O)NPh\}(S_2CNEt_2)]$ **4.7a** (1.08 g, 72%).

4.7a ¹H nmr (CDCl₃); δ 7.88 (d, 2H, J 7.2), 7.41 (d, 2H, J 7.4), 7.30 (t, 4H, J 7.2), 7.15 (t, 2H, J 7.3), 7.08 (d, 2H, J 7.4), 6.96 (t, 2H, J 7.4), 6.86 (t, 2H, J 7.3), 6.81-6.73 (m, 4H), 6.66 (t, 1H, J 7.3), 6.38 (d, 4H, J 7.3), 3.84 (m, 4H, CH₂), 3.65 (sextet, 2H, J 7.2, CH₂), 3.52 (sextet, 2H, J 7.1, CH₂), 1.20 (t, 6H, J 7.2, Me), 0.98 (t, 6H, J 7.2, Me): ir υ/cm⁻¹; 1710s, 1696s, 1538m, 1580m, 1512vs, 1474s, 1439s, 1355m, 1318s, 1274s, 1252s, 1205m, 1149m, 1072m, 1023m, 754s, 687s. Analysis Calculated for Mo₂C₄₁H₄₅N₇S₄O %C=50.67, %H=4.63, %N=10.09, %S=13.18. Found %C=49.93, %H=4.60, %N=9.72, %S=13.17.

Thermolysis of [Mo₂(NPh)₂(µ-NPh){µ-PhNC(O)NPh}(S₂CNEt₂)₂] 4.7a

 $[Mo_2(NPh)_2(\mu-NPh)\{\mu-PhNC(O)NPh\}(S_2CNEt_2)_2]$ **4.7a** (1.20 g, 1.23 mmol) was dissolved in toluene (100 ml) and refluxed for 18 hours. Which

upon cooling lead to the deposition of orange crystals. These were isolated by filtration of the solution, followed by washing with petrol (2x50 ml) and identified as $[Mo(\mu-NPh)(NPh)(S_2CNEt_2)]_2$ **4.6a** (0.35 g, 33%).

4.6a ¹H nmr (CDCl₃); δ 8.12 (d, 4H, J 7.3), 7.52 (t, 4H, J 7.4), 7.20 (t, 2H, J 7.2), 7.13 (t 4H, J 7.4), 6.74 (t, 2H, J 7.4), 6.67 (d, 4H, J 7.4), 3.68 (q, 8H, J 7.3, CH₂), 1.18 (t, 12H, J 7.2, Me): ir υ/cm⁻¹; 1578m, 1516s, 1474s, 1436m, 1354w, 1309m, 1274m, 1262m, 1201w, 1149m, 1067m, 1023w, 996w, 975w, 767s, 754s, 695m, 686m, 668m, 486w. Analysis calculated for Mo₂C₃₄H₄₀S₄N₆ %C=47.88, %H=4.72, %N=9.85, %S=15.10. Found %C=47.67, %H=4.70, %N=9.54, %S=15.10.

Reaction of [Mo(µ-NPh)(NPh)(S₂CNEt₂)]₂ 4.6a with PhNCO

To a solution of $[{Mo(\mu-NPh)(NPh)(S_2CNEt_2)}_2]$ **4.6a** (0.34 g, 0.40 mmol) in toluene (100 ml) was added via a degassed syringe phenylisocyanate (0.50 ml, 0.45 mmol). The resulting mixture was refluxed for three days after which time volatiles were removed at reduced pressure, and the products purified by chromatography. Elution with dichloromethane gave a red band $[Mo_2(NPh)_2(\mu-NPh){\mu-PhNC(O)NPh}(S_2CNEt_2)_2]$ **4.7a** (0.20 g, 50%).

Reaction of [Mo(O)₂(S₂CNEt₂)₂] 1.2 with 2 PhNCO

 $[Mo(O)_2(S_2CNEt_2)_2]$ **1.2** (2.44 g, 5.75 mmol) was dissolved in toluene. To this was added via a degassed syringe phenylisocyanate (1.40 ml, 11.7 mmol). The resulting solution was refluxed for 3 days, after which time volatiles were removed under reduced pressure. The remaining red solid was passed down a chromatography column. Eluting with 40% dichloromethane in petrols gave $[Mo(NPh)(S_2)(S_2CNEt_2)_2]$ **2.2a** (0.62 g, 20% (30% based on S)), further elution with 90% dichloromethane in petrols gave $[Mo_2(NPh)_2(\mu-NPh)\{\mu-PhNC(O)NPh\}(S_2CNEt_2)_2]$ **4.7a** (1.45 g, 52%). Finally eluting with methanol afforded a red compound identified as $[Mo_2(NPh)_2(\mu-NPh)\{\mu-PhNC(O)NPh\}(S_2CNEt_2)_2]$

PhNC(NPh)NPh}(S₂CNEt₂)₂] **4.8a** (0.67 g, 11%).

4.8a ¹H nmr (CDCl₃); δ 6.90-7.70 (m, 30H, Ph), 3.60-4.05 (m, 8H, CH₂), 0.95-1.20 (m, 12H, CH₃): ir ν /cm⁻¹ 1637s, 1588w, 1521s, 1494m, 1480m, 1439m, 1355w, 1295s, 1278s, 1204w, 1175w, 1096w, 1075w, 1011w, 993w, 977w, 940w, 764m, 750w, 691m, 681m, 563w, 511w; Mass spectrum (M⁺ 1048) Expected for Mo₂C₄₇H₅₀S₄N₈O 1046. Analysis calculated for Mo₂C₄₇H₅₀S₄N₈O %C=53.91, %H=4.78, %N=10.70, %S=12.23. Found %C=61.13, %H=5.38, %N=11.16, %S=10.26.

[Mo(O)(µ-O)(S₂CNEt₂)]₂ 4.1²¹⁷

 $[Mo(O)_2(S_2CNEt_2)_2]$ **1.2** (3.00 g, 7.08 mmol) and zinc dust (3.00 g) were placed into a schlenk and degassed. To this was added 1,2-dichloroethane (100 ml), and the thiophenol (0.16 ml, 1.46 mmol) was added via a degassed syringe. The resultant solution was refluxed for 3 hours, affording a yellow precipitate. The yellow precipitate was collected by filtration and washed with methanol, and ether, then dried under vacuum to afford **4.1** (1.26 g, 65%).

Reaction of [Mo(µ-O)(O)(S₂CNEt₂)]₂ 4.1 with PhNCO

To a toluene (100 ml) solution of $[Mo(\mu-O)(O)(S_2CNEt_2)]_2$ **4.1** (0.12 g, 0.22 mmol) was added via a degassed syringe phenylisocyanate (0.13 ml, 1.10 mmol). The resulting solution was refluxed for 16 hours during which time the colour changed from yellow to red. Solvents were removed at reduced pressure and the resultant red solid absorbed onto alumina and passed down a chromatography column. Elution with dichloromethane gave a red band identified as $[Mo_2(NPh)_2(\mu-NPh)\{\mu-PhNC(O)NPh\}(S_2CNEt_2)_2)]$ **4.7a** (0.31 g, 90%).

[Mo₂(NPh)₂(µ-NPh){µ-PhNC(O)NPh}(S₂CNEt₂)₂] 4.7a with PhNCO

To a solution of $[Mo_2(NPh)_2(\mu-NPh)\{\mu-PhNC(O)NPh\}(S_2CNEt_2)_2]$ **4.7a**. (0.40 g, 0.04 mmol) in toluene (100 ml) was added via a degassed syringe phenylisocyanate (0.05 ml, 0.04 mmol). The resulting mixture was refluxed for three days after which time volatiles were removed and the products purified by chromatography. Elution with dichloromethane gave a red band identified as **4.7a** (0.39 g, 97%).

Reaction of $[Mo(\mu-NPh)(O)(S_2CNEt_2)]_2$ 4.5a and $[Mo(NPh)(S_2)(S_2CNEt_2)_2]$ 2.2a in the presence of PhNCO

To a solution of $[Mo(\mu-NPh)(O)(S_2CNEt_2)]_2$ **4.5a**. (0.40 g, 0.57 mmol) and $[Mo(NPh)(S_2)(S_2CNEt_2)_2]$ **2.2a** (0.31 g, 0.57 mmol) in toluene (100 ml) was added via a degassed syringe phenylisocyanate (0.21 ml, 1.76 mmol). The resulting mixture was refluxed for three days after which time volatiles were removed and the products purified by chromatography. Elution with 40% dichloromethane in petrol afforded a purple band identified as **2.2a** (0.31 g, 97%). Further elution with dichloromethane gave a red band identified as **4.7a** (0.39 g, 98%).

Reaction of [Mo₂(µ-NPh)(µ-S)(O)₂(S₂CNEt₂)₂] 3.8a with PhNCO

To a solution of $[Mo_2(\mu-NPh)(\mu-S)(O)_2(S_2CNEt_2)_2]$ **3.8a** (0.11 g, 0.17 mmol) in toluene (100 ml) was added via a degassed syringe phenylisocyanate (0.04 ml, 0.50 mmol). The resulting mixture was refluxed for 1 day, after which time volatiles were removed under reduced pressure. The remaining orange solid was purified by chromatography. Elution with dichloromethane gave a orange band $[Mo_2(NPh)_2(\mu-S){\mu-PhNC(O)NPh}(S_2CNEt_2)_2]$ **4.9a** (0.14 g, 89%). Crystals were obtained by slow diffusion of methanol into a dichloromethane solution.

4.9a ¹H nmr (CDCl₃); δ 7.88 (d, 2H, J 7.3 o-C₆H₅), 7.25 (t, 2H, J 6.8, p-C₆H₅), 7.20 (t, 1H, J 7.1, p-C₆H₅), 7.04 (d, 2H, J 7.3, o-C₆H₅), 6.89 (t, 4H, J 7.8, m-C₆H₅), 6.79 (t, 4H, J 7.3, m-C₆H₅), 6.71 (t, 1H, J 7.3, p-C₆H₅), 6.56 (d, 4H, J 8.0, o-C₆H₅), 4.00-3.94 (m, 4H, CH₂), 3.66 (sext, 2H, J 7.2, CH₂), 3.57 (sext, 2H, J 7.2, CH₂) 1.29 (t, 6H, J 7.2, CH₃), 1.05 (t, 6H, J 7.2, CH₃): ir v/cm⁻¹; 1714s, 1521s, 1486s, 1474s, 1450m, 1438m, 1312s, 1277s, 1247m, 759m, 689m. Analysis calculated for Mo₂C₃₅H₄₀S₅N₆O %C=46.05, %H=4.42, %N=9.21, %S=17.56. Found %C=44.91, %H=4.36, %N=8.82, %S=17.17.

Reaction of $[Mo_2(\mu-S)(\mu-O)(O)_2(S_2CNEt_2)_2]$ 4.2 with PhNCO

To a toluene (100 ml) solution of $[Mo_2(\mu-S)(\mu-O)(O)_2(S_2CNEt_2)_2]$ **4.2** (0.22 g, 0.39 mmol) was added via a degassed syringe phenylisocyanate (0.19 ml, 1.60 mmol). The resulting solution was refluxed for 16 hours during which time the colour changed from yellow to red. Solvents were removed at reduced pressure and the resultant red solid absorbed onto alumina and passed down a chromatography column. Elution with 60% dichloromethane in petrol gave a red band identified as $[Mo_2(NPh)_2(\mu-S)\{\mu-PhNC(O)NPh\}(S_2CNEt_2)_2]$ **4.9a** (0.33 g, 93%).

Reaction of [Mo(NPh)(S₂)(S₂CNEt₂)₂] 2.2a with PhNCO

 $[Mo(NPh)(S_2)(S_2CNEt_2)_2]$ **2.2a** (0.22 g, 0.4 mmol) was dissolved in toluene (100 ml). To this was added phenylisocyanate (0.06 ml, 0.4 mmol). The resulting solution was refluxed for three days, the volatiles were then removed at reduced pressure and the products purified by chromatography. Eluting with 40% dichloromethane in petrols yielded **2.2a** (0.20 g, 93%), identified by comparison of nmr and ir spectra.

Protonation of $[Mo(\mu-NPh)(O)(S_2CNEt_2)]_2$ 4.5a with HBF₄

To a dichloromethane (30 ml) solution of $[Mo(\mu-NPh)(O)(S_2CNEt_2)]_2$ **4.5a** (0.20 g, 0.28 mmol) was added a few drops of an ethereal solution of HBF₄. The solution rapidly turned from yellow to red. The solvent was removed and the remaining red oil was washed with ether. The compound was dissolved in dichloromethane and a few drops of hexane were added. Upon refrigeration red crystals of $[Mo_2(\mu-NPh)_2(O)(S_2CNEt_2)_3][BF_4]$ **4.11a** (0.10 g, 38%) were formed.

4.11a ¹H nmr (CDCl₃); δ 7.49 (t, 4H, J 7.1, m-C₆H₅), 7.29 (d, 4H, J 7.0, o-C₆H₅), 7.10 (t, 2H, J 7.1, p-C₆H₅), 3.70-4.01 (m, 12H, CH₂), 1.00-1.31 (m, 18H, CH₃): ir v/cm⁻¹; 1526m, 1442m, 1382w, 1355w, 1280m, 1200w, 1154w, 1052br,s, 996w, 964w, 847w, 788w, 691w, 520w. Analysis Calculated for Mo₂C₂₉H₄₀S₆N₅OBF₄ %C=36.83, %H=4.26, %N=7.41, %S=20.29. Found %C=36.23, %H=4.23, %N=7.65, %S=21.10.

Reaction of $[Mo_2(NPh)_2(\mu-S){\mu-PhNC(O)NPh}(S_2CNEt_2)_2]$ 4.9a with 2,4-Dinitrophenylhydrazine

To a dichloromethane (50 ml) solution of $[Mo_2(NPh)_2(\mu-S){\mu-PhNC(O)NPh}(S_2CNEt_2)_2]$ **4.9a** (0.10 g, 0.11 mmol) was added a dichloromethane solution of 2,4-dinitrophenylhydrazine and the reaction stirred. The ir spectra of the resulting solution was monitored during the course of the reaction, which showed the loss of the C=O band from **4.9a** over a period of 30 minutes. The solvent was removed and the remaining orange oil **4.10a** was washed with ether. Attempts to recrystallize this oil were unsuccessful.

4.10a ¹H nmr (CDCl₃); δ 6.73-8.58 (m, 23H, Ph), 3.64-3.91 (m, 8H, CH₂), 1.14-1.40 (m, 12H, CH₃): ir υ/cm⁻¹; 1618s, 1594m, 1538m, 1519s, 1507s, 1499m, 1437m, 1355m, 1334s, 1310m, 1281m, 1249m, 1226m, 1205m, 1120br, 1063m, 750m, 734m.

Reaction of [{Mo(µ-O)(O)(S₂CNEt₂)]₂ 4.1 with 2-MeC₆H₄NCO

To a toluene (100 ml) solution of $[Mo(\mu-O)(O)(S_2CNEt_2)]_2$ **4.1** (0.21 g, 0.38 mmol) was added via a degassed syringe phenylisocyanate (0.2 ml, 1.88 mmol). The resulting solution was refluxed for 16 hours during which time the colour changed from yellow to orange. Solvents were removed at reduced pressure and the resultant orange solid absorbed onto alumina and passed down a chromatography column. Elution with 40% dichloromethane in petrol gave a orange band identified as [{Mo(μ -2-MeC_6H_4N)(2-MeC_6H_4N)(S₂CNEt₂)}₂] **4.6c** (0.31 g, 90%).

Reaction of $[Mo(\mu-2-MeC_6H_4N)(2-MeC_6H_4N)(S_2CNEt_2)_2]$ 4.6c and 2-MeC₆H₄NCO

To a toluene (100 ml) solution of $[Mo(\mu-2-MeC_6H_4N)(2-MeC_6H_4N)(S_2CNEt_2)]_2$ **4.6c** (0.30 g, 0.33 mmol) was added o-tolylisocyanate (0.05 ml, 0.35 mmol). The resulting solution was refluxed for 18 hours, volatiles were removed and the resulting solid passed down a chromatography column. Elution with 40% dichloromethane in petrol gave a yellow band identified as starting material (0.28 g, 93%).

Reaction of $[Mo(\mu-2-MeC_6H_4N)(2-MeC_6H_4N)(S_2CNEt_2)]_2$ 4.6c with CF₃COOH

To a dichloromethane (20 ml) solution of $[Mo(\mu-2-MeC_6H_4N)(2-MeC_6H_4N)(S_2CNEt_2)]_2$ **4.6c** (0.30 g, 0.33 mmol) was added a few drops of aqueous trifluoroacetic acid. An initial colour change from orange to red was observed, gradually becoming yellow over a period of a minute. The solvent was removed from this solution at a rotary evaporator, and the resulting oily yellow solid washed with ether. Crystals of $[Mo(\mu-MeC_6H_4N)(O)(S_2CNEt_2)]_2$ **4.5c** (0.20 g, 83%) were obtained by slow diffusion of methanol into a dichloromethane solution. **4.5c** ¹H nmr (CDCl₃); δ 7.38 (d,2H, J 7.1, C₆H₄), 7.15-7.10 (m, 4H, C₆H₄), 6.50 (d, 2H, J 7.1, C₆H₄), 3.86-3.78 (m, 8H, CH₂), 2.53 (s, 6H, C₆H₄*Me*), 1.27 (t, 12H, J 7.0, CH₂*Me*): ir v/cm⁻¹; 1580m, 1520s, 1481s, 1456s, 1439s, 1380w, 1351w, 1279s, 1201m, 1151m, 1076m, 948s, 932s, 756m, 718m. Analysis calculated for Mo₂C₂₂H₃₄S₄N₄O₂ %C=37.39, %H=4.85, %N=7.93, %S=18.15. Found %C=38.02, %H=4.40, %N=8.30, %S=18.40.

6.5 Experimental for Chapter 5

Thermolysis of $[Mo(O)_2(S_2CNEt_2)_2]$ 1.2

A toluene (100 ml) solution of $[Mo(O)_2(S_2CNEt_2)_2]$ **1.2** (1.82 g, 4.29 mmol) was refluxed in a roundbottom flask for 3 days. Volatiles were removed under reduced pressure and the resultant oily brown solid was absorbed onto alumina and passed down a chromatography column. Elution with 70% dichloromethane in petrol gave a yellow band identified as $[Mo_2(\mu-S)(\mu-O)(O)_2(S_2CNEt_2)_2]$ **4.2** by comparison of ir spectra and analysis with literature values²¹⁷ (1.21 g, 49%). Further elution with 100% dichloromethane in petrol gave a brown band **5.1**.

¹H nmr (CDCl₃); δ 3.98 (br, 18), 3.68 (br, 30), 1.21 (br, 30), 0.83 (br, 80): ir υ/cm⁻¹; 1523s, 1458m, 1439m, 1375w, 1358m, 1303w, 1282s, 1208m, 1153w, 1096w, 1077w, 1067w, 952w, 918w, 853w, 794w.

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Crystallographic Data

General

A suitable single crystal was mounted on a glass fibre. All geometric and intensity data were taken from this sample using an automated four-circle diffractometer (Nicolet R3mV) equipped with Mo-K α radiation (λ =0.71073 Å). Important crystallographic parameters are summarised in the tables.

The lattice vectors were identified by application of the automatic indexing routine of the diffractometer to the positions of reflections taken from a rotation photograph and centred by the diffractometer. The ω -20 technique was used to measure reflections unless one or more axial parameters were greater than 23 Å in which case the ω technique was used in the range 5°≤20≤50°. Except where noted, three standard reflections (remeasured every 97 scans) showed no significant loss in intensity during data collection. The data were corrected for Lorentz and polarisation effects, and empirically for absorption. Unique data with I≥3.0 σ (I) were used to solve and refine the structures in the space groups indicated.

The structures were solved by direct methods and developed by using alternating cycles of least-squares refinement and difference-fourier synthesis. The non-hydrogen atoms were refined anisotropically while hydrogens were placed in idealised positions (C-H 0.96 Å) and assigned a common isotropic thermal parameter (U=0.08 Å²). Structure solution used the SHELXTL PLUS program package on a microVax II computer.

Definitions

$$\begin{aligned} \mathsf{R} &= \Sigma[|\mathsf{F}_{o}| - |\mathsf{F}_{c}|] / \Sigma |\mathsf{F}_{o}| \\ \mathsf{R}_{w} &= \Sigma w^{\frac{1}{2}}. \ [|\mathsf{F}_{o}| - |\mathsf{F}_{c}|] / \Sigma w^{\frac{1}{2}}. |\mathsf{F}_{o}| \end{aligned}$$

Appendix 1.1.a Crystallographic data for $[Mo(2,6-{}^{i}Pr_{2}C_{6}H_{3}N)_{2}(S_{2}CNEt_{2})_{2}]$ 1.1f

Formula	Mo ₁ C ₃₄ H ₅₄ N ₄ S ₄
Colour	Brown
Space group	C 2/c
a, Å	16.336(2)
b, Å	12.977(2)
c, Å	19.230(2)
α, deg	90
β, deg	111.70(1)
γ, deg	90
V, Å ³	3787.84
Z	4
F(000)	1568
d _{calc} , g/cm ³	1.30
Cryst. size, mm	0.90 x 0.70 x 0.48
μ (Mo-K _{α}), cm ⁻¹	5.76
Orientation reflections: no.;range	20 ; 16.88 $\leq 2\theta \leq 30.31$
Data measured	4593
Unique data	4556
No. of unique with I≥3.0σ(I)	3059
No. of parameters	195
R	0.0314
R _w	0.0345
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.000403F^2$
Largest shift/esd, final cycle	0.002
Largest peak, e/Å ³	0.34

Appendix 1.1.b Atomic coordinates $(x10^4)$ and equivalent isotropic displacement parameters $(Å^2x10^3)$

	x	У	Z	U(eq)*
Mo(1)	5000	965(1)	2500	30(1)
S(1)	6212(1)	441(1)	3656(1)	41(1)
S(2)	4545(1)	-646(1)	3144(1)	46(1)
N(1)	5874(2)	-1116(2)	4415(1)	47(1)
N(2)	4407(1)	1797(2)	2870(1)	35(1)
C(1)	5566(2)	-524(2)	3811(1)	40(1)
C(2)	5348(2)	-1974(3)	4528(2)	61(1)
C(3)	5514(3)	-2959(3)	4192(2)	85(2)
C(4)	6711(2)	-909(3)	5027(2)	61(1)
C(5)	6585(3)	-202(4)	5595(2)	89(2)
C(11)	4056(2)	2571(2)	3162(1)	34(1)
C(12)	3137(2)	2583(2)	3009(1)	40(1)
C(13)	2809(2)	3371(2)	3321(2)	56(1)
C(14)	3352(2)	4099(3)	3775(2)	63(1)
C(15)	4244(2)	4086(2)	3922(2)	55(1)
C(16)	4618(2)	3329(2)	3620(1)	41(1)
C(17)	2547(2)	1801(2)	2483(2)	45(1)
C(18)	1722(2)	1546(3)	2654(2)	67(1)
C(19)	2278(2)	2172(3)	1678(2)	60(1)
C(20)	5600(2)	3342(2)	3784(2)	49(1)
C(21)	6138(3)	3162(5)	4582(2)	130(3)
C(22)	5894(3)	4295(4)	3513(4)	126(3)
* Equivale	ent isotropio	c U defined	as one third	of the trace
of the or	thogonalized	U _{ij} tensor		

Appendix I: Crystallographic Data

$\begin{array}{llllllllllllllllllllllllllllllllllll$	pths (Å) (1) (2) (1) (3) (3) (3) (5) (4) (5) (4) (5) (5) (5) (5)	$\begin{array}{l} Mo(1) - S(2) \\ Mo(1) - S(1A) \\ Mo(1) - N(2A) \\ S(2) - C(1) \\ N(1) - C(2) \\ N(2) - C(11) \\ C(4) - C(5) \\ C(11) - C(16) \\ C(12) - C(17) \\ C(14) - C(15) \\ C(16) - C(20) \\ C(17) - C(19) \\ C(20) - C(22) \end{array}$	2.672 2.464 1.766 1.694 1.470 1.376 1.497 1.505 1.377 1.517 1.523 1.489	<pre>(1) (1) (2) (2) (4) (3) (6) (3) (3) (5) (4) (4) (4) (7)</pre>
Appendix 1.1.d Bond ang S(1) -Mo(1) -S(2) S(2) -Mo(1) -N(2) S(2) -Mo(1) -N(2) S(2) -Mo(1) -S(1A) S(1) -Mo(1) -S(2A) N(2) -Mo(1) -N(2A) N(2) -Mo(1) -N(2A) S(2A) -Mo(1) -N(2A) Mo(1) -S(2) -C(1) C(1) -N(1) -C(4) Mo(1) -N(2) -C(11) S(1) -C(1) -N(1) N(1) -C(2) -C(3) N(2) -C(11) -C(12) C(12) -C(11) -C(16) C(11) -C(12) -C(17) C(12) -C(13) -C(14) C(14) -C(15) -C(16) C(11) -C(16) -C(20) C(12) -C(17) -C(18) C(16) -C(20) -C(22)	Hes (°) 68.6(1) 90.2(1) 86.2(1) 86.2(1) 162.4(1) 98.9(1) 104.7(1) 90.2(1) 85.0(1) 122.5(3) 169.9(2) 120.7(2) 112.0(4) 119.4(2) 121.1(2) 121.4(3) 122.1(3) 122.1(3) 113.4(3) 109.8(2) 113.0(3)	S(1) -Mo(1) -N(2) S(1) -Mo(1) -S(2) N(2) -Mo(1) -S(2) S(2) -Mo(1) -S(2) S(1A) -Mo(1) -S(2) S(1A) -Mo(1) -N(2) S(1A) -Mo(1) -N(2) C(1) -N(1) -C(2) C(2) -N(1) -C(2) C(2) -N(1) -C(2) S(2) -C(1) -N(1) N(1) -C(1) -S(2) S(2) -C(1) -N(1) N(1) -C(4) -C(2) S(2) -C(1) -N(1) N(1) -C(4) -C(2) C(11) -C(12) -C C(13) -C(12) -C C(13) -C(14) -C C(13) -C(14) -C C(15) -C(16) -C C(12) -C(17) -C C(16) -C(20) -C C(21) -C(20) -C	2) 1A) 1A) 2A) (2A) (2A) (2A) (2A) 1)) 16) (13) (15) (15) (15) (20) (19) (21) (22)	100.5(1) 148.0(1) 98.9(1) 77.0(1) 68.6(1) 162.4(1) 100.5(1) 91.0(1) 121.0(2) 116.4(2) 115.4(1) 123.8(2) 111.1(3) 119.5(2) 117.8(2) 122.2(2) 120.7(3) 120.0(2) 113.0(3) 110.4(4)

Formula	Mo ₁ C ₂₆ H ₃₈ N ₄ S ₄
Colour	Brown
Space group	P 2, 2, 2,
a, Å	10.753(2)
b, Å	10.761(1)
c, Å	26.872(5)
α, deg	90
β, deg	90
γ, deg	90
V, Å ³	3120.95
Z	4
F(000)	1312
d _{calc} , g/cm ³	1.34
Cryst. size, mm	0.40 x 0.30 x 0.30
μ (Mo-K _{α}), cm ⁻¹	6.87
Orientation reflections: no.;range	27 ; $18.19 \le 2\theta \le 26.03$
Data measured	3677
Unique data	3622
No. of unique with I≥3.0σ(I)	2871
No. of parameters	316
R	0.0405
R _w	0.0491
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.005713F^2$
Largest shift/esd, final cycle	0.001
Largest peak, e/ų	0.35
Data Collected, deg	5 - 53

Appendix 1.2.a Crystallographic data for $[Mo(2,6-Me_2C_6H_3N)_2(S_2CNEt_2)_2]$ 1.1d

Appendix	1.2.b	Atomic	coordinates	(x10 ⁴)	and	equivalent	isotropic
displaceme	ent para	ameters	(Å ² x10 ³)				
•	•		. ,				
	x		У		z	U (e	ed) *
Mo(1)	735	7(1)	4857(1)	12	50(1)	32 (1)
S(1)	793	7(2)	7007(2)	8	02(1)	46 (1)
S(2)	858	3(2)	4518(2)	4	91(1)	43 (1)
S(3)	950	6(2)	5437(2)	16	99(1)	46(1)
S(4)	702	3(2)	6083(2)	20	09(1)	43 (1)
N(1)	944	5(9)	6539(7)		39(3)	61(3)
N(2)	905	0(7)	6944(8)	24	67(3)	59 (2)
N(3)	746	0(6)	3300(5)	14	58(2)	44 (2)
N(4)	581	1(5)	4952(6)	10	42(2)	43 (2)
C(1)	873	3(7)	6111(7)	3	92(3)	40(2)
C(2)	964	4(12)	7905(9)	-	25(4)	74(4)
C(3)	1069	4(13)	8341(12)	3	08(5)	100(5)
C(4)	1004:	2(11)	5704(11)	-3:	25(4)	76 (4)
C(5)	924	0(16)	5356(16)	-7	50(4)	111(6)
C(6)	860	5(7)	6225(8)	21	01(3)	42 (2)
C(7)	1039	5(9)	7161(13)	25	17(4)	76 (4)
C(8)	1083	9(13)	8193(13)	22	08(5)	99 (5)
C(9)	824	2(11)	7573(12)	28	24(4)	80 (4)
C(10)	786	3(17)	6738(18)	32	62(4)	124 (7)
C(11)	716	9(8)	2085(6)	15	63(3)	42 (2)
C(12)	786	/(11)	1116(8)	13	47(3)	60 (3)
C(13)	754	6(14) 0(16)	-97(8)	14	85(5)	85 (5)
C(14)	658	8(16) 2(10)	-337(9)	18	0/(4)	93 (5)
C(15)	595.	3(12)	602(10)	20	16(4) 00(2)	/6(4)
C(16)	623	0(9)	1826(8)	19	02(3)	54 (3)
C(17)	886	4(13) 0(11)	1403(11)	91	90(4) 27/4)	88(5)
C(18)	246	8(II) 8(II)	2851(10)	21.	3/(4) 20/2)	/8((4)
C(21)	450	9(0)	40/1(8)	9. 11	39(3) F3(3)	40(2)
C(22)	241	8(8)	5353(10)		5∠(3) 51(4)	58 (00 (3)
C(23)	241	7 (Ö) 2 (Q)	5055(14)		41 (4) 00 (1)	80(41
C(24)	∠⊥0. 211	ム (ツ) 4 (0)	4104(10) 2450(10)	0.	30(4) 72 <i>(1</i>)	90 (70 /	(0)
C(25)	130	4 (フ) 6 / 0 \	343U(1Z) 3715(0)	4 5	/ J (4) 00/21		(4) (2)
C(20)	432	0(0)	5750(3)	1 5	00(3) 26(E)	55 (00 /	5)
C(27)	220	∪ (⊥ ⊥) ⊃ / 1 1 \	2002(14)	с т Э.	20()) 51/1)	99 (7 c /	3)
C(20)	228.	ム (エ エ)	2993(IU)	3	54(4)	/ 0 (4)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized $\rm U_{ij}$ tensor

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Appendix I: Crystallographic Data

Appendix 1.2.c Bond leng	ths (Å)			
$\begin{array}{llllllllllllllllllllllllllllllllllll$	<pre>(2) (2) (6) (8) (11) (14) (13) (9) (18) (19) (12) (13) (20) (14) (12) (13) (20) (13)</pre>	$ \begin{array}{l} \text{Mo}(1) - \text{S}(2) \\ \text{Mo}(1) - \text{S}(4) \\ \text{Mo}(1) - \text{N}(4) \\ \text{S}(2) - \text{C}(1) \\ \text{S}(4) - \text{C}(6) \\ \text{N}(1) - \text{C}(2) \\ \text{N}(2) - \text{C}(6) \\ \text{N}(2) - \text{C}(9) \\ \text{N}(4) - \text{C}(21) \\ \text{C}(4) - \text{C}(5) \\ \text{C}(9) - \text{C}(10) \\ \text{C}(11) - \text{C}(16) \\ \text{C}(12) - \text{C}(17) \\ \text{C}(14) - \text{C}(15) \\ \text{C}(16) - \text{C}(18) \\ \text{C}(21) - \text{C}(26) \\ \text{C}(22) - \text{C}(27) \\ \text{C}(24) - \text{C}(25) \\ \text{C}(26) - \text{C}(28) \\ \end{array} $	2.462 2.462 1.756 1.742 1.726 1.496 1.344 1.463 1.398 1.482 1.538 1.390 1.473 1.344 1.513 1.422 1.513 1.418 1.514	<pre>(2) (2) (6) (8) (13) (11) (14) (9) (18) (18) (18) (12) (16) (17) (14) (12) (17) (17) (14)</pre>
Appendix 1.2.d Bond angl	es (°)			
S(2) - Mo(1) - S(2) $S(2) - Mo(1) - S(3)$ $S(2) - Mo(1) - S(4)$ $S(1) - Mo(1) - N(3)$ $S(3) - Mo(1) - N(4)$ $S(3) - Mo(1) - N(4)$ $N(3) - Mo(1) - N(4)$ $Mo(1) - S(2) - C(1)$ $Mo(1) - S(4) - C(6)$ $C(1) - N(1) - C(4)$ $C(6) - N(2) - C(7)$ $C(7) - N(2) - C(9)$ $Mo(1) - N(4) - C(21)$ $S(1) - C(1) - N(1)$ $N(1) - C(2) - C(3)$ $S(3) - C(6) - S(4)$ $S(4) - C(6) - N(2)$ $N(2) - C(9) - C(10)$ $N(3) - C(11) - C(16)$ $C(11) - C(12) - C(13)$ $C(13) - C(12) - C(13)$ $C(13) - C(14) - C(15)$ $C(11) - C(16) - C(15)$ $C(15) - C(16) - C(18)$ $N(4) - C(21) - C(26)$ $C(21) - C(22) - C(23)$ $C(23) - C(24) - C(25)$ $C(21) - C(26) - C(25)$ $C(25) - C(26) - C(28)$	87.1(1) 148.1(1) 160.7(2) 91.3(2) 91.5(2) 160.9(2) 102.5(3) 91.8(2) 91.3(3) 121.7(8) 120.5(8) 162.8(6) 124.7(6) 110.0(9) 115.5(4) 120.4(6) 113.0(11) 119.4(7) 116.6(9) 123.3(10) 120.4(10) 119.5(8) 118.9(9) 117.7(7) 117.7(9) 122.3(9) 121.7(9) 128.5(8) 120.8(9)	S(1) - Mo(1) - S(2) $S(1) - Mo(1) - S(3)$ $S(3) - Mo(1) - S(3)$ $S(2) - Mo(1) - N(3)$ $S(2) - Mo(1) - N(3)$ $S(4) - Mo(1) - N(3)$ $S(4) - Mo(1) - N(3)$ $C(1) - N(1) - C(2)$ $Mo(1) - S(3) - C(3)$ $Mo(1) - S(3) - C(3)$ $Mo(1) - N(3) - C(3)$ $C(1) - N(1) - C(4)$ $C(6) - N(2) - C(9)$ $Mo(1) - N(3) - C(3)$ $S(1) - C(1) - S(2)$ $S(2) - C(1) - N(1)$ $N(1) - C(4) - C(5)$ $S(3) - C(6) - N(2)$ $N(2) - C(7) - C(8)$ $N(3) - C(11) - C(3)$ $C(12) - C(13) - C(3)$ $C(14) - C(15) - C(3)$ $C(14) - C(21) - C(3)$ $C(22) - C(21) - C(3)$ $C(22) - C(23) - C(3)$ $C(24) - C(25) - C(3)$ $C(21) - C(26) - C(3)$	2) 4) 3) 4) 1) 6)) 11))) 11))) 11))) (16) (17) (14) (15) (22) (26) (27) (24) (26) (27) (24) (26) (28)	<pre>% 3.0 (1) 86.9 (1) 95.2 (2) 104.7 (2) 104.7 (2) 104.5 (2) 95.5 (2) 85.4 (3) 84.9 (3) 121.0 (8) 117.3 (8) 122.7 (8) 162.0 (6) 114.4 (4) 120.8 (6) 114.5 (11) 124.0 (6) 112.9 (10) 119.8 (7) 120.7 (7) 120.1 (8) 121.9 (10) 120.8 (11) 121.5 (8) 120.9 (7) 121.3 (7) 119.9 (8) 122.3 (10) 118.4 (10) 120.7 (8)</pre>

Formula	Mo ₁ C ₂₂ H ₂₆ N ₄ S ₄ Cl ₄
Colour	Brown
Space group	P 2, 2, 2,
a, Å	10.690(4)
b, Å	10.700(3)
c, Å	26.728(5)
α , deg	90
β, deg	90
γ, deg	90
V, Å ³	3057.38
Z	4
F(000)	1440
d _{calc} , g/cm ³	1.55
Cryst. size, mm	0.40 x 0.20 x 0.40
μ (Mo-K _{α}), cm ⁻¹	10.54
Orientation reflections: no.;range	22 ; 15.23 ≤ 2θ ≤ 30.05
Data measured	3078
Unique data	3029
No. of unique with I≥3.0σ(I)	2362
No. of parameters	316
R	0.0404
R _w	0.0438
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.000633F^2$
Largest shift/esd, final cycle	0.001
Largest peak, e/ų	0.46

Appendix 1.3.a Crystallographic data for $[Mo(2,6-Cl_2C_6H_3N)_2(S_2CNEt_2)_2]$ **1.1e**
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	displacement parameters (A-x10°)				
$\begin{array}{llllllllllllllllllllllllllllllllllll$		x	У	Z	U(eq)*
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Mo(1)	7358(1)	9858(1)	1250(1)	54(1)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	S(1)	9491(2)	10424(2)	1701(1)	67(1)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	S(2)	6999(2)	11111(2)	2004(1)	63(1)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	S(3)	7920(2)	11993(2)	799(1)	67(1)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	S(4)	8615(2)	9497(2)	498(1)	64(1)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Cl(1)	3885(3)	11414(3)	1582(1)	106(1)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Cl(2)	5512(3)	7900(3)	304(1)	105(1)
C1 (4) $8910(3)$ $6384(3)$ $918(1)$ $106(1)$ N(1) $9032(8)$ $11946(9)$ $2472(3)$ $77(3)$ N(2) $9435(10)$ $11524(9)$ $27(3)$ $81(3)$ N(3) $5805(6)$ $9937(7)$ $1033(3)$ $65(2)$ N(4) $7439(7)$ $8296(6)$ $1463(3)$ $63(2)$ C(1) $8595(9)$ $11246(9)$ $2111(3)$ $65(3)$ C(2) $10395(11)$ $12111(15)$ $2534(5)$ $102(5)$ C(3) $10859(12)$ $13128(15)$ $2227(5)$ $113(6)$ C(4) $8196(11)$ $12558(12)$ $2824(4)$ $92(4)$ C(5) $7887(15)$ $11730(17)$ $3264(5)$ $130(7)$ C(6) $8751(9)$ $11092(9)$ $394(3)$ $63(3)$ C(7) $9599(15)$ $12877(11)$ $-31(5)$ $102(5)$ C(8) $10639(15)$ $13377(13)$ $290(6)$ $124(7)$ C(9) $10058(12)$ $10690(13)$ $-323(4)$ $99(5)$ C(10) $9218(16)$ $10373(16)$ $-760(5)$ $130(7)$ C(11) $4589(8)$ $9635(8)$ $929(3)$ $60(3)$ C(12) $4302(9)$ $8702(10)$ $584(4)$ $74(3)$ C(13) $3097(10)$ $8415(13)$ $460(4)$ $94(4)$ C(14) $2153(10)$ $9038(14)$ $677(4)$ $99(5)$	Cl(3)	5401(3)	8012(3)	2197(1)	106(1)
N(1) $9032(8)$ $11946(9)$ $2472(3)$ $77(3)$ N(2) $9435(10)$ $11524(9)$ $27(3)$ $81(3)$ N(3) $5805(6)$ $9937(7)$ $1033(3)$ $65(2)$ N(4) $7439(7)$ $8296(6)$ $1463(3)$ $63(2)$ C(1) $8595(9)$ $11246(9)$ $2111(3)$ $65(3)$ C(2) $10395(11)$ $12111(15)$ $2534(5)$ $102(5)$ C(3) $10859(12)$ $13128(15)$ $2227(5)$ $113(6)$ C(4) $8196(11)$ $12558(12)$ $2824(4)$ $92(4)$ C(5) $7887(15)$ $11730(17)$ $3264(5)$ $130(7)$ C(6) $8751(9)$ $11092(9)$ $394(3)$ $63(3)$ C(7) $9599(15)$ $12877(11)$ $-31(5)$ $102(5)$ C(8) $10639(15)$ $13377(13)$ $290(6)$ $124(7)$ C(9) $10058(12)$ $10690(13)$ $-323(4)$ $99(5)$ C(10) $9218(16)$ $10373(16)$ $-760(5)$ $130(7)$ C(11) $4589(8)$ $9635(8)$ $929(3)$ $60(3)$ C(12) $4302(9)$ $8702(10)$ $584(4)$ $74(3)$ C(13) $3097(10)$ $8415(13)$ $460(4)$ $94(4)$ C(14) $2153(10)$ $9038(14)$ $677(4)$ $99(5)$	Cl(4)	8910(3)	6384(3)	918(1)	106(1)
N(2) $9435(10)$ $11524(9)$ $27(3)$ $81(3)$ N(3) $5805(6)$ $9937(7)$ $1033(3)$ $65(2)$ N(4) $7439(7)$ $8296(6)$ $1463(3)$ $63(2)$ C(1) $8595(9)$ $11246(9)$ $2111(3)$ $65(3)$ C(2) $10395(11)$ $12111(15)$ $2534(5)$ $102(5)$ C(3) $10859(12)$ $13128(15)$ $2227(5)$ $113(6)$ C(4) $8196(11)$ $12558(12)$ $2824(4)$ $92(4)$ C(5) $7887(15)$ $11730(17)$ $3264(5)$ $130(7)$ C(6) $8751(9)$ $11092(9)$ $394(3)$ $63(3)$ C(7) $9599(15)$ $12877(11)$ $-31(5)$ $102(5)$ C(8) $10639(15)$ $13377(13)$ $290(6)$ $124(7)$ C(9) $10058(12)$ $10690(13)$ $-323(4)$ $99(5)$ C(10) $9218(16)$ $10373(16)$ $-760(5)$ $130(7)$ C(11) $4589(8)$ $9635(8)$ $929(3)$ $60(3)$ C(12) $4302(9)$ $8702(10)$ $584(4)$ $74(3)$ C(13) $3097(10)$ $8415(13)$ $460(4)$ $94(4)$ C(14) $2153(10)$ $9038(14)$ $677(4)$ $99(5)$	N(1)	9032(8)	11946(9)	2472(3)	77(3)
N(3) $5805(6)$ $9937(7)$ $1033(3)$ $65(2)$ N(4) $7439(7)$ $8296(6)$ $1463(3)$ $63(2)$ C(1) $8595(9)$ $11246(9)$ $2111(3)$ $65(3)$ C(2) $10395(11)$ $12111(15)$ $2534(5)$ $102(5)$ C(3) $10859(12)$ $13128(15)$ $2227(5)$ $113(6)$ C(4) $8196(11)$ $12558(12)$ $2824(4)$ $92(4)$ C(5) $7887(15)$ $11730(17)$ $3264(5)$ $130(7)$ C(6) $8751(9)$ $11092(9)$ $394(3)$ $63(3)$ C(7) $9599(15)$ $12877(11)$ $-31(5)$ $102(5)$ C(8) $10639(15)$ $13377(13)$ $290(6)$ $124(7)$ C(9) $10058(12)$ $10690(13)$ $-323(4)$ $99(5)$ C(10) $9218(16)$ $10373(16)$ $-760(5)$ $130(7)$ C(11) $4589(8)$ $9635(8)$ $929(3)$ $60(3)$ C(12) $4302(9)$ $8702(10)$ $584(4)$ $74(3)$ C(13) $3097(10)$ $8415(13)$ $460(4)$ $94(4)$ C(14) $2153(10)$ $9038(14)$ $677(4)$ $99(5)$	N(2)	9435(10)	11524(9)	27(3)	81(3)
N(4) $7439(7)$ $8296(6)$ $1463(3)$ $63(2)$ C(1) $8595(9)$ $11246(9)$ $2111(3)$ $65(3)$ C(2) $10395(11)$ $12111(15)$ $2534(5)$ $102(5)$ C(3) $10859(12)$ $13128(15)$ $2227(5)$ $113(6)$ C(4) $8196(11)$ $12558(12)$ $2824(4)$ $92(4)$ C(5) $7887(15)$ $11730(17)$ $3264(5)$ $130(7)$ C(6) $8751(9)$ $11092(9)$ $394(3)$ $63(3)$ C(7) $9599(15)$ $12877(11)$ $-31(5)$ $102(5)$ C(8) $10639(15)$ $13377(13)$ $290(6)$ $124(7)$ C(9) $10058(12)$ $10690(13)$ $-323(4)$ $99(5)$ C(10) $9218(16)$ $10373(16)$ $-760(5)$ $130(7)$ C(11) $4589(8)$ $9635(8)$ $929(3)$ $60(3)$ C(12) $4302(9)$ $8702(10)$ $584(4)$ $74(3)$ C(13) $3097(10)$ $8415(13)$ $460(4)$ $94(4)$ C(14) $2153(10)$ $9038(14)$ $677(4)$ $99(5)$	N(3)	5805(6)	9937(7)	1033(3)	65(2)
C(1) $8595(9)$ $11246(9)$ $2111(3)$ $65(3)$ $C(2)$ $10395(11)$ $12111(15)$ $2534(5)$ $102(5)$ $C(3)$ $10859(12)$ $13128(15)$ $2227(5)$ $113(6)$ $C(4)$ $8196(11)$ $12558(12)$ $2824(4)$ $92(4)$ $C(5)$ $7887(15)$ $11730(17)$ $3264(5)$ $130(7)$ $C(6)$ $8751(9)$ $11092(9)$ $394(3)$ $63(3)$ $C(7)$ $9599(15)$ $12877(11)$ $-31(5)$ $102(5)$ $C(8)$ $10639(15)$ $13377(13)$ $290(6)$ $124(7)$ $C(9)$ $10058(12)$ $10690(13)$ $-323(4)$ $99(5)$ $C(10)$ $9218(16)$ $10373(16)$ $-760(5)$ $130(7)$ $C(11)$ $4589(8)$ $9635(8)$ $929(3)$ $60(3)$ $C(12)$ $4302(9)$ $8702(10)$ $584(4)$ $74(3)$ $C(13)$ $3097(10)$ $8415(13)$ $460(4)$ $94(4)$ $C(14)$ $2153(10)$ $9038(14)$ $677(4)$ $99(5)$	N(4)	7439(7)	8296(6)	1463(3)	63(2)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(1)	8595(9)	11246(9)	2111(3)	65(3)
C (3) $10859(12)$ $13128(15)$ $2227(5)$ $113(6)$ C (4) $8196(11)$ $12558(12)$ $2824(4)$ $92(4)$ C (5) $7887(15)$ $11730(17)$ $3264(5)$ $130(7)$ C (6) $8751(9)$ $11092(9)$ $394(3)$ $63(3)$ C (7) $9599(15)$ $12877(11)$ $-31(5)$ $102(5)$ C (8) $10639(15)$ $13377(13)$ $290(6)$ $124(7)$ C (9) $10058(12)$ $10690(13)$ $-323(4)$ $99(5)$ C (10) $9218(16)$ $10373(16)$ $-760(5)$ $130(7)$ C (11) $4589(8)$ $9635(8)$ $929(3)$ $60(3)$ C (12) $4302(9)$ $8702(10)$ $584(4)$ $74(3)$ C (13) $3097(10)$ $8415(13)$ $460(4)$ $94(4)$ C (14) $2153(10)$ $9038(14)$ $677(4)$ $99(5)$	C(2)	10395(11)	12111(15)	2534(5)	102(5)
C(4) $8196(11)$ $12558(12)$ $2824(4)$ $92(4)$ $C(5)$ $7887(15)$ $11730(17)$ $3264(5)$ $130(7)$ $C(6)$ $8751(9)$ $11092(9)$ $394(3)$ $63(3)$ $C(7)$ $9599(15)$ $12877(11)$ $-31(5)$ $102(5)$ $C(8)$ $10639(15)$ $13377(13)$ $290(6)$ $124(7)$ $C(9)$ $10058(12)$ $10690(13)$ $-323(4)$ $99(5)$ $C(10)$ $9218(16)$ $10373(16)$ $-760(5)$ $130(7)$ $C(11)$ $4589(8)$ $9635(8)$ $929(3)$ $60(3)$ $C(12)$ $4302(9)$ $8702(10)$ $584(4)$ $74(3)$ $C(13)$ $3097(10)$ $8415(13)$ $460(4)$ $94(4)$ $C(14)$ $2153(10)$ $9038(14)$ $677(4)$ $99(5)$	C(3)	10859(12)	13128(15)	2227(5)	113(6)
C(5) $7887(15)$ $11730(17)$ $3264(5)$ $130(7)$ $C(6)$ $8751(9)$ $11092(9)$ $394(3)$ $63(3)$ $C(7)$ $9599(15)$ $12877(11)$ $-31(5)$ $102(5)$ $C(8)$ $10639(15)$ $13377(13)$ $290(6)$ $124(7)$ $C(9)$ $10058(12)$ $10690(13)$ $-323(4)$ $99(5)$ $C(10)$ $9218(16)$ $10373(16)$ $-760(5)$ $130(7)$ $C(11)$ $4589(8)$ $9635(8)$ $929(3)$ $60(3)$ $C(12)$ $4302(9)$ $8702(10)$ $584(4)$ $74(3)$ $C(13)$ $3097(10)$ $8415(13)$ $460(4)$ $94(4)$ $C(14)$ $2153(10)$ $9038(14)$ $677(4)$ $99(5)$	C(4)	8196(11)	12558(12)	2824(4)	92(4)
C (6) $8751(9)$ $11092(9)$ $394(3)$ $63(3)$ C (7) $9599(15)$ $12877(11)$ $-31(5)$ $102(5)$ C (8) $10639(15)$ $13377(13)$ $290(6)$ $124(7)$ C (9) $10058(12)$ $10690(13)$ $-323(4)$ $99(5)$ C (10) $9218(16)$ $10373(16)$ $-760(5)$ $130(7)$ C (11) $4589(8)$ $9635(8)$ $929(3)$ $60(3)$ C (12) $4302(9)$ $8702(10)$ $584(4)$ $74(3)$ C (13) $3097(10)$ $8415(13)$ $460(4)$ $94(4)$ C (14) $2153(10)$ $9038(14)$ $677(4)$ $99(5)$	C(5)	7887(15)	11730(17)	3264(5)	130(7)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(6)	8751(9)	11092(9)	394(3)	63(3)
C(8) $10639(15)$ $13377(13)$ $290(6)$ $124(7)$ C(9) $10058(12)$ $10690(13)$ $-323(4)$ $99(5)$ C(10) $9218(16)$ $10373(16)$ $-760(5)$ $130(7)$ C(11) $4589(8)$ $9635(8)$ $929(3)$ $60(3)$ C(12) $4302(9)$ $8702(10)$ $584(4)$ $74(3)$ C(13) $3097(10)$ $8415(13)$ $460(4)$ $94(4)$ C(14) $2153(10)$ $9038(14)$ $677(4)$ $99(5)$	C(7)	9599(15)	12877(11)	-31(5)	102(5)
C(9) $10058(12)$ $10690(13)$ $-323(4)$ $99(5)$ $C(10)$ $9218(16)$ $10373(16)$ $-760(5)$ $130(7)$ $C(11)$ $4589(8)$ $9635(8)$ $929(3)$ $60(3)$ $C(12)$ $4302(9)$ $8702(10)$ $584(4)$ $74(3)$ $C(13)$ $3097(10)$ $8415(13)$ $460(4)$ $94(4)$ $C(14)$ $2153(10)$ $9038(14)$ $677(4)$ $99(5)$	C(8)	10639(15)	13377(13)	290(6)	124(7)
C(10) $9218(16)$ $10373(16)$ $-760(5)$ $130(7)$ $C(11)$ $4589(8)$ $9635(8)$ $929(3)$ $60(3)$ $C(12)$ $4302(9)$ $8702(10)$ $584(4)$ $74(3)$ $C(13)$ $3097(10)$ $8415(13)$ $460(4)$ $94(4)$ $C(14)$ $2153(10)$ $9038(14)$ $677(4)$ $99(5)$	C(9)	10058(12)	10690(13)	-323(4)	99(5)
C(11) $4589(8)$ $9635(8)$ $929(3)$ $60(3)$ $C(12)$ $4302(9)$ $8702(10)$ $584(4)$ $74(3)$ $C(13)$ $3097(10)$ $8415(13)$ $460(4)$ $94(4)$ $C(14)$ $2153(10)$ $9038(14)$ $677(4)$ $99(5)$	C(10)	9218(16)	103/3(16)	-/60(5)	130(7)
C(12) $4302(9)$ $8702(10)$ $584(4)$ $74(3)$ $C(13)$ $3097(10)$ $8415(13)$ $460(4)$ $94(4)$ $C(14)$ $2153(10)$ $9038(14)$ $677(4)$ $99(5)$ $C(14)$ $20520(0)$ $20250(10)$ $1005(4)$ $202(10)$	C(11)	4589(8)	9635(8)	929(3)	60(3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(12)	4302(9)	8/UZ(LU) 9/1E(12)	284(4) 460(4)	74(3)
C(14) 2155(10) 9056(14) 077(4) 99(5)	C(13)	3097(10) 2152(10)	8413(13) 0020(14)	400(4) 677(4)	94(4)
C(T, K) = C(T,	C(14)	2133(10)	9038(14)	0//(4)	99(5)
C(15) $2570(9)$ $9900(12)$ $1025(4)$ $09(4)C(16)$ $3590(9)$ $10265(10)$ $11/(13)$ $71/(3)$	C(15)	2570(9)	10265(12)	1023(4)	09(4) 71(3)
C(10) = 5555(6) = 10205(10) = 1141(5) = 71(5) C(21) = 7151(6) = 7102(9) = 1572(3) = 60(3)	C(10)	7151(0)	7102(2)	1572(3)	$f_{1}(3)$
C(21) 7151(5) 7102(8) 1572(5) 00(5) C(22) 7747(10) 6088(9) 1354(3) 74(3)	C(21)	$7 \pm 3 \pm (3)$ $7 \mp 4 \mp (10)$	6088(9)	1351(3)	74(3)
C(22) 7/97(10) 0000(9) 1004(0) 74(0) C(23) 7/92(13) /876(9) 1/81(5) 92(/)	C(22)	7/92(13)	4876(9)	1/81(5)	92(1)
C(24) $6534(14)$ $4651(10)$ $1826(5)$ $101(5)$	C(24)	6534(14)	4651(10)	1826(5)	101(5)
C(25) = 5906(13) = 5596(10) = 2037(5) = 94(4)	C(25)	5906(13)	5596(10)	2037(5)	94(4)
C(26) $6223(10)$ $6806(9)$ $1917(4)$ $77(3)$	C(26)	6223(10)	6806(9)	1917(4)	77(3)

Appendix 1.3.b Atomic coordinates $(x10^4)$ and equivalent isotropic displacement parameters $(Å^2x10^3)$

$\begin{array}{llllllllllllllllllllllllllllllllllll$	$ \begin{array}{c} \text{(A)} \\ (3) \\ (3) \\ (7) \\ (10) \\ (9) \\ (10) \\ (11) \\ (13) \\ (15) \\ (15) \\ (15) \\ (15) \\ (11) \\ (20) \\ (21) \\ (14) \\ (15) \\ (18) \\ (13) \\ (13) \\ (17) \end{array} $	$\begin{array}{l} \text{Mo}(1) - \text{S}(2) \\ \text{Mo}(1) - \text{S}(4) \\ \text{Mo}(1) - \text{N}(4) \\ \text{S}(2) - \text{C}(1) \\ \text{S}(4) - \text{C}(6) \\ \text{Cl}(2) - \text{C}(12) \\ \text{Cl}(4) - \text{C}(22) \\ \text{N}(1) - \text{C}(2) \\ \text{N}(2) - \text{C}(6) \\ \text{N}(2) - \text{C}(6) \\ \text{N}(2) - \text{C}(9) \\ \text{N}(4) - \text{C}(21) \\ \text{C}(4) - \text{C}(5) \\ \text{C}(9) - \text{C}(10) \\ \text{C}(11) - \text{C}(16) \\ \text{C}(13) - \text{C}(14) \\ \text{C}(15) - \text{C}(16) \\ \text{C}(21) - \text{C}(26) \\ \text{C}(23) - \text{C}(24) \\ \text{C}(25) - \text{C}(26) \\ \end{array}$	2.452 2.449 1.769 1.735 1.735 1.733 1.477 1.308 1.455 1.346 1.510 1.512 1.385 1.342 1.377 1.391 1.376	<pre>(3) (3) (7) (9) (10) (10) (10) (10) (14) (13) (14) (19) (12) (17) (13) (14) (19) (15)</pre>
Appendix 1.3.d Bond ang S(1) -Mo(1) - S(2) S(2) -Mo(1) - S(3) S(2) -Mo(1) - S(4) S(1) -Mo(1) -N(3) S(3) -Mo(1) -N(3) S(3) -Mo(1) -N(4) S(3) -Mo(1) -N(4) N(3) -Mo(1) -N(4) Mo(1) - S(2) - C(1) Mo(1) - S(4) - C(6) C(1) -N(1) - C(4) C(6) -N(2) - C(7) C(7) -N(2) - C(9) Mo(1) -N(4) - C(21) S(1) - C(1) - N(1) N(1) - C(2) - C(3) S(3) - C(6) - S(4) S(3) - C(6) - S(4) S(3) - C(6) - S(4) S(3) - C(6) - S(4) S(3) - C(1) - C(10) N(3) - C(11) - C(16) C1(2) - C(12) - C(11) C(11) - C(12) - C(13) C(13) - C(14) - C(15) C1(1) - C(16) - C(11) C(11) - C(16) - C(15) N(4) - C(21) - C(26) C1(4) - C(22) - C(23) C(23) - C(24) - C(25) C1(3) - C(26) - C(21) C(21) - C(26) - C(25)	<pre>les (°)</pre>	S(1) - Mo(1) - S(S(1) - Mo(1) - S(S(2) - Mo(1) - N(S(2) - Mo(1) - N(S(2) - Mo(1) - N(S(2) - Mo(1) - N(S(2) - Mo(1) - N(Mo(1) - S(1) - C(Mo(1) - S(3) - C(C(1) - N(1) - C(2) C(2) - N(1) - C(4) C(6) - N(2) - C(9) Mo(1) - N(3) - C(S(1) - C(1) - S(2) S(2) - C(1) - N(3) - C(S(3) - C(6) - N(2) N(2) - C(7) - C(8) N(3) - C(11) - C(C(12) - C(11) - C(C(12) - C(11) - C(C(12) - C(11) - C(C(12) - C(12) - C(11) - C(C(12) - C(12) - C(12) - C(C(14) - C(15) - C C(14) - C(21) - C(C(22) - C(21) - C(C(22) - C(23) - C(C(24) - C(25) - C(C(24) - C(26) - C(3) 4) 3) 3) 4) 4) 1) 6)) 11)) 11)) 12) (16) (13) (14) (16) (15) 22) (26) (22) (25)	79.3(1) 86.4(1) 68.8(1) 95.5(2) 104.8(2) 105.0(2) 95.1(2) 85.8(3) 85.3(3) 120.3(9) 118.6(9) 121.5(9) 162.2(7) 113.9(5) 121.3(7) 122.0(11) 124.7(8) 112.3(11) 120.9(8) 116.7(8) 119.4(9) 119.5(12) 118.5(10) 119.4(8) 123.1(8) 115.4(8) 118.3(10) 119.3(12) 118.4(9)

Formula	Mo ₁ C ₁₆ H ₂₅ N ₃ S ₆
Colour	Purple
Space group	P2 ₁ /c
a, Å	10.436(2)
b, Å	9.963(2)
c, Å	23.406(7)
α, deg	90
β, deg	96.63(2)
γ, deg	90
V, Å ³	2405.74
Z	4
F(000)	1120
d _{calc} , g/cm ³	1.51
Cryst. size, mm	0.68 x 0.40 x 0.40
$\mu(Mo-K_{\alpha}), \ cm^{-1}$	10.40
Orientation reflections: no.;range	36 ; 14.27 $\le 2\theta \le 27.93$
Data measured	4761
Unique data	4717
No. of unique with I≥3.0σ(I)	3268
No. of parameters	235
R	0.0390
R _w	0.0410
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.000239F^2$
Largest shift/esd, final cycle	0.001
Largest peak, e/Å ³	0.52

Appendix 1.4.a Crystallographic data for $[Mo(S_2)(NPh)(S_2CNEt_2)_2]$ 2.2a

displacement parameters (Ųx10³)				
	x	v	z	U(eq) *
Mo(1)	2032(1)	8203(1)	3924(1)	40(1)
S(1)	4023(1)	6701(1)	4104(1)	50(1)
S(2)	3300(1)	8644(1)	4893(1)	51(1)
S(3)	1407(1)	6406(1)	3183(1)	51(1)
S(4)	966(1)	6172(1)	4373(1)	46(1)
S(5)	696(1)	9761(1)	4348(1)	61(1)
S(6)	-161(1)	8972(2)	3585(1)	63(1)
N(1)	5562(4)	7297(4)	5109(2)	56(1)
N(2)	294(4)	4240(4)	3577(2)	52(1)
N(3)	2915(4)	9156(4)	3485(2)	50(1)
C(1)	4468(4)	7509(4)	4752(2)	45(2)
C(2)	5835(5)	7953(5)	5676(2)	65(2)
C(3)	5408(6)	7106(6)	6146(3)	78(2)
C(4)	6562(5)	6414(6)	4934(3)	70(2)
C(5)	7497(6)	7175(7)	4623(3)	91(3)
C(6)	802(4)	5444(5)	3700(2)	43(1)
C(7)	-203(6)	3408(5)	4022(2)	70(2)
C(8)	-1628(7)	3370(9)	3959(3)	122(4)
C(9)	212(5)	3634(5)	3000(2)	62(2)
C(10)	1344(6)	2765(7)	2937(3)	94(3)
C(11)	3777(5)	9595(5)	3130(2)	53(2)
C(12)	3334(6)	10118(6)	2589(3)	77(2)
C(13)	4180(8)	10596(8)	2239(3)	105(3)
C(14)	5470(10)	10525(9)	2436(4)	120(4)
C(15)	5965(7)	10023(8)	2974(4)	104(4)
C(16)	5099(6)	9543(6)	3321(3)	79(2)

Appendix 1.4.b Atomic coordinates $(x10^4)$ and equivalent isotropic displacement parameters ($Å^2x10^3$)

2.487 (1) 2.605 (1)

2.431 (2)

1.718 (5) 1.736 (5) 2.033 (2)

1.469 (7)

1.326 (6)

1.470 (6) 1.505 (8)

1.472 (9) 1.383 (7)

1.376 (11) 1.382 (12)

Mo(1)-S(2) Mo(1)-S(4)

Mo(1) - S(6)

S(1) - C(1)

S(3)-C(6) S(5)-S(6)

N(1) - C(2)N(2) - C(6)

N(2) - C(9)

C(2)-C(3)

C(7)-C(8) C(11)-C(12) C(12)-C(13)

C(14)-C(15)

Appendix 1.4.c Bond lengths (A)

Mo(1)-S(1)	2.544	(1)
Mo(1)-S(3)	2.511	(1)
Mo(1)-S(5)	2.398	(2)
Mo(1)-N(3)	1.759	(4)
S(2)-C(1)	1.731	(5)
S(4)-C(6)	1.718	(5)
N(1)-C(1)	1.326	(6)
N(1)-C(4)	1.470	(7)
N(2)-C(7)	1.484	(7)
N(3)-C(11)	1.383	(7)
C(4)-C(5)	1.507	(9)
C(9)-C(10)	1.490	(9)
C(11)-C(16)	1.385	(7)
C(13)-C(14)	1.358	(13)
C(15)-C(16)	1.387	(11)

Appendix 1.4.d Bond angles (°)

S(1)-Mo(1)-S(2)	69.1(1)	S(1)-Mo(1)-S(3)	79.4(1)
S(2) - Mo(1) - S(3)	143.5(1)	S(1)-Mo(1)-S(4)	82.2(1)
S(2) - Mo(1) - S(4)	88.3(1)	S(3) - Mo(1) - S(4)	69.0(1)
S(1) - Mo(1) - S(5)	145.4(1)	S(2)-Mo(1)-S(5)	76.8(1)
S(3) - Mo(1) - S(5)	129.9(1)	S(4) - Mo(1) - S(5)	91.5(1)
S(1) - Mo(1) - S(6)	160.9(1)	S(2)-Mo(1)-S(6)	126.0(1)
S(3) - Mo(1) - S(6)	82.2(1)	S(4)-Mo(1)-S(6)	86.5(1)
S(5)-Mo(1)-S(6)	49.8(1)	S(1)-Mo(1)-N(3)	85.9(1)
S(2) - Mo(1) - N(3)	100.6(1)	S(3)-Mo(1)-N(3)	94.9(1)
S(4) - Mo(1) - N(3)	161.4(1)	S(5)-Mo(1)-N(3)	106.3(1)
S(6)-Mo(1)-N(3)	100.9(1)	Mo(1)-S(1)-C(1)	88.7(2)
Mo(1)-S(2)-C(1)	90.3(2)	Mo(1)-S(3)-C(6)	89.7(2)
Mo(1)-S(4)-C(6)	87.1(2)	Mo(1) - S(5) - S(6)	65.9(1)
Mo(1)-S(6)-S(5)	64.3(1)	C(1) - N(1) - C(2)	122.0(4)
C(1) - N(1) - C(4)	120.0(4)	C(2) - N(1) - C(4)	118.0(4)
C(6)-N(2)-C(7)	121.6(4)	C(6)-N(2)-C(9)	122.4(4)
C(7) - N(2) - C(9)	115.9(4)	Mo(1)-N(3)-C(11)	165.2(3)
S(1) - C(1) - S(2)	111.7(2)	S(1)-C(1)-N(1)	125.1(4)
S(2) - C(1) - N(1)	123.2(4)	N(1)-C(2)-C(3)	111.8(4)
N(1)-C(4)-C(5)	111.8(5)	S(3)-C(6)-S(4)	114.2(2)
S(3)-C(6)-N(2)	121.6(3)	S(4) - C(6) - N(2)	124.2(4)
N(2)-C(7)-C(8)	113.5(5)	N(2) - C(9) - C(10)	113.1(4)
N(3)-C(11)-C(12)	120.7(5)	N(3)-C(11)-C(16)	120.0(5)
C(12)-C(11)-C(16)	119.3(6)	C(11)-C(12)-C(13)	121.3(6)
C(12)-C(13)-C(14)	118.1(7)	C(13)-C(14)-C(15)	123.0(9)
C(14)-C(15)-C(16)	118.1(7)	C(11)-C(16)-C(15)	120.2(6)

Formula	Mo ₁ C ₁₀ H ₂₁ N ₃ S ₆
Colour	Purple
Space group	ΡĪ
a, Å	8.232(1)
b, Å	9.058(1)
c, Å	13.402(1)
α, deg	95.94(1)
β, deg	94.14(1)
γ, deg	100.55(1)
V, Å ³	972.88
Z	2
F(000)	480
d _{calc} , g/cm ³	1.61
Cryst. size, mm	0.50 x 0.30 x 0.25
μ (Mo-K _{α}), cm ⁻¹	12.72
Orientation reflections: no.;range	36 ; $22.16 \le 2\theta \le 32.17$
Data measured	3694
Unique data	3682
No. of unique with I≥3.0σ(I)	3000
No. of parameters	181
R	0.0297
R _w	0.0391
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.002292F^2$
Largest shift/esd, final cycle	0.002
Largest peak, e/Å ³	0.28

Appendix 1.5.a Crystallographic data for $[Mo(S_2)(N^tBu)(S_2CNMe_2)_2]$ 2.2h'

Appendix displaceme	1.5.b Atomic ent parameters	coordinates (Å ² x10 ³)	(x10 ⁴) and	equivalent isotropic
				/
	x	У	Z	U(eq)*
Mo(1)	1508(1)	6811(1)	2306(1)	42(1)
S(1)	-802(1)	8303(1)	2278(1)	51(1)
S(2)	578(2)	7127(1)	565(1)	64(1)
S(3)	1707(1)	7943(1)	4111(1)	52(1)
S(4)	3337(1)	9558(1)	2595(1)	52(1)
S(5)	3529(1)	5864(1)	1350(1)	78(1)
S(6)	4025(1)	5996(1)	2870(1)	81(1)
N(1)	-2055(5)	8494(4)	414(3)	72(1)
N(2)	3240(3)	10812(3)	4481(2)	52(1)
N(3)	103(3)	5246(3)	2500(2)	46(1)
C(1)	-919(5)	8041(4)	998(3)	53(1)
C(2)	-2042(8)	8236(6)	-684(3)	106(2)
C(3)	-3285(6)	9251(6)	802(5)	101(2)
C(4)	2832(4)	9609(4)	3807(2)	44(1)
C(5)	4111(5)	12238(4)	4223(3)	69(1)
C(6)	2749(5)	10809(5)	5502(3)	65(1)
C(7)	-1176(4)	4125(4)	2817(3)	56(1)
C(8)	-409(8)	2827(5)	3078(5)	106(3)
C(9)	-2529(6)	3665(6)	1944(4)	93(2)
C(10)	-1854(5)	4853(5)	3732(3)	69(1)

Appendix 1.5.cBond ler $Mo(1) - S(1)$ 2.527 $Mo(1) - S(3)$ 2.509 $Mo(1) - S(5)$ 2.399 $Mo(1) - N(3)$ 1.713 $S(2) - C(1)$ 1.709 $S(4) - C(4)$ 1.704 $N(1) - C(1)$ 1.325 $N(1) - C(3)$ 1.423 $N(2) - C(5)$ 1.446 $N(3) - C(7)$ 1.423 $C(7) - C(9)$ 1.523	agths (Å) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1) (1) (2) (4) (5) (4) (6)	Mo(1) - S(2) Mo(1) - S(4) Mo(1) - S(6) S(1) - C(1) S(3) - C(4) S(5) - S(6) N(1) - C(2) N(2) - C(4) N(2) - C(6) C(7) - C(8) C(7) - C(10)	2.464 2.636 2.421 1.701 1.723 2.035 1.467 1.317 1.455 1.493 1.523	<pre>(1) (1) (1) (3) (3) (2) (6) (4) (5) (7) (6)</pre>
Appendix 1.5.d Bond an S(1) -Mo(1) -S(2) S(2) -Mo(1) -S(3) S(2) -Mo(1) -S(3) S(1) -Mo(1) -S(5) S(3) -Mo(1) -S(5) S(3) -Mo(1) -S(6) S(3) -Mo(1) -S(6) S(2) -Mo(1) -N(3) S(4) -Mo(1) -N(3) S(4) -Mo(1) -N(3) Mo(1) -S(2) -C(1) Mo(1) -S(2) -C(1) Mo(1) -S(6) -S(5) C(1) -N(1) -C(3) C(4) -N(2) -C(5) C(5) -N(2) -C(6) S(1) -C(1) -S(2) S(2) -C(1) -N(1) S(3) -C(4) -N(2) N(3) -C(7) -C(8) C(8) -C(7) -C(10)	gles (°) 69.1(1) 144.0(1) 91.8(1) 145.3(1) 130.6(1) 159.7(1) 82.7(1) 50.0(1) 100.9(1) 160.5(1) 98.5(1) 90.2(1) 86.3(1) 64.4(1) 123.0(4) 121.5(3) 116.4(3) 112.3(2) 124.6(3) 120.9(2) 107.9(3) 112.2(4) 110.9(4)	$\begin{array}{c} S(1) - Mo(1) - S(1) \\ S(1) - Mo(1) - S(1) \\ S(3) - Mo(1) - S(1) \\ S(2) - Mo(1) - S(1) \\ S(3) - Mo(1) - N(1) \\ S(3) - Mo(1) - N(1) \\ S(3) - Mo(1) - N(1) \\ S(5) - Mo(1) - N(1) \\ Mo(1) - S(1) - C(1) \\ Mo(1) - S(3) - C(1) \\ Mo(1) - S(3) - C(1) \\ Mo(1) - S(3) - C(1) \\ Mo(1) - S(2) - S(1) \\ C(1) - N(1) - C(2) \\ C(2) - N(1) - C(3) \\ C(4) - N(2) - C(6) \\ Mo(1) - N(3) - C(1) \\ S(3) - C(4) - S(4) \\ S(4) - C(4) - N(2) \\ N(3) - C(7) - C(1) \\ \end{array}$	3) 4) 5) 5) 6) 3) 3) 3) 1) 4)))))))))))))))))	78.2(1) 81.4(1) 68.3(1) 77.2(1) 91.7(1) 126.9(1) 85.2(1) 89.3(1) 93.0(1) 105.4(1) 88.3(1) 90.0(1) 65.6(1) 119.2(4) 117.8(4) 122.0(3) 168.7(2) 123.2(3) 115.0(2) 124.1(2) 107.8(3) 105.(3)

Appendix 1.6.a

Crystallographic data for $[Mo(S_2)(2,6-{}^{i}Pr_2C_6H_3N)(S_2CNMe_2)_2]$ 2.2f'

Formula	Mo ₁ C ₁₈ H ₂₉ N ₃ S ₆
Colour	Purple
Space group	P2 ₁ /c
a, Å	9.471(3)
b, Å	17.974(4)
c, Å	14.505(2)
α, deg	90
β, deg	94.62(2)
γ, deg	90
V, Å ³	2461.17
Z	4
F(000)	1184
d _{calc} , g/cm ³	1.55
Cryst. size, mm	0.30 x 0.30 x 0.60
μ (Mo-K _{α}), cm ⁻¹	10.20
Orientation reflections: no.;range	29 ; 22.99 $\leq 2\theta \leq$ 29.99
Data measured	4815
Unique data	4796
No. of unique with I≥3.0σ(I)	3505
No. of parameters	253
R	0.0365
R _w	0.0473
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.006521F^2$
Largest shift/esd, final cycle	0.001
Largest peak, e/ų	0.40

displacement parameters (A xTU)				
Mo(1) S(1) S(2) S(3) S(4) S(5) S(6) N(1) N(2) N(3) C(1) C(2)	x 7506(1) 9673(1) 9002(1) 6774(1) 6451(1) 6451(1) 5068(1) 11494(3) 5590(5) 8203(3) 10253(4) 12006(6)	Y 4385(1) 3645(1) 4305(1) 3616(1) 3105(1) 4974(1) 4974(1) 4761(1) 3645(2) 2329(2) 5154(2) 3837(2) 3864(3)	z 2263(1) 2698(1) 963(1) 3577(1) 1703(1) 1059(1) 2209(1) 1402(3) 3120(5) 2861(2) 1649(3) 543(3)	U(eq)* 32(1) 42(1) 44(1) 61(1) 59(1) 63(1) 63(1) 53(1) 93(2) 31(1) 40(1) 73(2)
C(3)	12440(5)	3199(3)	2012(4)	72(2)
C(4)	6202(5)	2940(2)	2812(4)	66(2)
C(5) C(6)	5043(7) 5429(9)	1/61(3) 2185(4)	2448(8) 4071(6)	143(4)
C(7)	8748(4)	5756(2)	3347(3)	32(1)
C(8)	8315(4)	5910(2)	4231(3)	42(1)
C(9)	8948(5)	6498(3)	4705(3)	53(1)
C(10) C(11)	10362(5)	6767(2)	3473(3)	53(1)
C(12)	9772(4)	6192(2)	2950(3)	39(1)
C(13)	7244(5)	5442(3)	4658(3)	50(1)
C(14) C(15)	6202(7) 7975(7)	5883(5)	5151(5) 5304(4)	112(3)
C(15)	10228(4)	6029(2)	2006(3)	43(1)
C(17)	11571(6)	5589(3)	2070(4)	70(2)
C(18)	10402(7)	6733(3)	1428(3)	69(2)

Appendix 1.6.b Atomic coordinates $(x10^4)$ and equivalent isotropic displacement parameters $(Å^2x10^3)$

Appendix 1.6.c Bond leng	ths (Å)		
$\begin{array}{llllllllllllllllllllllllllllllllllll$	<pre>(1) (2) (2) (3) (4) (7) (5) (7) (10) (4) (5) (6) (7) (6) (8) (6)</pre>	Mo(1) - S(2) $Mo(1) - S(4)$ $Mo(1) - S(6)$ $S(1) - C(1)$ $S(3) - C(4)$ $S(5) - S(6)$ $N(1) - C(2)$ $N(2) - C(4)$ $N(2) - C(6)$ $C(7) - C(8)$ $C(8) - C(9)$ $C(9) - C(10)$ $C(11) - C(12)$ $C(13) - C(14)$ $C(16) - C(17)$	2.452 (1) 2.612 (1) 2.402 (1) 1.695 (4) 1.705 (5) 2.011 (2) 1.428 (7) 1.334 (7) 1.424 (11) 1.405 (5) 1.371 (6) 1.374 (6) 1.492 (9) 1.495 (7)
Appendix 1.6.d Bond angle S(1) -Mo(1) - S(2) S(2) -Mo(1) - S(3) S(2) -Mo(1) - S(4) S(1) -Mo(1) - S(5) S(3) -Mo(1) - S(5) S(3) -Mo(1) - S(6) S(3) -Mo(1) - S(6) S(2) -Mo(1) - N(3) S(4) -Mo(1) - N(3) S(6) -Mo(1) - N(3) Mo(1) - S(2) - C(1) Mo(1) - S(4) - C(4) Mo(1) - S(6) - S(5) C(1) - N(1) - C(3) C(4) - N(2) - C(5) C(5) - N(2) - C(6) S(1) - C(1) - S(2) S(2) - C(1) - N(1) S(3) - C(4) - N(2) N(3) - C(7) - C(8) C(7) - C(13) C(4) - C(1) - C(13) C(7) - C(13) C(1) - C(1) - C(13) C(7) - C(13) C(1) - C(1) - C(13) C(1) - C(1) - C(13) C(2) - C(1) - C(13) C(2) - C(1) - C(13) C(2) - C(1) - C(13)	es (°) 69.4(1) 140.1(1) 86.5(1) 147.3(1) 128.7(1) 158.7(1) 81.7(1) 49.7(1) 102.2(1) 168.1(1) 96.8(1) 89.8(1) 89.8(1) 86.4(2) 64.7(1) 120.4(4) 119.1(7) 117.0(6) 111.4(2) 124.7(3) 119.5(5) 120.0(3) 121.7(4) 121.7(4) 121.7(4) 121.9(4)	S(1) - Mo(1) - S(3) S(1) - Mo(1) - S(4) S(3) - Mo(1) - S(4) S(2) - Mo(1) - S(5) S(4) - Mo(1) - S(5) S(2) - Mo(1) - S(6) S(4) - Mo(1) - S(6) S(1) - Mo(1) - N(3) S(3) - Mo(1) - N(3) S(5) - Mo(1) - N(3) S(5) - Mo(1) - N(3) S(5) - Mo(1) - N(3) Mo(1) - S(1) - C(1) Mo(1) - S(3) - C(4) Mo(1) - S(5) - S(6) C(1) - N(1) - C(2) C(2) - N(1) - C(3) C(4) - N(2) - C(6) Mo(1) - N(3) - C(7) S(1) - C(1) - N(1) S(3) - C(4) - S(4) S(4) - C(4) - N(2) N(3) - C(7) - C(12) C(7) - C(8) - C(9) C(9) - C(8) - C(13)	$\begin{array}{c} 77.5(1) \\ 84.0(1) \\ 68.1(1) \\ 78.4(1) \\ 88.8(1) \\ 127.2(1) \\ 84.0(1) \\ 91.5(1) \\ 100.2(1) \\ 100.2(1) \\ 100.8(1) \\ 89.0(1) \\ 89.0(1) \\ 89.5(2) \\ 65.6(1) \\ 122.9(4) \\ 116.6(4) \\ 123.9(6) \\ 179.1(3) \\ 123.9(3) \\ 115.9(3) \\ 124.6(5) \\ 118.3(3) \\ 117.5(4) \\ 120.7(4) \\ 120.7(4) \end{array}$
C(3) - C(1) - C(10) C(10) - C(11) - C(12) C(7) - C(12) - C(16) C(8) - C(13) - C(14) C(14) - C(13) - C(15) C(12) - C(16) - C(18)	121.9(4) 122.0(4) 121.6(3) 113.4(5) 109.8(5) 113.0(3)	C(9) - C(10) - C(1) C(7) - C(12) - C(1) C(11) - C(12) - C(1) C(8) - C(13) - C(1) C(12) - C(16) - C(1) C(17) - C(16) - C(1)	$\begin{array}{cccc} 1, & 119.7(4) \\ 1) & 117.1(4) \\ 16) & 121.2(4) \\ 5) & 109.6(4) \\ 17) & 110.7(4) \\ 18) & 109.9(4) \end{array}$

Appendix 1.7.a Crystallographic data for $[Mo_2(\mu-S)(\mu-NPh)(O)_2(S_2CNEt_2)_2]$ 3.8a

Formula	$Mo_2 C_{16} H_{26} N_3 S_5 O_1$
Colour	Yellow
Space group	ΡĪ
a, Å	8.859(2)
b, Å	8.940(2)
c, Å	16.583(4)
α, deg	87.31(2)
β, deg	74.43(2)
γ, deg	86.88(2)
V, Å ³	1262.65
Z	2
F(000)	644
d _{calc} , g/cm ³	1.69
Cryst. size, mm	0.10 x 0.20 x 0.24
μ (Mo-K _{α}), cm ⁻¹	13.85
Orientation reflections: no.;range	28 ; 17.51 ≤ 2θ ≤ 26.54
Data measured	4811
Unique data	4725
No. of unique with I≥3.0σ(I)	3330
No. of parameters	253
R	0.0364
R _w	0.0385
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.000433F^2$
Largest shift/esd, final cycle	0.001
Largest peak, e/ų	0.58

displacement parameters (Å²x10³) U(eq)* x z 3556(1) Mo(1) 3080(1)3350(1)41(1)Mo(2) 1799(1)5698(1) 2472(1)40(1)S(1) 3279(2) 3449(1) 53(1) 5809(2) S(2) 4845(1)53(1)3073(2) 3227(2)S(3) 55(2) 7989(2) 62(1) 2822(1) S(4) 62(1) 3143(2)7874(2) 1695(1)S(5) 4992(2)769(2) 3865(1) 50(1) N(1) 5980(6) 2642(5)5026(3) 49(2) N(2) 1179(6) 10305(5) 1775(3)56(2) N(3) 3955(5) 4848(5)2354(3)44(2)0(1)2638(5)1897(4)3056(3) 63(2)0(2) 1010(5)4771(4)1837(3) 60(2) 4519(3) 2967(5) C(1) 5084(6) 44(2)C(2) 5307(8) 2504(7)5940(4)58(2)96(4) C(3) 4858(11) 6248(5)941(8) C(4) 7706(7) 2569(7) 4711(4)63(3) C(5) 8455(10) 1112(10) 4733(7) 135(6) C(6) 1408(7)8932(6) 2047(3) 51(2) C(7) -289(9)11182(7) 72(3) 2105(5) C(8) -1351(12)11224(13)131(5)1550(6)C(9) 2439(10)11058(7)1135(5)78(3) C(10) 2590(13)10625(10)269(5)114(5)C(11) 5364(7) 5022(6) 1737(3)50(2) C(12) 5578(9) 4344(9) 974(4) 76(3) 6911(12) 4589(12) C(13) 332(5) 106(4)C(14) 8021(10) 5455(12)422(6) 103(4)C(15) 7880(9) 6097(10) 1178(5)89(4) C(16) 6547(8) 5887(8) 1843(4) 69(3) * Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ii} tensor

Appendix 1.7.b Atomic coordinates $(x10^4)$ and equivalent isotropic displacement parameters $(Å^2x10^3)$

2.465 (2) 2.334 (2)

1.681 (4) 2.460 (2)

1.979 (5) 1.732 (5)

1.727 (5)

1.315 (8)

1.477 (8) 1.467 (8) 1.396 (6) 1.432 (11)

1.475(12)

1.388 (10)

1.327 (15) 1.396 (9)

Mo(1)-S(1) Mo(1)-S(5) Mo(1)-O(1)

Mo(2) - S(4)

Mo(2) - N(3)S(1) - C(1)

S(3)-C(6) N(1)-C(1)

N(1) - C(4)

N(2)-C(7) N(3)-C(11) C(4)-C(5)

C(9) - C(10)

C(11) - C(16)

C(13)-C(14) C(15)-C(16)

Appendix 1.7.c Bond lengths (Å)

Mo(1)-Mo(2)	2.732	(1)
Mo(1)-S(2)	2.481	(2)
Mo(1)-N(3)	1.974	(4)
Mo(2)-S(3)	2.491	(2)
Mo(2)-S(5)	2.315	(2)
Mo(2)-O(2)	1.681	(5)
S(2)-C(1)	1.723	(6)
S(4)-C(6)	1.735	(6)
N(1)-C(2)	1.475	(7)
N(2)-C(6)	1.313	(7)
N(2)-C(9)	1.485	(8)
C(2)-C(3)	1.502	(9)
C(7)-C(8)	1.480	(14)
C(11)-C(12)	1.391	(9)
C(12)-C(13)	1.381	(11)
C(14)-C(15)	1.377	(13)

Appendix 1.7.d Bond angles (°)

	• • •		
Mo(2) - Mo(1) - S(1)	128.0(1)	Mo(2)-Mo(1)-S(2)	133.4(1)
S(1) - Mo(1) - S(2)	70.9(1)	Mo(2)-Mo(1)-S(5)	53.7(1)
S(1) - Mo(1) - S(5)	140.9(1)	S(2)-Mo(1)-S(5)	84.5(1)
Mo(2)-Mo(1)-N(3)	46.4(1)	S(1)-Mo(1)-N(3)	84.7(1)
S(2) - Mo(1) - N(3)	140.5(1)	S(5)-Mo(1)-N(3)	96.9(1)
Mo(2) - Mo(1) - O(1)	106.1(2)	S(1)-Mo(1)-O(1)	106.7(2)
S(2)-Mo(1)-O(1)	106.6(2)	S(5)-Mo(1)-O(1)	109.2(2)
N(3) - Mo(1) - O(1)	110.1(2)	Mo(1)-Mo(2)-S(3)	135.8(1)
Mo(1) - Mo(2) - S(4)	125.8(1)	S(3)-Mo(2)-S(4)	70.8(1)
Mo(1) - Mo(2) - S(5)	54.3(1)	S(3)-Mo(2)-S(5)	84.9(1)
S(4) - Mo(2) - S(5)	136.4(1)	Mo(1) - Mo(2) - N(3)	46.2(1)
S(3) - Mo(2) - N(3)	144.3(1)	S(4) - Mo(2) - N(3)	84.0(1)
S(5) - Mo(2) - N(3)	97.4(1)	Mo(1)-Mo(2)-O(2)	106.1(1)
S(3)-Mo(2)-O(2)	104.3(1)	S(4)-Mo(2)-O(2)	109.2(1)
S(5)-Mo(2)-O(2)	111.7(1)	N(3)-Mo(2)-O(2)	107.7(2)
Mo(1) - S(1) - C(1)	88.4(2)	Mo(1)-S(2)-C(1)	88.0(2)
Mo(2)-S(3)-C(6)	87.5(2)	Mo(2)-S(4)-C(6)	88.3(2)
Mo(1)-S(5)-Mo(2)	72.0(1)	C(1) - N(1) - C(2)	121.2(5)
C(1) - N(1) - C(4)	121.2(5)	C(2) - N(1) - C(4)	117.3(5)
C(6) - N(2) - C(7)	122.2(5)	C(6) - N(2) - C(9)	120.7(5)
C(7)-N(2)-C(9)	117.1(5)	Mo(1)-N(3)-Mo(2)	87.4(2)
Mo(1) - N(3) - C(11)	139.3(4)	Mo(2)-N(3)-C(11)	132.8(4)
S(1) - C(1) - S(2)	112.2(3)	S(1) - C(1) - N(1)	123.5(4)
S(2) - C(1) - N(1)	124.2(4)	N(1)-C(2)-C(3)	113.6(5)
N(1) - C(4) - C(5)	115.9(6)	S(3) - C(6) - S(4)	111.9(3)
S(3) - C(6) - N(2)	124.3(4)	S(4) - C(6) - N(2)	123.7(4)
N(2)-C(7)-C(8)	113.3(6)	N(2)-C(9)-C(10)	114.2(7)
N(3) - C(11) - C(12)	119.0(6)	N(3)-C(11)-C(16)	122.7(5)
C(12)-C(11)-C(16)	118.3(5)	C(11)-C(12)-C(13)	120.1(8)
C(12)-C(13)-C(14)	121.7(8)	C(13)-C(14)-C(15)	119.9(7)
C(14) - C(15) - C(16)	120.3(8)	C(11)-C(16)-C(15)	119.6(7)

Appendix 1.8.a

```
Crystallographic data for [Mo_2(NPh)_2(\mu-NPh)(\mu-PhNC(O)NPh)(S_2CNEt_2)_2].
MeOH 4.7a
```

Formula	Mo ₂ C ₄₂ H ₄₉ N ₇ S ₄ O ₁	
Colour	Brown	
Space group	P 2 ₁ 2 ₁ 2 ₁	
a, Å	11.852(5)	
b, Å	17.782(7)	
c, Å	22.518(6)	
α, deg	90	
β, deg	90	
γ, deg	90	
V, Å ³	4746.99	
Z	4	
F(000)	2056	
d _{calc} , g/cm ³	1.40	
Cryst. size, mm	0.52 x 0.42 x 0.30	
μ (Mo-K _{α}), cm ⁻¹	7.24	
Orientation reflections: no.;range	29 ; 16.74 \leq 20 \leq 25.47	
Data measured	4816	
Unique data	3317	
No. of unique with I≥3.0σ(I)	2757	
No. of parameters	267	
R	0.0762	
R _w	0.0810	
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.003578F^2$	
Largest shift/esd, final cycle	0.001	
Largest peak, e/ų	1.02	
Standards showed a drop of 20% during data collection		
No empirical Absorbtion correction was perforn	ned	

Appendix 1.8.b Atomic coordinates $(x10^4)$ and equivalent isotropic displacement parameters $(Å^2x10^3)$

C(71)	3342(16)	3456(10)	1857(7)	41(4)
C(72)	4319(20)	3839(14)	2084(10)	66(6)
C(73)	4935(25)	3491(15)	2496(13)	83(7)
C(74)	4643(28)	2799(17)	2689(12)	95(9)
C(75)	3694(26)	2431(17)	2452(13)	96(9)
C(76)	3061(22)	2774(13)	2003(10)	69(6)
0(90)	1728(29)	845(19)	1635(14)	84(9)
0(91)	783(30)	1122(18)	617(15)	86(10)
C(90)	681(54)	917(33)	1836(26)	97(18)
C(91)	-415(43)	1186(26)	1103(19)	68(12)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized $\rm U_{ij}$ tensor

Appendix 1.8.c Bond lengths (Å)

$\begin{array}{llllllllllllllllllllllllllllllllllll$	2.625 2.533 2.147 2.740 2.483 2.169 2.742 2.755 2.773 2.298 2.451 2.524 2.484 2.461 2.484 2.421 2.380 2.332 2.380 2.334 2.420 2.386 2.300 2.5000 2.5000	<pre>(3) (5) (13) (15) (6) (13) (14) (21) (20) (26) (34) (30) (24) (23) (22) (23) (38) (51) (34) (38) (43) (37) (50) (52) (25) (32) (33) (29) (35) (35) (29)</pre>	$\begin{array}{l} \text{Mo}(1) - S(1) \\ \text{Mo}(1) - N(3) \\ \text{Mo}(2) - S(3) \\ \text{Mo}(2) - N(3) \\ \text{Mo}(2) - N(5) \\ \text{S}(1) - C(1) \\ \text{S}(3) - C(6) \\ \text{O}(1) - C(11) \\ \text{N}(1) - C(2) \\ \text{N}(2) - C(6) \\ \text{C}(31) - C(32) \\ \text{C}(32) - C(33) \\ \text{C}(34) - C(35) \\ \text{C}(41) - C(42) \\ \text{C}(42) - C(43) \\ \text{C}(44) - C(45) \\ \text{C}(51) - C(52) \\ \text{C}(52) - C(53) \\ \text{C}(54) - C(55) \\ \text{C}(61) - C(62) \\ \text{C}(62) - C(63) \\ \text{C}(64) - C(65) \\ \text{C}(71) - C(72) \\ \text{C}(72) - C(73) \\ \end{array}$	2.466 1.973 2.386 2.546 1.991 2.338 1.712 1.701 1.211 1.572 1.262 1.420 1.386 1.365 1.3473 1.526 1.399 1.395 1.301 1.342 1.496 1.208 1.383 1.354 1.384 1.384 1.289 1.334	<pre>(6) (15) (14) (5) (14) (21) (22) (20) (31) (22) (20) (31) (20) (22) (23) (47) (37) (32) (36) (44) (31) (46) (50) (26) (31) (37) (32) (34) (36) (29) (36)</pre>
$\begin{array}{c} C(73) - C(76) & 1 \\ C(71) - C(76) & 1 \\ C(73) - C(74) & 1 \\ C(75) - C(76) & 1 \\ O(91) - C(91) & 1 \end{array}$		(29) (41) (38) (60)	C(72) - C(73) C(74) - C(75) O(90) - C(90)	1.334 1.406 1.327	(29) (36) (44) (72)
Appendix 1.8.d Bor Mo(2)-Mo(1)-S(1	nd angle	es(°) 128.9(2)	Mo(2)-Mo(1)-S	(2)	136.8(1)
$\begin{array}{c} S(1) - Mo(1) - S(2) \\ S(1) - Mo(1) - N(3) \\ Mo(2) - Mo(1) - N(4) \\ S(2) - Mo(1) - N(4) \\ Mo(2) - Mo(1) - N(5) \\ S(2) - Mo(1) - N(5) \\ N(4) - Mo(1) - N(5) \\ S(1) - Mo(1) - N(7) \\ N(3) - Mo(1) - N(7) \end{array}$	L) 5)	70.6(2) 85.4(5) 52.9(4) 91.9(4) 55.4(3) 85.7(4) 56.9(5) 103.1(5) 103.2(7)	$\begin{array}{c} Mo(2) - Mo(1) - N \\ S(2) - Mo(1) - N \\ S(1) - Mo(1) - N \\ S(2) - M \\ S(2$	(3) 3) 4) 5) 5) (7) 7) 7)	48.8(4) 148.6(5) 153.0(4) 101.8(6) 100.2(4) 78.6(6) 108.1(5) 101.9(5) 100.5(6)

$N_{1}(\Gamma) = N_{2}(1) = N_{1}(7)$	156 7161	$M_{2}(1) = M_{2}(2) = C(2)$	126 7/1)
N(5) - MO(1) - N(7)	150.7(0)	MO(1) - MO(2) - S(3)	130.7(1)
Mo(1) - Mo(2) - S(4)	128.4(1)	S(3) - MO(2) - S(4)	70.2(2)
Mo(1)-Mo(2)-N(3)	48.2(4)	S(3)-Mo(2)-N(3)	152.7(5)
S(4)-Mo(2)-N(3)	88.0(5)	Mo(1) - Mo(2) - N(4)	52.2(3)
S(3) - Mo(2) - N(4)	90.6(4)	S(4) - Mo(2) - N(4)	147.6(4)
N(3) - MO(2) - N(4)	100.4(6)	$M_{O}(1) - M_{O}(2) - N(5)$	57.1(3)
S(3) - MO(2) - N(5)	85 8(4)	S(4) - MO(2) - N(5)	$94 \ 3(4)$
$N(2) M_{0}(2) N(5)$	70.4(5)	$N(4) M_{0}(2) N(5)$	57 1 (5)
N(3) - MO(2) - N(3)	19.4(J)	N(4) - MO(2) - N(3)	17.4(3)
MO(1) - MO(2) - N(6)	105.8(5)	S(3) - MO(2) - N(6)	99.8(5)
S(4) - Mo(2) - N(6)	110.9(5)	N(3) - MO(2) - N(6)	103.4(7)
N(4)-Mo(2)-N(6)	97.6(6)	N(5)-Mo(2)-N(6)	154.7(6)
Mo(1) - S(1) - C(1)	89.7(7)	Mo(1) - S(2) - C(1)	86.6(7)
Mo(2)-S(3)-C(6)	87.5(7)	Mo(2)-S(4)-C(6)	88.0(7)
C(1) - N(1) - C(2)	120.6(18)	C(1) - N(1) - C(4)	120.7(19)
C(2) - N(1) - C(4)	118.7(18)	C(6) - N(2) - C(7)	121.8(19)
C(6) = N(2) = C(9)	123 6(18)	C(7) = N(2) = C(9)	113 9(18)
$M_{0}(1) = M_{1}(2) = M_{0}(2)$	92 9(6)	$M_{O}(1) = N(3) = C(31)$	133 7(12)
$M_{O}(1) = N(3) = MO(2)$ $M_{O}(2) = N(3) = O(21)$	140 2(12)	MO(1) N(3) C(31) MO(1) N(4) MO(2)	$74 \circ (12)$
MO(2) = N(3) = C(31)	140.2(12)	MO(1) - N(4) - MO(2)	74.5(4)
MO(1) - N(4) - C(11)	96.3(10)	MO(2) = N(4) = C(11)	90.0(10) 120.0(10)
MO(1) - N(4) - C(41)	130.3(10)	MO(2) - N(4) - C(41)	129.8(10)
C(11) - N(4) - C(41)	117.7(13)	Mo(1) - N(5) - Mo(2)	67.5(4)
Mo(1) - N(5) - C(11)	87.2(10)	Mo(2)-N(5)-C(11)	90.4(9)
Mo(1)-N(5)-C(51)	139.1(11)	Mo(2)-N(5)-C(51)	132.9(11)
C(11)-N(5)-C(51)	121.6(13)	Mo(2)-N(6)-C(61)	168.4(15)
Mo(1)-N(7)-C(71)	175.1(13)	S(1)-C(1)-S(2)	112.9(11)
S(1) - C(1) - N(1)	123.7(16)	S(2) - C(1) - N(1)	123.0(16)
N(1) - C(2) - C(3)	115.1(22)	N(1) - C(4) - C(5)	113.6(22)
S(3) - C(6) - S(4)	112.7(11)	S(3) - C(6) - N(2)	126.0(16)
S(4) - C(6) - N(2)	121 3(16)	N(2) - C(7) - C(8)	112 0(20)
N(2) = C(9) = C(10)	116 3(25)	O(1) = C(11) = N(4)	127 1(15)
N(2) = C(3) = C(10)	121 2(15)	N(4) = C(11) N(5)	101 3(13)
V(1) = C(11) = N(3)	101.5(10)	N(4) = C(11) = N(3)	110 - 5(10)
N(3) = C(31) = C(32)	121.5(19)	N(3) = C(31) = C(30)	119.5(19)
C(32) - C(31) - C(36)	118.8(21)	C(31) - C(32) - C(33)	122.2(24)
C(32) - C(33) - C(34)	116.9(24)	C(33) - C(34) - C(35)	125.9(28)
C(34)-C(35)-C(36)	118.9(29)	C(31)-C(36)-C(35)	117.1(24)
N(4) - C(41) - C(42)	119.4(18)	N(4)-C(41)-C(46)	120.7(19)
C(42)-C(41)-C(46)	119.8(23)	C(41)-C(42)-C(43)	123.0(25)
C(42)-C(43)-C(44)	110.8(29)	C(43)-C(44)-C(45)	126.0(36)
C(44)-C(45)-C(46)	120.8(35)	C(41)-C(46)-C(45)	119.5(28)
N(5) - C(51) - C(52)	119.7(15)	N(5)-C(51)-C(56)	120.8(16)
C(52) - C(51) - C(56)	118.5(17)	C(51) - C(52) - C(53)	124.1(18)
C(52) - C(53) - C(54)	116.7(22)	C(53) - C(54) - C(55)	117.9(23)
C(54) - C(55) - C(56)	125 7(23)	C(51) = C(56) = C(55)	1167(20)
N(6) = C(61) = C(62)	120.6(18)	N(6) = C(61) = C(66)	120.7(20)
R(0) = C(01) = C(02)	110 2(20)	C(61) C(62) C(63)	110 1(22)
C(02) - C(01) - C(00)	120.2(20)	C(01) - C(02) - C(03)	110 0/04
C(02) - C(03) - C(04)	$\pm 20.7(24)$	C(03) - C(04) - C(03)	110.7(24)
U(04) - U(05) - U(06)	$\pm 24. \pm (24)$	C(bI) - C(bb) - C(b5)	$\pm \pm 0.\pm (22)$
N(7) - C(71) - C(72)	119.3(16)	N(7) - C(71) - C(76)	116./(18)
C(72) - C(71) - C(76)	124.0(19)	C(71) - C(72) - C(73)	117.9(22)
C(72)-C(73)-C(74)	120.4(27)	C(73)-C(74)-C(75)	120.5(28)
C(74)-C(75)-C(76)	120.0(27)	C(71)-C(76)-C(75)	116.9(23)

Appendix 1.9.a

Crystallographic data for $[Mo_2(O)(\mu-NPh)_2(S_2CNEt_2)_3][BF_4]$ 4.11a

Formula	$Mo_2 C_{27} H_{42} N_5 S_6 B_1 F_4$
Colour	Red
Space group	ΡĪ
a, Å	11.058(3)
b, Å	14.773(4)
c, Å	14.853(4)
α, deg	63.24(2)
β, deg	69.27(2)
γ, deg	69.93(2)
V, Å ³	1976.46
Z	2
F(000)	936
d _{calc} , g/cm ³	1.55
Cryst. size, mm	0.52 x 0.16 x 0.26
μ (Mo-K _{α}), cm ⁻¹	9.70
Orientation reflections: no.;range	24 ; 11.27 $\leq 2\theta \leq 21.15$
Data measured	7390
Unique data	7161
No. of unique with I≥3.0σ(I)	3569
No. of parameters	415
R	0.0684
R _w	0.0719
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.001945F^2$
Largest shift/esd, final cycle	0.002
Largest peak, e/ų	1.07

(x10⁴) Appendix 1.9.b Atomic coordinates and equivalent isotropic displacement parameters (Å²x10³) U(eq)* x z Y 4056(1) 2846(1) 3409(1) 36(1) Mo(1) Mo(2) 4614(1)4429(1) 3462(1) 42(1) 4854(3) 44(2) S(1) 3376(3)1202(3)S(2) 1634(3)3166(3) 3999(3) 56(2) S(3) 6124(3)1806(3)2749(3) 49(2) S(4) 3707(3) 2252(3)2155(3)48(2)S(5) 6782(4)4290(3)3675(3) 67(2)S(6) 5693(4) 5730(3) 1920(3)58(2) 5526(9) N(1) 705(12) 1487(9) 54(6)N(2) 5933(11) 1007(8)1508(8) 47(6) N(5) 4846(10) 2884(8) 4364(8) 41(5)N(4) 3883(10) 4284(7) 2451(8) 44(6) 2075(11) 8006(13) N(3) 5783(9) 65(8) 0(1)3392(10) 5015(7)4181(8) 62(6)C(1) 1765(12) 4871(11) 48(8)1868(11)C(2) 849(14) 444(10)6349(11) 52(7) C(3) 630(16) -378(12)6111(14)73(10)65(9) -644(13)2104(12)5505(14)C(4) C(5) -1107(17)2680(16) 6222(18) 103(15) C(6) 5342(13) 1599(9)2028(10) 41(7)C(7) 7360(13) 444(11)1427(12) 56(8) C(8) 7483(17) -722(11)2116(13)69(10)893(10) 57(8) C(9) 5223(16) 879(12) C(10) 5429(19) 1609(13) -200(12) 75(10) 6995(15) 2514(13) C(11) 5315(11) 60(9) 1068(15) 76(11) C(12) 8161(18) 6661(13) 169(18) 111(16) C(13) 8783 (22) 6367(17) C(14) 9149(18) 5367(14) 2596(16) 89(12) 3274(17) C(15) 8947(18) 5909(16) 97(14)C(20) 5351(13) 2291(10)5253(10) 42(7)C(21) 5482(11) 47(7)5961(13) 1236(10)C(22) 6414(14)691(10) 6372(10) 46(7)7060(12) 61(9) C(23) 6271(14)1132(12)60(9) C(24) 5654(16) 2154(13) 6838(11) C(25) 5957(12) 5177(14) 2747(11) 54(8)C(30) 3271(12) 5060(10) 1688(11)44(7)C(31) 2548(13) 6012(11) 1778(12) 55(8) C(32) 999(14) 66(9) 1953(14) 6818(12) C(33) 2072(16)6704(14)111(14)69(10)5753(14) -1(13)C(34) 2814(18)72(10)774(13) C(35) 3406(17) 4938(12) 67(9) B(1) 1300(26) 638(21) 900(26) 103(18) F(1) 1303(13)-369(9)1280(10) 125(8)F(2) 2476(14)842(11) 244(13)151(11)F(3) 434(21) 1220(13) 443(30)339(32) 1230(36) 943(18) 1593(16) 301(28) F(4)

Appendix 1.9.cBond leng $Mo(1) - Mo(2)$ 2.654 $Mo(1) - S(2)$ 2.451 $Mo(1) - S(4)$ 2.568 $Mo(1) - N(4)$ 1.941 $Mo(2) - S(6)$ 2.458 $Mo(2) - N(4)$ 2.055 $S(1) - C(1)$ 1.712 $S(3) - C(6)$ 1.766 $S(5) - C(11)$ 1.711 $N(1) - C(4)$ 1.461 $N(2) - C(7)$ 1.500 $N(1) - C(4)$ 1.462 $N(3) - C(14)$ 1.519 $C(4) - C(5)$ 1.500 $C(9) - C(10)$ 1.477 $C(14) - C(15)$ 1.466 $C(20) - C(25)$ 1.307 $C(30) - C(35)$ 1.400 $C(32) - C(33)$ 1.360 $C(34) - C(35)$ 1.396 $B(1) - F(2)$ 1.355 $B(1) - F(4)$ 1.267	ths $(Å)$ (2) (4) (6) (9) (4) (15) (12) (14) (17) (17) (17) (17) (17) (17) (17) (17	$\begin{array}{l} \text{Mo}(1) - \text{S}(1) \\ \text{Mo}(1) - \text{N}(3) \\ \text{Mo}(2) - \text{S}(3) \\ \text{Mo}(2) - \text{N}(5) \\ \text{Mo}(2) - \text{N}(5) \\ \text{Mo}(2) - \text{O}(1) \\ \text{S}(2) - \text{C}(1) \\ \text{S}(2) - \text{C}(1) \\ \text{S}(4) - \text{C}(6) \\ \text{S}(6) - \text{C}(11) \\ \text{N}(1) - \text{C}(2) \\ \text{N}(2) - \text{C}(6) \\ \text{N}(2) - \text{C}(30) \\ \text{N}(3) - \text{C}(12) \\ \text{C}(2) - \text{C}(3) \\ \text{C}(7) - \text{C}(8) \\ \text{C}(12) - \text{C}(13) \\ \text{C}(20) - \text{C}(21) \\ \text{C}(21) - \text{C}(22) \\ \text{C}(23) - \text{C}(24) \\ \text{C}(30) - \text{C}(31) \\ \text{C}(31) - \text{C}(32) \\ \text{C}(33) - \text{C}(34) \\ \text{B}(1) - \text{F}(1) \\ \text{B}(1) - \text{F}(3) \end{array}$	2.547 2.431 1.939 2.455 2.039 1.650 1.720 1.741 1.472 1.283 1.501 1.376 1.474 1.518 1.545 1.453 1.402 1.371 1.364 1.398 1.396 1.412 1.332 1.219	<pre>(3) (4) (15) (6) (9) (10) (13) (13) (20) (15) (20) (26) (16) (19) (30) (19) (35) (17) (21) (23) (20) (21) (27) (32) (42)</pre>
Appendix 1.10.d Bond and Mo(2) -Mo(1) - S(1) S(1) -Mo(1) - S(2) S(1) -Mo(1) - S(3) Mo(2) -Mo(1) - S(4) S(2) -Mo(1) -N(5) S(2) -Mo(1) -N(5) S(4) -Mo(1) -N(5) S(1) -Mo(1) -N(4) S(3) -Mo(1) -N(4) N(5) -Mo(1) -N(4) Mo(1) -Mo(2) -S(6) Mo(1) -Mo(2) -N(5) S(6) -Mo(2) -N(5) S(6) -Mo(2) -N(4) N(5) -Mo(2) -N(4) S(5) -Mo(2) -N(4) S(5) -Mo(2) -O(1) Mo(1) -S(1) -C(1) Mo(1) -S(3) -C(6) Mo(2) -S(5) -C(11) C(1) -N(1) -C(2) C(2) -N(1) -C(4) C(6) -N(2) -C(9) Mo(1) -N(5) -Mo(2) Mo(1) -N(5) -C(20) Mo(1) -N(4) -C(30) C(11) -N(3) -C(12) C(12) -N(3) -C(14) S(3) -C(6) -S(4) S(4) -C(6) -N(2) N(2) -C(9) -C(10) S(5) -C(11) -N(3)	ples (°) 131.4(1) 70.5(1) 90.1(1) 141.6(1) 84.2(2) 49.8(3) 111.3(3) 159.8(3) 159.8(3) 159.0(3) 109.6(3) 99.9(5) 123.5(1) 46.6(4) 143.8(3) 137.9(3) 93.0(5) 111.6(5) 105.1(4) 87.4(4) 90.9(4) 88.3(7) 121.3(11) 116.7(11) 120.5(12) 83.7(4) 131.5(12) 145.7(12) 125.1(16) 115.6(14) 124.9(9) 114.2(15) 111.3(9) 125.6(14) 13.0(16) 126.6(14)	$\begin{array}{l} \text{Mo}(2) - \text{Mo}(1) - \text{S} \\ \text{Mo}(2) - \text{Mo}(1) - \text{S} \\ \text{S}(2) - \text{Mo}(1) - \text{S}(2) \\ \text{S}(3) - \text{Mo}(1) - \text{S}(2) \\ \text{S}(3) - \text{Mo}(1) - \text{S}(2) \\ \text{S}(3) - \text{Mo}(1) - \text{N}(2) \\ \text{S}(2) - \text{Mo}(1) - \text{N}(2) \\ \text{S}(3) - \text{Mo}(2) - \text{S}(3) \\ \text{S}(5) - \text{Mo}(2) - \text{S}(3) \\ \text{S}(5) - \text{Mo}(2) - \text{N}(2) \\ \text{S}(5) - \text{Mo}(2) - \text{N}(2) \\ \text{S}(6) - \text{Mo}(2) - \text{N}(2) \\ \text{S}(6) - \text{Mo}(2) - \text{O}(2) \\ \text{Mo}(1) - \text{Mo}(2) - \text{O}(2) \\ \text{Mo}(1) - \text{Mo}(2) - \text{O}(2) \\ \text{Mo}(1) - \text{S}(2) - \text{C}(2) \\ \text{Mo}(1) - \text{S}(2) - \text{C}(2) \\ \text{Mo}(1) - \text{S}(4) - \text{C}(2) \\ \text{Mo}(1) - \text{S}(4) - \text{C}(2) \\ \text{Mo}(1) - \text{N}(1) - \text{C}(4) \\ \text{C}(6) - \text{N}(2) - \text{C}(7) \\ \text{Mo}(1) - \text{N}(4) - \text{Mo} \\ \text{Mo}(2) - \text{N}(4) - \text{C}(2) \\ \text{Mo}(1) - \text{N}(4) - \text{Mo} \\ \text{Mo}(2) - \text{N}(4) - \text{C}(2) \\ \text{S}(3) - \text{C}(1) - \text{S}(2) \\ \text{S}(3) - \text{C}(6) - \text{N}(2) \\ \text{N}(1) - \text{C}(4) - \text{C}(5) \\ \text{S}(3) - \text{C}(6) - \text{N}(2) \\ \text{N}(2) - \text{C}(7) - \text{C}(8) \\ \text{S}(5) - \text{C}(11) - \text{S}(6) \\ \text{S}(6) - \text{C}(11) - \text{N}(3) \\ \text{S}(6) - \text{C}(11) - \text{N}(3) \\ \text{S}(6) - \text{C}(1) - \text{N}(2) \\ \text{S}(6) - \text{C}(1) - \text{S}(2) \\ \text{S}(6) - \text{C}(1) - \text{N}(2) \\ \text{S}$	$(2) \\ (3) \\ 3) \\ 4) \\ 5) \\ 5) \\ (4) \\ 4) \\ (5) \\ 5) \\ (4) \\ (1) \\ 1) \\ (1) \\ 1) \\ (1) \\ 1) \\ (2) \\ 30) \\ (2) \\ 30) \\ 14) \\) \\) \\) \\) \\) \\) \\) \\) \\) \\$	$\begin{array}{c} 103.1(1)\\ 107.9(1)\\ 148.9(2)\\ 86.8(1)\\ 70.2(1)\\ 86.5(3)\\ 90.7(3)\\ 50.3(4)\\ 88.6(3)\\ 93.0(5)\\ 121.1(1)\\ 71.5(1)\\ 86.3(4)\\ 46.6(3)\\ 85.6(3)\\ 113.2(4)\\ 109.5(3)\\ 109.1(5)\\ 89.5(4)\\ 87.5(6)\\ 87.6(5)\\ 121.9(10)\\ 123.7(16)\\ 115.7(13)\\ 144.9(10)\\ 83.2(4)\\ 128.3(11)\\ 119.2(12)\\ 112.6(7)\\ 122.4(9)\\ 10.8(18)\\ 123.0(11)\\ 110.9(12)\\ 112.5(10)\\ 120.9(11)\\ \end{array}$

N(3) - C(12) - C(13)	114.8(16)	N(3) - C(14) - C(15)	110.8(14)
N(5)-C(20)-C(21)	120.9(16)	N(5)-C(20)-C(25)	119.6(11)
C(21)-C(20)-C(25)	119.4(14)	C(20)-C(21)-C(22)	118.3(17)
C(21)-C(22)-C(23)	122.9(13)	C(22)-C(23)-C(24)	118.2(15)
C(23)-C(24)-C(25)	121.9(20)	C(20)-C(25)-C(24)	119.3(14)
N(4) - C(30) - C(31)	121.4(16)	N(4)-C(30)-C(35)	120.8(13)
C(31)-C(30)-C(35)	117.7(13)	C(30)-C(31)-C(32)	122.1(18)
C(31)-C(32)-C(33)	120.5(16)	C(32)-C(33)-C(34)	118.2(15)
C(33)-C(34)-C(35)	121.9(20)	C(30)-C(35)-C(34)	119.4(16)
F(1) - B(1) - F(2)	111.8(21)	F(1) - B(1) - F(3)	115.3(34)
F(2) - B(1) - F(3)	107.3(24)	F(1) - B(1) - F(4)	112.2(25)
F(2) - B(1) - F(4)	101.1(33)	F(3) - B(1) - F(4)	108.0(32)

Appendix 1.10.a

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Crystallographic data for [{Mo(\mu-N-o-Tolyl)(N-o-Tolyl)(S<sub>2</sub>CNEt<sub>2</sub>)}<sub>2</sub>]
4.6c
```

Formula	Mo ₂ C ₃₈ H ₄₈ N ₆ S ₄
Colour	Orange
Space group	C 2/c
a, Å	20.639(3)
b, Å	10.810(1)
c, Å	20.425(2)
α, deg	90
β, deg	113.21(1)
γ, deg	90
V, Å ³	4188.34
Z	4
F(000)	1864
d _{calc} , g/cm ³	1.44
Cryst. size, mm	0.80 x 0.40 x 0.40
μ (Mo-K _a), cm ⁻¹	8.09
Orientation reflections: no.;range	29 ; 15.16 ≤ 2θ ≤ 31.22
Data measured	5871
Unique data	5754
No. of unique with I≥3.0σ(I)	3030
No. of parameters	246
R	0.0351
R _w	0.0392
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.000375F^2$
Largest shift/esd, final cycle	0.001
Largest peak, e/Å ³	0.61

The methyl substituent on the phenyl imido ligands exhibit a disorder over the ortho sites. Occupancies were refined [C(17) 60%, C(17A) 40%, C(27) 62%, C(27A) 38%] but fixed in the final cycle of least squares refinement. In the space group Cc such a disorder need not be present. However, refinement in that non-centrosymmetric space group gave significant correlation without resolving the problem. Hence, we report the structure in the higher symmetry space group C 2/c

Appendix 1.10.b Atomic coordinates $(x10^4)$ and equivalent isotropic displacement parameters $(Å^2x10^3)$

	x	У	Z	U(eq)*
Mo(1)	664(1)	2328(1)	2951(1)	38(1)
S(1)	1742(1)	3344(1)	2951(1)	65(1)
S(2)	1273(1)	3445(1)	4100(1)	54(1)
N(1)	2571(2)	4142(3)	4244(2)	60(1)
N(2)	946(2)	803(3)	3144(2)	50(1)
N(3)	224(2)	2657(3)	1926(2)	44(1)
C(1)	1955(2)	3697(3)	3830(2)	50(1)
C(2)	3133(2)	4328(5)	3980(3)	80(2)
C(4)	2731(3)	4516(5)	4984(2)	70(2)
C(3)	3598(3)	3218(7)	4093(4)	107(3)
C(5)	2593(3)	5886(6)	5024(3)	90(3)
C(11)	423(2)	2918(4)	1356(2)	55(2)
C(12)	571(3)	4107(6)	1211(3)	84(3)
C(13)	754(4)	4310(9)	631(5)	121(4)
C(14)	797(4)	3401(13)	227(5)	149(6)
C(15)	634(3)	2208(10)	338(3)	124(4)
C(16)	447(3)	1938(7)	910(3)	79(2)
C(17)	514(5)	5089(8)	1568(6)	85(5)
C(17A)	254(7)	872(12)	980(7)	70(5)
C(21)	1120(3)	-430(4)	3144(2)	62(2)
C(22)	1753(4)	-737(5)	3024(3)	92(3)
C(23)	1898(5)	-1987(8)	3030(4)	134(5)
C(24)	1487(6)	-2838(7)	3131(4)	125(5)
C(25)	925(6)	-2612(7)	3265(4)	121(4)
C(26)	724(4)	-1324(6)	3269(3)	92(3)
C(27)	2225(5)	182(9)	2990(6)	92(5)
C(27A)	269(8)	-1163(13)	3483(8)	78(6)

Appendix 1.10.c Bond lengths (Å)

2.481	(1)
1.741	(3)
2.633	(1)
1.715	(4)
1.310	(5)
1.471	(6)
1.407	(6)
1.497	(9)
1.379	(8)
1.395	(12)
1.309	(16)
1.398	(10)
1.459	(10)
1.383	(11)
1.322	(15)
1.454	(10)
	2.481 1.741 2.633 1.715 1.310 1.471 1.407 1.397 1.395 1.309 1.398 1.459 1.383 1.322 1.454

Appendix 1.10.d Bond angles (°) S(1) - MO(1) - S(2) 70.5(1)

S(I) - MO(I) - S(Z)	/0.5(1)
S(2) - Mo(1) - N(2)	104.2(1)
S(2) - Mo(1) - N(3)	140.1(1)
S(1)-Mo(1)-Mo(1A)	133.4(1)
N(2) - Mo(1) - Mo(1A)	108.7(1)
S(1) - Mo(1) - N(3A)	142.8(1)
N(2) - Mo(1) - N(3A)	112.6(2)
Mo(1A) - Mo(1) - N(3A)	47.7(1)
$M_0(1) - S(2) - C(1)$	87.0(1)
C(1) - N(1) - C(4)	122.0(4)
Mo(1) - N(2) - C(21)	167.9(3)
Mo(1) - N(3) - Mo(1A)	83.9(1)
S(1) - C(1) - S(2)	113.3(2)
S(2) - C(1) - N(1)	124.0(4)
N(1) - C(4) - C(5)	110.7(4)
N(3) - C(11) - C(16)	118.7(4)
C(11) - C(12) - C(13)	119.1(7)
C(13) - C(12) - C(17)	117.0(8)
C(13) - C(14) - C(15)	121.3(10)
C(11) - C(16) - C(15)	118.3(7)
C(15) - C(16) - C(17A)	119.7(9)
N(2) - C(21) - C(26)	120.8(5)
C(21) - C(22) - C(23)	115.3(7)
C(23) - C(22) - C(27)	122.4(8)
C(23) - C(24) - C(25)	125.2(8)
C(21) - C(26) - C(25)	119.2(8)
C(25) - C(26) - C(27A)	114.2(10)
·····	(10)

$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccc} (1/A) & 1.246 & (1) \\ (2(26) & 1.354 & (9) \\ (2(27) & 1.414 & (1) \\ (2(25) & 1.315 & (1) \\ (2(27A) & 1.194 & (2) \\ (2(17A) & -N(3) & 1) \\ (2(17A) & -N(3) & 1) \\ (2(17A) & -N(3) & 1) \\ (1(1) - N(1) & 1) \\ (1(1) - C(12) & 1) \\ (2(12) - C(17) & 1) \\ (2(15) - C(16) & 1) \\ \end{array}$
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Appendix 1.11.a Crystallographic data for $[Mo(O)(\mu-N-o-Tolyl)(S_2CNEt_2)]_2$ 4.5c

Formula	Mo ₂ C ₂₄ H ₃₄ N ₄ S ₄ O ₂
Colour	Yellow
Space group	P2 ₁ /c
a, Å	9.963(2)
b, Å	13.706(2)
c, Å	22.213(4)
α, deg	90
β, deg	97.85(2)
γ, deg	90
V, Å ³	3004.77
Z	4
F(000)	1480
d _{calc} , g/cm ³	1.61
Cryst. size, mm	0.35 x 0.55 x 0.25
μ (Mo-K _{α}), cm ⁻¹	11.10
Orientation reflections: no.;range	30 ; 21.25 \leq 2 θ \leq 39.43
Data measured	5899
Unique data	5845
No. of unique with I≥3.0σ(I)	4308
No. of parameters	325
R	0.0323
R _w	0.0411
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.002817F^2$
Largest shift/esd, final cycle	0.001
Largest peak, e/ų	0.37

Mo(1) Mo(2) S(1) S(2) S(3) S(4) N(1) N(2) N(3) N(4) O(1) O(2) C(1) C(2) C(1) C(2) C(1) C(2) C(3) C(4) C(5) C(6) C(7) C(6) C(7) C(8) C(9) C(11) C(12) C(13)	x 2842(1) 1787(1) 5177(1) 2919(1) 2953(1) 486(1) 5206(3) 1557(4) 3605(3) 1408(3) 2151(3) 786(3) 4538(4) 6589(5) 6568(6) 4604(5) 4884(6) 1643(4) 2538(5) 3424(6) 380(5) -669(6) 4835(4) 4949(5) 6217(5)	Y 7742(1) 7596(1) 7713(1) 6562(1) 7228(1) 6325(1) 6715(3) 5951(3) 8000(2) 6895(3) 8763(2) 8589(2) 6962(3) 7062(4) 7929(6) 6079(3) 5015(4) 6433(3) 6084(4) 5198(5) 5316(3) 5846(4) 8274(3) 9188(3) 9427(4)	z 4019(1) 2872(1) 4590(1) 4858(1) 1990(1) 2242(1) 5643(1) 1226(1) 3266(1) 3266(1) 3599(1) 4271(1) 2738(1) 5107(2) 5853(2) 6276(3) 6059(2) 5964(2) 1736(2) 789(2) 748(3) 1025(2) 599(3) 3067(2) 2802(2) 2621(2)	U(eq)* 32(1) 34(1) 48(1) 41(1) 47(1) 50(1) 41(1) 48(1) 36(1) 36(1) 52(1) 55(1) 36(1) 60(2) 87(3) 50(1) 70(2) 39(1) 59(2) 79(2) 57(2) 79(2) 38(1) 46(1) 58(2)		
C(9) C(10) C(11)	380(5) -669(6) 4835(4)	5316(3) 5846(4) 8274(3)	1025(2) 599(3) 3067(2)	57(2) 79(2) 38(1)		
C(12) C(13) C(14)	4949(5) 6217(5) 7298(5) 7152(5)	9188(3) 9427(4) 8797(4) 7002(5)	2802(2) 2621(2) 2693(2)	46(1) 58(2) 64(2)		
C(15) C(16) C(17) C(21)	5929(4) 3788(6) 651(4)	7642(3) 9885(3) 6088(3)	3128 (2) 2730 (3) 3764 (2)	50(2) 50(2) 72(2) 41(1)		
C(22) C(23) C(24)	-353(4) -1012(5) -739(5)	6198(4) 5345(5) 4447(5)	4140(2) 4295(2) 4071(3)	54(2) 76(2) 72(2)		
C(25) C(26) C(27)	229(5) 919(4) -677(6)	4349(4) 5168(3) 7181(5)	3693(2) 3550(2) 4384(3)	58(2) 46(1) 78(2)		

Appendix 1.11.b Atomic coordinates $(x10^4)$ and equivalent isotropic displacement parameters $(Å^2x10^3)$

Appendix 1.11.c Bond leng	gths (Å)			
Appendix 1.11.cBond leng $Mo(1) - Mo(2)$ 2.628 $Mo(1) - S(2)$ 2.461 $Mo(1) - N(4)$ 1.974 $Mo(2) - S(3)$ 2.462 $Mo(2) - N(3)$ 1.980 $Mo(2) - O(2)$ 1.689 $S(2) - C(1)$ 1.722 $S(4) - C(6)$ 1.723 $N(1) - C(2)$ 1.472 $N(2) - C(6)$ 1.304 $N(2) - C(9)$ 1.479 $N(4) - C(21)$ 1.415 $C(4) - C(5)$ 1.504 $C(9) - C(10)$ 1.498 $C(11) - C(16)$ 1.385 $C(12) - C(17)$ 1.492 $C(14) - C(15)$ 1.362 $C(21) - C(22)$ 1.396 $C(22) - C(24)$ 1.368 $C(25) - C(26)$ 1.376	gths (Å) (1) (1) (3) (1) (3) (4) (6) (5) (6) (7) (6) (7) (6) (7) (6) (7) (6) (7) <	$\begin{array}{l} \text{Mo}(1) - S(1) \\ \text{Mo}(1) - N(3) \\ \text{Mo}(1) - O(1) \\ \text{Mo}(2) - S(4) \\ \text{Mo}(2) - N(4) \\ \text{S}(1) - C(1) \\ \text{S}(3) - C(6) \\ \text{N}(1) - C(1) \\ \text{N}(1) - C(1) \\ \text{N}(2) - C(7) \\ \text{N}(3) - C(11) \\ \text{C}(2) - C(3) \\ \text{C}(7) - C(8) \\ \text{C}(11) - C(12) \\ \text{C}(12) - C(13) \\ \text{C}(12) - C(13) \\ \text{C}(13) - C(14) \\ \text{C}(15) - C(16) \\ \text{C}(21) - C(26) \\ \text{C}(22) - C(27) \\ \text{C}(24) - C(25) \end{array}$	2.493 1.962 1.688 2.485 1.960 1.727 1.735 1.326 1.458 1.458 1.451 1.517 1.511 1.395 1.415 1.373 1.384 1.387 1.503 1.369	<pre>(1) (3) (3) (1) (3) (4) (4) (4) (5) (6) (6) (5) (9) (8) (6) (7) (7) (7) (6) (8) (8) (8)</pre>
Appendix 1.11.d Bond and	lles (°)			
Mo(2) - Mo(1) - S(1) $S(1) - Mo(1) - S(2)$ $S(1) - Mo(1) - N(3)$ $Mo(2) - Mo(1) - N(4)$ $S(2) - Mo(1) - O(1)$ $S(2) - Mo(1) - O(1)$ $N(4) - Mo(1) - O(1)$ $Mo(1) - Mo(2) - S(4)$ $Mo(1) - Mo(2) - N(3)$ $S(3) - Mo(2) - N(3)$ $S(3) - Mo(2) - N(4)$ $N(3) - Mo(2) - N(4)$ $N(3) - Mo(2) - O(2)$ $Mo(1) - S(1) - C(1)$ $Mo(2) - S(3) - C(6)$ $C(1) - N(1) - C(2)$ $C(2) - N(1) - C(4)$ $C(6) - N(2) - C(9)$ $Mo(1) - N(3) - Mo(2)$ $Mo(2) - N(3)$ $Mo(2) - O(2)$ $Mo(1) - N(3) - Mo(2)$ $Mo(1) - N(3) - Mo(2)$ $Mo(2) - N(3) - C(11)$ $Mo(1) - N(4) - C(21)$ $S(1) - C(1) - S(2)$ $S(2) - C(1) - N(1)$ $N(1) - C(4) - C(5)$ $S(3) - C(6) - N(2)$ $N(2) - C(7) - C(8)$ $N(3) - C(11) - C(12)$ $C(12) - C(11) - C(12)$ $C(12) - C(13) - C(14)$ $C(14) - C(15) - C(16)$ $N(4) - C(21) - C(22)$ $C(22) - C(21) - C(26)$ $C(21) - C(22) - C(27)$ $C(22) - C(23) - C(24)$	$\begin{array}{c} 135.5(1)\\ 71.0(1)\\ 89.6(1)\\ 47.8(1)\\ 85.3(1)\\ 104.8(1)\\ 105.5(1)\\ 110.0(1)\\ 135.0(1)\\ 47.9(1)\\ 145.1(1)\\ 136.0(1)\\ 92.3(1)\\ 110.9(1)\\ 109.6(1)\\ 86.8(1)\\ 88.4(1)\\ 122.4(4)\\ 116.1(3)\\ 121.1(4)\\ 83.6(1)\\ 135.9(2)\\ 135.5(2)\\ 113.0(2)\\ 122.7(3)\\ 113.0(4)\\ 123.9(3)\\ 112.6(4)\\ 119.8(4)\\ 122.5(5)\\ 120.0(5)\\ 121.5(4)\\ 119.4(4)\\ 121.3(5)\\ 122.5(5)$	$ \begin{array}{l} Mo(2) - Mo(1) - S \\ Mo(2) - Mo(1) - N \\ S(2) - Mo(1) - N \\ S(2) - Mo(1) - N \\ S(1) - Mo(1) - N \\ S(1) - Mo(1) - N \\ S(1) - Mo(1) - O \\ Mo(1) - Mo(2) - S \\ S(3) - Mo(2) - S \\ S(3) - Mo(2) - N \\ S(3) - Mo(2) - N \\ S(3) - Mo(2) - N \\ S(4) - Mo(2) - O \\ S(4) - M \\ O \\ C(1) - S \\ S(4) - C \\ S(1) - C \\ Mo(1) - N \\ S(1) - C \\ S(1) - C$	(2) (3) (3) (4) (1) (2) (3) (4) (1) (2) (2) (2) (1) (1) (1) (1) (1) (1) (1) (1) (2) (1) (1) (2) (2) (2) (2) (2) (2) (2) (2) (2) (2	130.6(1) 48.5(1) 142.1(1) 142.7(1) 92.4(1) 103.9(1) 110.8(1) 128.1(1) 71.0(1) 84.6(1) 48.3(1) 88.6(1) 105.0(1) 102.4(1) 111.4(1) 87.9(1) 121.5(3) 122.4(4) 16.2(3) 140.3(2) 83.8(1) 140.3(2) 83.8(1) 140.3(2) 111.0(4) 112.4(2) 123.6(3) 111.2(4) 122.0(4) 112.5(4) 122.5(4) 112.5(4) 119.2(5) 121.5(4) 119.1(4) 120.2(5) 121.8(4) 120.

Appendix 1.12.a

Crystallographic data for $[Mo_2(\mu-S)_2(O)(N^tBu)(S_2CNEt_2)_2]$ 4.12h

Formula	$Mo_2 C_{14} H_{29} N_3 S_6 O_1$
Colour	Yellow
Space group	P 2,/a
a, Å	12.711(2)
b, Å	11.882(3)
c, Å	17.193(3)
α, deg	90
β, deg	96.91(1)
γ, deg	90
V, Å ³	2578.37
Z	4
F(000)	1288
d _{calc} , g/cm ³	1.65
Cryst. size, mm	0.50 x 0.30 x 0.22
μ (Mo-K _{α}), cm ⁻¹	14.27
Orientation reflections: no.;range	30 ; $20.92 \le 2\theta \le 29.01$
Data measured	5054
Unique data	5022
No. of unique with I≥3.0σ(I)	3963
No. of parameters	235
R	0.0345
R _w	0.0380
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.000590F^2$
Largest shift/esd, final cycle	0.001
Largest peak, e/ų	1.24

Appendix 1.12.b Atomic coordinates $(x10^4)$ and equivalent isotropic displacement parameters $(Å^2x10^3)$

	x	У	Z	U(eq)*
Mo(1)	1955(1)	2045(1)	7843(1)	39(1)
Mo(2)	1822(1)	30(1)	6968(1)	36(1)
S(1)	854(2)	2939(1)	8774(1)	56(1)
S(2)	3070(2)	2445(1)	9089(1)	50(1)
S(3)	2873(1)	-1744(1)	7064(1)	47(1)
S(4)	612(2)	-1632(1)	6929(1)	52(1)
S(5)	439(1)	995(1)	7456(1)	48(1)
S(6)	3310(1)	754(1)	7722(1)	43(1)
N(1)	2021(4)	3588(4)	10100(2)	46(2)
N(2)	1683(4)	-3592(3)	7191(2)	40(2)
N(3)	1851(4)	519(3)	6039(2)	49(2)
0(1)	2069(4)	3083(3)	7204(2)	58(2)
C(1)	1992(5)	3075(4)	9423(3)	40(2)
C(2)	3015(6)	3653(6)	10650(3)	57(3)
C(3)	3698(7)	4614(7)	10472(4)	84(4)
C(4)	1084(5)	4136(5)	10345(3)	52(3)
C(5)	474(6)	3397(6)	10824(4)	76(3)
C(6)	1723(5)	-2495(4)	7065(3)	39(2)
C(7)	2655(5)	-4242(4)	7397(3)	49(2)
C(8)	2904(6)	-4405(6)	8270(4)	74(3)
C(9)	680(5)	-4200(4)	7165(3)	54(3)
C(10)	324(6)	-4684(6)	6362(4)	70(3)
C(11)	1871(7)	1159(5)	5320(3)	68(3)
C(12)	1728(9)	325(7)	4639(4)	128(5)
C(13)	2918(8)	1746(7)	5353(5)	109(5)
C(14)	1001(8)	2014(6)	5257(4)	100(4)

Appendix 1.12.c I	Bond lengths (Å)				
Mo(1) - Mo(2) $Mo(1) - S(2)$ $Mo(1) - S(6)$ $Mo(2) - S(3)$ $Mo(2) - S(5)$ $Mo(2) - N(3)$ $S(2) - C(1)$ $S(4) - C(6)$ $N(1) - C(2)$ $N(2) - C(6)$ $N(2) - C(9)$ $C(2) - C(3)$ $C(7) - C(8)$ $C(11) - C(12)$ $C(11) - C(14)$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Mo(1)-5 Mo(1)-6 Mo(2)-5 Mo(2)-5 S(1)-C S(3)-C N(1)-C N(1)-C N(2)-C N(3)-C C(4)-C C(9)-C C(11)-0	S(1) 2 S(5) 2 O(1) 1 S(4) 2 S(6) 2 (1) 1 (6) 1 (1) 1 (4) 1 (7) 1 (11) 1 (5) 1 (10) 1 C(13) 1	.485 (2) .326 (2) .670 (4) .499 (2) .326 (2) .726 (6) .713 (6) .311 (6) .463 (8) .464 (8) .464 (8) .454 (7) .483 (10) .515 (8) .499 (13)	
Appendix 1.12.d $M_{O}(2) - M_{O}(1) - S(2)$ $S(1) - M_{O}(1) - S(2)$ $S(1) - M_{O}(1) - S(2)$ $M_{O}(2) - M_{O}(1) - O(1)$ $S(6) - M_{O}(1) - O(1)$ $S(6) - M_{O}(1) - O(1)$ $M_{O}(1) - M_{O}(2) - S(2)$ $S(4) - M_{O}(2) - S(2)$ $S(3) - M_{O}(2) - S(3)$ $S(5) - M_{O}(2) - N(3)$ $S(5) - M_{O}(2) - N(3)$ C(1) - N(1) - C(2) C(2) - N(1) - C(4) C(6) - N(2) - C(9) $M_{O}(2) - N(3) - C(1)$ S(1) - C(1) - N(1) N(1) - C(2) - C(3) S(3) - C(6) - S(4) S(4) - C(6) - N(2) N(2) - C(9) - C(10) N(3) - C(11) - C(1)	Bond angles (°) (1) $134.7(1)$ $2)$ $70.6(1)$ $5)$ $84.4(1)$ $5)$ $84.4(1)$ $6)$ $52.6(1)$ $5)$ $81.4(1)$ (1) $106.3(1)$ (1) $106.3(1)$ (1) $107.7(2)$ (4) $133.0(1)$ (5) $52.6(1)$ $5)$ $84.9(1)$ $5)$ $83.2(1)$ $5)$ $84.9(1)$ $5)$ $83.2(1)$ $5)$ $84.9(1)$ $5)$ $84.9(1)$ $5)$ $89.4(2)$ $6)$ $105.7(2)$ $105.7(2)$ $105.7(2)$ $105.7(2)$ $105.7(2)$ $110.87.9(2)$ $5)$ $89.4(2)$ $6)$ $122.1(5)$ $111.9(3)$ $123.8(5)$ $111.9(3)$ $123.8(5)$ $112.4(5)$ $112.4(5)$ $112.4(5)$ $112.4(5)$ $112.4(5)$ $112.4(5)$ $112.4(5)$ $112.4(5)$ $112.4(5)$ $112.4(5)$ $112.4(5)$ $112.4(5)$ $112.4(5)$ $112.4(5)$ $112.4(5)$ $123.8(5)$ $123.8(5)$ $123.8(5)$ $124.8(5)$ $124.8(5)$ $124.8(5)$ $124.8(5)$ $124.8(5)$ $124.8(5)$ $124.8(5)$ $124.8(5)$ $124.8(5)$ $124.8(5)$ $124.8(5)$ $124.8(5)$ $124.8(5)$ $124.8(5)$	$\begin{array}{c} Mo(2) - H\\ Mo(2) - H\\ S(2) - Mc\\ S(1) - Mc\\ S(5) - Mc\\ S(5) - Mc\\ S(5) - Mc\\ S(3) - Mc\\ S(3) - Mc\\ S(3) - Mc\\ Mo(1) - H\\ S(4) - Mc\\ Mo(1) - H\\ S(4) - Mc\\ Mo(1) - H\\ S(4) - Mc\\ S(6) - Mc\\ Mo(1) - S\\ S(4) - Mc\\ S(6) - Mc\\ Mo(1) - S\\ S(6) - Mc\\ S(6)$	Mo(1) - S(2) Mo(1) - S(5) o(1) - S(6) o(1) - S(6) o(1) - O(1) o(1) - O(1) Mo(2) - S(3) o(2) - S(4) o(2) - S(6) Mo(2) - S(6) Mo(2) - N(3) o(2) - C(1) S(4) - C(6) S(6) - Mo(2) (1) - C(4) (2) - C(7) (2) - C(9) (1) - S(2) (1) - N(1) (4) - C(5) (6) - N(2) (7) - C(8) (11) - C(12) C(11) - C(1) $128.1(1)$) $52.9(1)$ 136.3(1) 144.7(1) 102.5(1) 102.0(1) 110.0(1) 133.2(1) 69.9(1) 144.3(1) 152.9(1) 139.8(1) 101.8(1) 109.0(2) 106.8(2) 88.6(2) 88.6(2) 106.8(2) 88.6(2) 121.6(5) 120.8(5) 117.0(4) 112.5(3) 124.0(5) 124.2(5) 124.2(5) 124.2(5) 122.3(5) 107.4(5) 101.8(5) 107.4(5) 10.8(5) 10.8(5) 112.5(3) 10.8(5) 113.2(5) 124.2(5) 112.3(5) 10.8(5) 112.3(5) 10.8(5) 112.3(5) 10.8(5) 112.3(5) 10.8(5) 112.3(5) 10.8(5) 10.8(5) 112.3(5) 10.8(5) 112.3(5) 10.8(5) 10.8(5) 10.8(5) 112.3(5) 10.8(5) 1	

Appendix 1.13.a

Crystallographic data for $[Mo_2(\mu-S)_2(O)(2,6-Me_2C_6H_3N)(S_2CNEt_2)_2]$ 4.12d

Formula	$Mo_2 C_{18} H_{29} N_3 S_6 O_1$
Colour	Orange
Space group	C 2/c
a, Å	15.979(2)
b, Å	13.805(3)
c, Å	24.897(3)
α, deg	90
β, deg	95.53(1)
γ, deg	90
V, Å ³	5466.60
Z	8
F(000)	2768
d _{calc} , g/cm ³	1.67
Cryst. size, mm	0.70 x 0.40 x 0.40
μ (Mo-K _{α}), cm ⁻¹	13.50
Orientation reflections: no.;range	30 ; $21.65 \le 2\theta \le 30.36$
Data measured	6341
Unique data	6318
No. of unique with I≥3.0σ(I)	3878
No. of parameters	271
R	0.0325
R _w	0.0348
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.000179F^2$
Largest shift/esd, final cycle	0.001
Largest peak, e/ų	0.36

Appendix 1.13.b Atomic coordinates $(x10^4)$ and equivalent isotropic displacement parameters $(Å^2x10^3)$

	х	У	Z	U(eq)*
Mo(1)	6082(1)	1495(1)	6714(1)	46(1)
Mo(2)	7656(1)	1755(1)	6323(1)	43(1)
S(1)	4804(1)	2497(1)	6654(1)	60(1)
S(2)	4860(1)	489(1)	6402(1)	59(1)
S(3)	8402(1)	1007(1)	5600(1)	64(1)
S(4)	8308(1)	3026(1)	5803(1)	76(1)
S(5)	6708(1)	2951(1)	6503(1)	58(1)
S(6)	6796(1)	400(1)	6218(1)	52(1)
N(1)	3398(2)	1437(3)	6453(2)	56(1)
N(2)	9283 (3)	2308(3)	5083(2)	71(2)
N(3)	8323 (2)	1642(3)	6901(1)	48(1)
0(1)	6315(2)	1238(3)	7364(1)	72(1)
C(1)	4222(3)	1465(3)	6503(2)	51(1)
C(2)	2910(3)	2302(4)	6545(3)	81(2)
C(3)	2727(5)	2913(5)	6070(3)	121(3)
C(4)	2933(3)	535(4)	6340(2)	77(2)
C(5)	2488(5)	463(5)	5806(3)	134(4)
C(6)	8749(3)	2129(4)	5443(2)	59(2)
C(7)	9556(4)	3294(5)	4967(3)	94(3)
C(8)	10307(5)	3633(5)	5291(3)	112(3)
C(9)	9623(4)	1545(5)	4767(2)	94(3)
C(10)	10472(5)	1252(6)	4968(3)	120(4)
C(11)	8738(2)	1588(3)	7419(2)	52(2)
C(12)	8974(3)	2459(5)	7692(2)	69(2)
C(13)	9397(3)	2374(6)	8195(2)	91(3)
C(14)	9574(4)	1490(7)	8426(2)	107(4)
C(15)	9341(3)	645(6)	8163(2)	89(3)
C(16)	8914(3)	675(4)	7644(2)	64(2)
C(17)	8773(4)	3427(4)	7436(3)	88(2)
C(18)	8655(4)	-217(4)	7340(2)	86(2)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized $\rm U_{ij}$ tensor

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Appendix 1.13.c Bond lengths (Å)				
$\begin{array}{llllllllllllllllllllllllllllllllllll$	<pre>(1) (1) (1) (1) (1) (1) (3) (5) (5) (5) (7) (6) (8) (9) (10) (7) (7) (7) (12) (7)</pre>	$ \begin{array}{l} Mo(1) - S(1) \\ Mo(1) - S(5) \\ Mo(1) - O(1) \\ Mo(2) - S(4) \\ Mo(2) - S(6) \\ S(1) - C(1) \\ S(3) - C(6) \\ N(1) - C(1) \\ N(1) - C(4) \\ N(2) - C(7) \\ N(3) - C(11) \\ C(4) - C(5) \\ C(9) - C(10) \\ C(11) - C(16) \\ C(12) - C(17) \\ C(14) - C(15) \\ C(16) - C(18) \end{array} $	2.460 2.328 1.663 2.471 2.320 1.724 1.704 1.464 1.466 1.394 1.449 1.457 1.398 1.501 1.371 1.482	<pre>(1) (1) (3) (2) (1) (4) (5) (5) (6) (8) (5) (9) (10) (7) (8) (12) (8)</pre>
Appendix 1.13.d Bond angles (°)				
$\begin{array}{c} Mo(2) - Mo(1) - S(1) \\ S(1) - Mo(1) - S(2) \\ S(1) - Mo(1) - S(5) \\ Mo(2) - Mo(1) - S(6) \\ S(2) - Mo(1) - O(1) \\ S(6) - Mo(1) - O(1) \\ Mo(1) - Mo(2) - S(4) \\ Mo(1) - Mo(2) - S(5) \\ S(3) - Mo(2) - S(5) \\ S(3) - Mo(2) - S(6) \\ S(5) - Mo(2) - S(6) \\ S(5) - Mo(2) - S(6) \\ S(3) - Mo(2) - N(3) \\ Mo(1) - S(1) - C(1) \\ Mo(1) - S(1) - C(1) \\ Mo(2) - S(3) - C(6) \\ Mo(1) - S(5) - Mo(2) \\ C(1) - N(1) - C(2) \\ C(2) - N(1) - C(4) \\ C(6) - N(2) - C(9) \\ Mo(2) - N(3) - C(11) \\ S(1) - C(1) - N(1) \\ N(1) - C(2) - C(3) \\ S(3) - C(6) - S(4) \\ S(4) - C(6) - N(2) \\ N(2) - C(9) - C(10) \\ N(3) - C(11) - C(16) \\ C(11) - C(12) - C(13) \\ C(13) - C(12) - C(17) \\ C(13) - C(14) - C(15) \\ C(11) - C(16) - C(15) \\ C(11) - C(16) - C(18) \\ \end{array}$	132.3(1) 70.7(1) 82.7(1) 52.8(1) 83.1(1) 103.9(1) 106.5(1) 107.7(1) 135.3(1) 53.1(1) 84.9(1) 84.4(1) 101.9(1) 105.5(1) 105.6(1) 88.6(1) 88.7(2) 74.4(1) 120.6(4) 117.2(4) 122.2(5) 169.6(3) 124.2(3) 114.5(5) 112.2(3) 122.9(4) 113.7(5) 118.6(4) 116.9(6) 122.1(6) 121.6(5) 117.2(5) 122.	$ \begin{array}{l} \text{Mo}(2) - \text{Mo}(1) - \text{S} \\ \text{Mo}(2) - \text{Mo}(1) - \text{S} \\ \text{S}(2) - \text{Mo}(1) - \text{S}(3) \\ \text{S}(1) - \text{Mo}(1) - \text{S}(6) \\ \text{S}(1) - \text{Mo}(1) - \text{S}(6) \\ \text{S}(5) - \text{Mo}(1) - \text{O}(2) \\ \text{S}(5) - \text{Mo}(1) - \text{O}(2) \\ \text{S}(5) - \text{Mo}(1) - \text{O}(2) \\ \text{S}(3) - \text{Mo}(2) - \text{S}(6) \\ \text{Mo}(1) - \text{Mo}(2) - \text{N}(2) \\ \text{S}(6) - \text{MO}(2) - \text{N}(2) \\ \text{Mo}(1) - \text{S}(2) - \text{C}(7) \\ \text{Mo}(1) - \text{S}(6) - \text{MO} \\ \text{C}(1) - \text{N}(1) - \text{C}(4) \\ \text{C}(6) - \text{N}(2) - \text{C}(7) \\ \text{C}(7) - \text{N}(2) - \text{C}(9) \\ \text{S}(1) - \text{C}(1) - \text{S}(2) \\ \text{S}(2) - \text{C}(1) - \text{N}(1) \\ \text{N}(1) - \text{C}(4) - \text{C}(5) \\ \text{S}(3) - \text{C}(6) - \text{N}(2) \\ \text{N}(3) - \text{C}(11) - \text{C}(12) \\ \text{N}(3) - \text{C}(11) - \text{C}(12) \\ \text{C}(12) - \text{C}(11) - \text{C} \\ \text{C}(12) - \text{C}(13) - \text{C} \\ \text{C}(14) - \text{C}(15) - \text{C} \\ \text{C}(11) - \text{C}(16) - \text{C} \end{array} $	$(2) \\ (5) \\ (5) \\ (5) \\ (5) \\ (5) \\ (1) \\ (3) \\ (4) \\ (5) \\ (3) \\ (4) \\ (5) \\ (3) \\ (3) \\ (3) \\ (3) \\ (3) \\ (3) \\ (1) $	$132.3(1) \\ 52.6(1) \\ 139.5(1) \\ 141.4(1) \\ 101.4(1) \\ 106.6(1) \\ 110.1(1) \\ 135.1(1) \\ 70.0(1) \\ 143.9(1) \\ 52.8(1) \\ 142.0(1) \\ 142.0(1) \\ 104.2(1) \\ 104.2(1) \\ 104.2(1) \\ 109.6(1) \\ 88.6(1) \\ 88.6(1) \\ 88.7(2) \\ 74.4(1) \\ 122.1(4) \\ 122.2(5) \\ 115.6(5) \\ 111.3(2) \\ 124.5(3) \\ 115.4(5) \\ 124.9(4) \\ 115.7(5) \\ 118.7(4) \\ 122.7(4) \\ 122.7(4) \\ 122.7(7) \\ 120.0(7) \\ 120.6(4) \\ 120.6(4) \\ 120.6(4) \\ 120.6(1) \\ 120.6$