Some reactions of a-phenyl-1,2,3,5-dithiadiazole

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SOME REACTIONS OF 4-PHENYL-1,2,3,5-DITHIADIAZOLE

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A thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Durham.

April 1989

TO MY MOTHER

AND

TO MY FATHER'S MEMORY

ACKNOWLEDGEMENTS

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MEMORANDUM

The work described in this thesis was carried out by me in the Department of Chemistry of the University of Durham during the periods October 1983 - September 1985 (part-time) and October 1985 - September 1987 (full-time). I declare that the work has not been submitted previously for a degree at this or any other University. This thesis is my original work, except where stated otherwise in the text or acknowledged by reference. The copyright of this thesis rests with the author. No quotation from it should be published without his prior written consent and information derived from it should be acknowledged.

ABBREVIATIONS

The presentation of this thesis, in particular the layout of the experimental sections and the references, is based upon that adopted by the Royal Society of Chemistry in its Journal and given in the 'Instructions for authors' printed annually at the beginning of each of the Journal's constituent Transactions.

The following abbreviations are used in this thesis:

Ar	aryl
^{t}Bu	tertiary butyl
Bz	benzyl
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
C.I.	chemical ionisation
D.C.I.	desorption chemical ionisation
D.S.C.	differential scanning calorimetry
E.I.	electron ionisation
ESCA	electron spectroscopy for chemical analysis
e.s.d.	estimated standard deviation
e.s.r.	electron spin resonance
Et	ethyl
EXAFS	extended X-ray absorption fine structure
F.A.B.	fast atom bombardment
f.w.h.h.	frequency width at half-height
i.r.	infrared
LUMO	lowest unoccupied molecular orbital
Me	methyl
MNDO	modified neglect of differential overlap
m.pt.	melting point
n.m.r.	nuclear magnetic resonance

Ph	phenyl
^{i}Pr	iso-propyl
r.t.	room temperature
SOMO	singly occupied molecular orbital
TCNE	tetracyanoethene
thf	tetrahydrofuran
u.v.	ultraviolet

Some Reactions of 4-Phenyl-1,2,3,5-Dithiadiazole

I B Gorrell Ph.D. 1989

ABSTRACT

The reactivity of the above compound, hereafter referred to as phenyl dithiadiazole, $(PhCN_2S_2)_2$, toward the following transition metal carbonyl species has been investigated: $V(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, $Fe(CO)_5$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, $Co_2(CO)_8$, $CpV(CO)_4$, $[CpMo(CO)_3]_2$, $CpMn(CO)_3$, $[CpFe(CO)_2]_2$, $CpCo(CO)_2$ and $[CpNi(CO)]_2$ and the following new compounds characterised: $Mn_2(CO)_8PhCN_2S_2$, $Fe_2(CO)_6PhCN_2S_2{}^*$, $[CpV(PhCN_2S_2)]_2$, $[CpCo(PhCN_2S)]_2$ and $Cp_2Ni_2(PhCN_2S_2)^*$; those marked with an asterisk by X-ray analysis (W Clegg). Reactivity studies of $(PhCN_2S_2)_2$ with the following transition metal phosphine and halogeno- compounds were also carried out: MCl_2 (M=Cr,Mn,Co,Ni,Pd,Cu), $FeBr_2$, $TiCl_4$(+Mg), Cp_2TiCl_2(+Mg) and $NiCl_2$(+Mg), $MoCl_4(CH_3CN)_2$, CuCl, $(Ph_3P)_4M$ (M=Pd,Pt) and $(Ph_3P)_3RhCl$ and the following new complexes prepared: $[PhCN_2S_2]_2PdCl_4$, $[PhCN_2S_2]_2CuCl_2$, $PhCN_2S_2(CuCl)_2$, $(Ph_3P)_2M(PhCN_2S_2)_2$ (M=Pd,Pt) and $[(Ph_3P)Pt(PhCN_2S)]_2$. Also, the reactivity of phenyl dithiadiazole toward R_3P (R=Ph,Me), Ph_3As, S_8, Me_3NO, $N_3{}^-$, H^-, Me_nNH_{3-n} (n=0-3), MeX (X=I,OSO_2F), MeCOBr, Me_3SiX (X=Cl,Br), HX (X=Cl,BF_4), NO, N_2O_4, N_2F_4, $(Me_3Sn)_2$, AgF_2 and TCNQ has been studied and gave rise to the following novel species: $[PhC(NHMe)_2]_2S_6$, $[PhC(NH_2)_2][S_2N_3S.\overline{N.Ph_2C_2N_3S}]$, $[PhC(NH)_2S_2]X$ (X=Cl,BF_4), $[PhCN_2S_2]SO_2F_3$, $[PhCN_2S_2]_3F$, $PhCN_2S_2F$ and $PhCN_2S_2(TCNQ)_2$. Finally, $[MoCl_2(PhCN_2S_2)(thf)]_2$ and $[Na(C_{12}H_{24}O_6)]PhCN_2S_2$ are reported as are the unusual magnetic properties of some of the above transition-metal complexes.

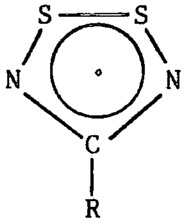
CONTENTS

CHAPTER 1

THE CHEMISTRY OF THE 1,2,3,5 - DITHIADIAZOLE RING SYSTEM

1.1 INTRODUCTION

This chapter reviews the chemistry of the 1,2,3,5 - dithiadiazoles, I, and the 1,2,3,5 - dithiadiazolium salts, II, from which they are prepared.



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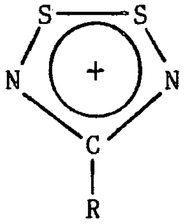

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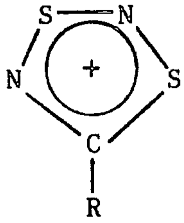


III

The related class of compounds based on the 1,3,2,4 - dithiadiazolium ring, III, and usually prepared[1] by the reaction of a nitrile with S_2N^+ are not considered.

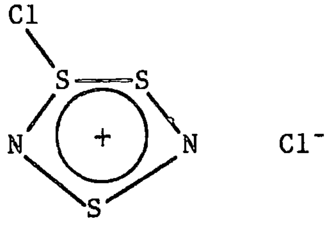
Firstly, the preparations of the cations are discussed; this is followed by an account of their reactions which includes the preparation of the neutral free radicals. There follows a summary of the, thus far observed, limited reactivity of the radicals and then sections on the structural and theoretical studies carried out on both the cations and the radicals. The final paragraphs are devoted to a brief overview of this thesis.

1.2 SYNTHESES OF THE 1,2,3,5 - DITHIADIAZOLIUM RING

This heterocycle was first prepared in Durham, in 1977, from a reaction[2] of trichlorocyclotrithiazene, $(NSCl)_3$, with a variety of nitriles, RCN (R = CCl_3, ^{t}Bu, Ph). The reactions were carried out in the hope of obtaining the five-membered $RCN_2S_2^+$ ring by analogy with the reactions between a source of sulphur and (i)$(NSCl)_3$ to give $S_3N_2Cl_2$, IV, and (ii)RCN to give $R_2C_2N_2S$, V, according to:

$$S_2Cl_2 + 2/3(NSCl)_3 \longrightarrow S_3N_2Cl_2 + SCl_2$$

$$1/8S_8 + 2RCN \longrightarrow R_2C_2N_2S$$



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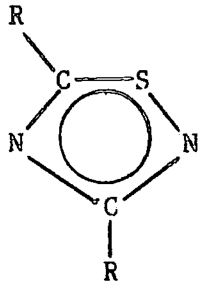


V

Initially, elemental sulphur was added to the reaction mixture but this caused the co-formation of S_4N_3Cl and S_8 contaminated the product and so, subsequently, the sulphur was provided 'in situ' by the thermal decomposition of $(NSCl)_3$. An X-ray analysis[3] on the trichloromethyl derivative confirmed the formation of the anticipated product (Section 1.5).

Later, Roesky[4] obtained the phenyl and tert-butyl derivatives from $(NSCl)_3$ and the corresponding azines:

$$3\ RCH{=}N{-}N{=}CHR + 4(NSCl)_3 \longrightarrow 6[RCN_2S_2]Cl + 3N_2 + 6HCl$$

The range of preparative routes to dithiadiazolium cations was extended with the report[5] of three new syntheses:

(1) Reaction of $(NSCl)_3$ with tetrachloroethene (which gave the trichloromethyl derivative in a complex mixture).

(2) Reaction of a nitrile, $RCN(R = Ph, CCl_3)$, an ammonium salt and SCl_2. (the use of $S_3N_2Cl_2$ as a source of NSCl also gave S_4N_3Cl and so NH_4^+ and SCl_2 were used to form 'in situ' NSCl instead.)

(3) Reaction of a benzamidine salt with SCl_2.

Syntheses from $(NSCl)_3$ and nitriles with α C-H bands were found to give sticky black solids and were not investigated further in this work although S_4N_3Cl was later isolated[10] from the reaction with acetonitrile.

An improved version[6] of Reaction (2) (using chlorine to prevent formation of $S_3N_2Cl_2$ as a side-product) was subsequently reported for aceto-, benzo- and 4-chlorobenzonitrile, but the cyano- and nitro-derivatives could not be prepared. The phenyl derivative was also prepared from NH_4Cl, SCl_2, and toluene, albeit in very low yield (3%). (It is now known that toluene-SCl_2 mixtures can be explosive[7]).

Halogeno- derivatives of this ring system were first prepared by Mews[8] who obtained $[XCN_2S_2]X$ (X = Cl,Br) in reacting bis (trimethylsilyl) carbodiimide with SCl_2, or N-cyanosulphurdifluoroimide with an excess of SCl_2 or S_2Br_2:

$$N\equiv C\text{-}NSF_2 + SCl_2 \longrightarrow [ClCN_2S_2]Cl + S(F,Cl)_x$$

$$N\equiv C\text{-}NSF_2 + S_2Br_2 \longrightarrow [BrCN_2S_2]Br + S(Br,F)_x$$

$$R_3SiN{=}C{=}NSiR_3 + 2SCl_2 \longrightarrow [ClCN_2S_2]Cl + 2Me_3SiCl$$

The trifluoromethyl species, $[CF_3CN_2S_2]Cl$ was prepared[9] from a reaction between $(NSCl)_3$ and CF_3CN in a Teflon autoclave at 55°C, and $[MeCN_2S_2]Cl$ was obtained[1b] from the reaction between S_2Cl_2 and sodium azide in acetonitrile (lithium azide gave a mixture of products). The $[MeCN_2S_2]^+$ cation has also been obtained, as $[MeCN_2S_2]_5\,[CoCl_4]Cl_3$, from a reaction[10] between $(NSCl)_3$, $CoCl_2$ and acetonitrile. Addition of Ph_4AsCl to this salt gave $[MeCN_2S_2]Cl$ and $[Ph_4As]_2CoCl_4$.

The first dithiadiazolium salt with an electron releasing substituent at carbon, $[Et_2NCN_2S_2]Cl$ was synthesised[11] via reaction of the six-membered ring compound, $(Et_2NCN)(NSCl)_2$, itself prepared[12] from Et_2NCN and $(NSCl)_3$, with sodium azide.

Finally, dithiadiazolium salts have occasionally been obtained as

by-products. $[MeCN_2S_2]Cl$ was obtained[13] in very low yield in a mixture with S_4N_4, isolated from the reaction of S_2Cl_2 with a large excess of Me_3SiN_3 in acetonitrile (S_3N_2Cl, S_4N_3Cl, S_4N_4 and $(SN)_x$ were the major products). The analogous reaction, using NaN_3, also gave $[MeCN_2S_2]Cl$ in a mixture with S_4N_3Cl, in somewhat higher yield. The phenyl derivative has been formed in the reaction of $(NSCl)_3$ with $PhC{:}NH(NH_2)$ which gave[14a] $Ph_2C_2N_3SCl$ as the major product, and also in the chlorination of $PhCS_3N_5$ which gave[14b] $PhCN(NSCl)_2$ as the major product.
The report of a previous reaction between benzamidine hydrochloride and $(NSCl)_3$ in this paper is incorrect. Thermal decomposition[15a] of $CF_3CN(NSCl)_2$ (itself prepared[9,15a] from CF_3CN and $(NSCl)_3$) at 120°C gave $[CF_3CN_2S_2]Cl$ and reaction[15b] of $(NSCl)_3$ with trichloroacetic anhydride gave $[CCl_3CN_2S_2]Cl$ with $S_3N_2NCOCl_3$ as the major product. All of the above-mentioned preparations, except those in which the dithiadiazolium salts are side-products, are presented in Table 1.1.

The mechanism for the formation of dithiadiazolium salts from an ammonium salt, a nitrile and SCl_2, has received attention. Early proposals[5] included reaction of the ammonium halide with the nitrile to give an amidine and amidinium salt, which then condensed with SCl_2, to form the desired product. Initial formation of a nitrile addition product such as $RC(Cl){=}NH$ or $RC(Cl){=}NSCl$ was also postulated as well as the following reaction:

$$NH_4Cl + 2SCl_2 \xrightarrow[-4HCl]{} NSCl + S \xrightarrow{RCN} [RCN_2S_2]Cl$$

Later work[6] shed more light on the mechanism when it was discovered that the presence of electron withdrawing substituents such as nitro- or nitrile groups at the para position in substituted benzonitriles,

TABLE 1.1

PREPARATIONS OF DITHIADIAZOLIUM CATIONS

STARTING MATERIALS	PRODUCT	YIELD(%)	CONDITIONS	REF
$(NSCl)_3$+RCN				
R=^tBu	$[^tBuCN_2S_2]Cl$		60°C for 24h	2
CCl_3	$[CCl_3CN_2S_2]Cl$	42	Reflux for 24h	2,5
Ph	$[PhCN_2S_2]Cl$	50	60°C for 48h in CCl_4	
CF_3	$[CF_3CN_2S_2]Cl$#	30	55°C for 40h in liquid SO_2	9
$(NSCl)_3$+MeCN+$CoCl_2$	$[MeCN_2S_2]Cl$	54.5	Stir at r.t.	10
$(NSCl)_3$+RCH=N-N=CHR				4
R=Ph	$[PhCN_2S_2]Cl$	92	Stir in CH_2Cl_2 at r.t.	
^tBu	$[^tBuCN_2S_2]Cl$	28	Stir in CCl_4 at r.t.	
$(NSCl)_3$+C_2Cl_4	$[CCl_3CN_2S_2]Cl$	13	60-80°C for 48h	5
NH_4Cl+SCl_2+PhCN	$[PhCN_2S_2]Cl$	25	140°C for 5h in $PhNO_2$	5
		30	Reflux for 10h under Cl_2	6
4-ClC_6H_4CN	$[ClC_6H_4CN_2S_2]Cl$	15	Reflux for 5h under Cl_2	
MeCN	$[MeCN_2S_2]Cl$	10	Reflux for 8h under Cl_2	
CCl_3CN	$[CCl_3CN_2S_2]Cl$	30	120°C for 5h in $PhNO_2$ under Cl_2	5
^tBuCN	$[^tBuCN_2S_2]Cl$	-	as above	
+$PhCH_3$	$[PhCN_2S_2]Cl$	3	140°C for 10h	6
$PhC(NH_2)_2Cl$+SCl_2	$[PhCN_2S_2]Cl$	19	105°C for 5h in $PhNO_2$	5
$NCNSF_2$+SCl_2	$[ClCN_2S_2]Cl$	50	Stir for 20h at 40°C	8
+ S_2Br_2	$[BrCN_2S_2]Br$	56	Stir for 21d at 45°C	
$Me_3SiNCNSiMe_3$+SCl_2	$[ClCN_2S_2]Cl$	81	50°C for 20h in CCl_4	
$(Et_2NCN)(NSCl)_2$+NaN_3	$[Et_2NCN_2S_2]Cl$	22	23°C for 2h in MeCN	11

$S_4N_4O_2$ and $[CF_3CN_4S_3][S_3N_4O_4]$ also isolated.

prevented formation of the corresponding dithiadiazolium salt. This was explained by invoking nucleophilic attack by the nitrile on SCl_2 as the rate-determining step. Such a process was thought to lead to an ionic intermediate [RCNSCl]Cl which could then cyclise with NSCl with concomitant loss of chlorine to form $[RCN_2S_2]Cl$.

1.3 THE CHEMISTRY OF 1,2,3,5 - DITHIADIAZOLIUM SALTS INCLUDING THE PREPARATION OF 1,2,3,5 - DITHIADIAZOLES.

The most common reaction of the salts (usually the chlorides) is simple anion exchange, and the new species obtained by this method are presented in Table 1.2.

The preparation of $[PhCN_2S_2]SbCl_6$ can also be carried out in refluxing thionyl chloride or in liquid sulphur dioxide at room temperature. Interestingly, the reactions between $[PhCN_2S_2]Cl$ and KBr or NaI also occur when the materials are ground together in the solid state.[16]

In order to probe the extent of covalent bonding between the cation and anion in $[RCN_2S_2]Cl$ several reactions typical of sulphenyl chlorides were carried out.[5] However, the phenyl derivative did not react with cyclohexene oxide, acetonitrile or tetrachloroethene and the trichloromethyl derivative did not react with diphenylethyne. Also, the latter derivative did not react with sulphur.

The reaction of $[PhCN_2S_2]Cl$ with diphenyl mercury gave[5] a small quantity of a black material, analysing as $Ph_2CN_2S_2$, which decomposed in sunlight to give Ph_2S_2 and a black tar. However it now seems likely that a mixture of $(PhCN_2S_2)_2$ (see later) and biphenyl were obtained.[16] Ethanol and ethanethiol gave complicated mixtures when reacted with dithiadiazolium chlorides.

TABLE 1.2

ANION EXCHANGE REACTIONS OF DITHIADIAZOLIUM SALTS

STARTING MATERIALS	$[RCN_2S_2]$ PRODUCT	YIELD (%)	CONDITIONS	REF
$[PhCN_2S_2]Cl+SbCl_5$	$[PhCN_2S_2]SbCl_6$	42	Stir in CH_2Cl_2	4,5,16
CF_3SO_3H	CF_3SO_3	32		4
$HN(SO_2F)_2$	$N(SO_2F)_2$	34		
$Et_3O^+BF_4^-$	BF_4	45		
$NO^+PF_6^-$	PF_6	55		
$FeCl_3$	$FeCl_4$	89	Stir in $SOCl_2$	6
KBr	Br	71	Stir in liquid SO_2	
NH_4NCS	NCS	71		
LiBr	Br	-	Reflux in thf	16
NaI	I	-	Stir in thf	
KI	I	-	Stir in liquid SO_2	6,16
$NH_4^+PhCO_2^-$	$PhCO_2$	-		
$NH_4^+MeCO_2^-$	$MeCO_2$	-		
BCl_3	BCl_4	97		
$SnCl_4$	$[PhCN_2S_2]_2\ SnCl_6$	-	Stir in $SOCl_2$	
$[CCl_3CN_2S_2]Cl+SbCl_5$	$[CCl_3CN_2S_2]SbCl_6$	-	Reflux in $SOCl_2$	5
$[MeCN_2S_2]Cl+SnCl_4$	$[MeCN_2S_2]_2\ SnCl_6$	81	Stir in $SOCl_2$	17
$[ClCN_2S_2]Cl+HSO_3F$	$[ClCN_2S_2]SO_3F$	96	Stir in CH_2Cl_2	8
$Ag^+AsF_6^-$	AsF_6	79	Stir in liquid SO_2	
$SbCl_5$	$SbCl_6$	90		
$SnCl_4$	$[ClCN_2S_2]_2\ SnCl_6$	95		
$[FCN_2S_2]Cl+AgAsF_6$	$[FCN_2S_2]AsF_6$	88		9

The salts are slowly hydrolysed in the atmosphere and rapidly hydrolysed in solution. In dioxan, $[CCl_3CN_2S_2]Cl$ gave [5] the amidine hydrate and recrystallisation from water converted the latter to CCl_3CONH_2. Later work[17] identified an amidine hydrochloride, sulphur and sulphur dioxide as the hydrolysis products.

There is one example of reaction at carbon; $[ClCN_2S_2]Cl$ was found[9] to give $[FCN_2S_2]Cl$ on treatment with AgF_2 at -60°C. At higher temperatures only $CF_2(NSF_2)_2$ was obtained. Attempts using AgF, HF, NaF or KF (also in the presence of crown ethers) failed.

During the X-ray analysis[3] of $[CCl_3CN_2S_2]Cl$, the salt was found to decompose in the X-ray beam to give a twinned crystal of an unidentified product.

Most dithiadiazolium salts are bright yellow, orange, or red in colour but $[PhCN_2S_2]X$ ($X=I,NCS,PhCO_2,MeCO_2$) were found to be purple-black. This observation[6,18] pointed the way to what is undoubtedly, the most important reaction of the salts; that is their facile reduction to the stable free-radical species, the dithiadiazoles. The colour was explained in terms of significant charge transfer from these softer, more polarisable anions to the dithiadiazolium cation. If solutions of the thiocyanate or benzoate in monoglyme are refluxed for ca. 8h, or, for the iodide in liquid sulphur dioxide and the acetate in thf, simply stirred at room temperature for 12h, then total electron transfer occurs with the formation of the neutral dithiadiazole. Some evidence for anion-cation interaction in the iodide was obtained by measuring the I(3d) binding energy by photoelectron spectroscopy. The value obtained, 620.7eV, lies between that of KI(618.6eV) and PhI(622.1eV).

Preparations of dithiadiazoles are presented in Table 1.3. Their essentially dimeric nature in the solid state has been revealed by X-ray analysis.[9,18] (Section 1.5)

The methyl compound $(MeCN_2S_2)_2$, has also been prepared[21] as a by-product during the reduction of $(NSCl)_3$ to $(SN)_x$ using Me_3SiN_3 in acetonitrile and reduction[15a] of $CF_3CN(NSCl)_2$ with zinc in liquid sulphur dioxide at room temperature gave $(CF_3CN_2S_2)_2$ in 26% yield.

Finally, $(RCN_2S_2)_2$ (R=Me,CF_3,I) have been obtained[22], via isomerisation of the corresponding, thermodynamically unstable 1,3,2,4 - dithiadiazoles in dilute solution at r.t. Also, the t-butyl derivative of the 1,3 isomer has been quantitatively photochemically isomerised to the 1,2 isomer which is a paramagnetic liquid at r.t.[23]

TABLE 1.3

PREPARATIONS OF DITHIADIAZOLES

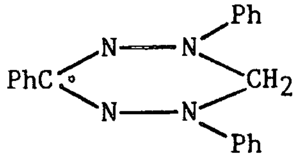
STARTING MATERIALS	PRODUCT	YIELD(%)	CONDITIONS	REF
$[PhCN_2S_2]Cl+NaNCS$	$(PhCN_2S_2)_2$	-	Reflux in monoglyme	16,18
$[RCN_2S_2]Cl^{*}+Na$	$(RCN_2S_2)_2$	-	Stir in benzene or thf	19
TPV**		-		
TMPD#		-		
$[PhCN_2S_2]MeCO_2$	$(PhCN_2S_2)_2$	-	Stir in thf	6,16
$PhCO_2$		-	Reflux in monoglyme	
NCS		-	Sublime	
$[PhCN_2S_2]Cl+LiN_3$		-		
KCN		-	Stir in AsF_3, recrystallise from SO_2	
PhMgBr		-	Stir in toluene-ether	
^{n}Buli		-		
MeLi		-	Stir in monoglyme-ether	
$SnCl_2$		-	Stir in monoglyme, extract with pentane	
Zn-Cu		41	Stir in thf	
Hg		-		
Fe		-		16
K		-	Reflux in monoglyme	
$[XCN_2S_2]Y^{\circ}+Zn$	$(XCN_2S_2)_2$		Stir in liquid SO_2	9
X = CF_3		99		
F		82		
Cl		81		
Br		74		
$[MeCN_2S_2]Cl+e^-$	$(MeCN_2S_2)_2$	36		20

* R = CCl_3,Ph

** Triphenylverdazyl radical

\# Tetramethylparaphenylenediamine

° Y = Cl,Br



1.4 THE CHEMISTRY OF 1,2,3,5 - DITHIADIAZOLES

Just as reduction to dithiadiazoles is, by far, the most common reaction of dithiadiazolium salts, so oxidation to the latter is the most common reaction of dithiadiazoles. Reactions of this type are summarised in Table 1.4.

TABLE 1.4

OXIDATIONS OF DITHIADIAZOLES

STARTING MATERIALS	PRODUCTS	YIELD(%)	CONDITIONS	REF
$(PhCN_2S_2)_2+Br_2$	$[PhCN_2S_2]Br$	46	Stir in CCl_4	6
$+SO_2Cl_2$	Cl	83	Stir at r.t.	
$+SOCl_2$				6,16
$(NSCl)_3$			Stir in benzene	
Cl_2				
I_2	I*		Stir in toluene	
$[Se_4](AsF_6)_2$	AsF_6		Stir in liquid SO_2	
$[S_8](AsF_6)_2$	AsF_6			
$SbCl_5$	$SbCl_6$			16
$SnCl_4$	$[PhCN_2S_2]_2\ SnCl_6$		Stir in toluene	6,16
$(BrCN_2S_2)_2+SOCl_2$	$[BrCN_2S_2]Cl$	99	Stir in liquid SO_2	9

* In the presence of excess iodine, the tri-iodide salt was obtained.

Phenyl dithiadiazole did not react[6,16] with diphenylethyne or S_4N_4. The reactivity of chloro dithiadiazole towards other free radicals has been investigated.[9] Only the chloride salt could be isolated from reactions with oxygen, nitric oxide and bis (trifluoromethyl) nitroxide. When the last-mentioned reaction is carried out in liquid sulphur dioxide the fluorosulphate salt is obtained:

$$(ClCN_2S_2)_2 + 2(CF_3)_2NO \xrightarrow{SO_2} 2[ClCN_2S_2]SO_3F + 2CF_3N{=}CF_2$$

More interesting reactions occur between the dithiadiazoles and their parent chlorides:

$$(XCN_2S_2)_2 + [XCN_2S_2]Cl \longrightarrow [XCN_2S_2]_3Cl$$

This reaction only occurs when X = CF_3(91%) or Cl(74%); the anion also seems to be important since use of a hexachloroantimonate (V) salt only leads to reduction to a pentachloroantimonate (III) salt:

$$(ClCN_2S_2)_2 + [ClCN_2S_2]SbCl_6 \longrightarrow [ClCN_2S_2]_2\ SbCl_5 + [ClCN_2S_2]Cl$$

The structure of $[CF_3CN_2S_2]_3Cl$ is given in Section 1.5.

Finally, the phenyl and 4-chlorophenyl derivatives have been found[24] to undergo a nitrogen insertion reaction in a cool d.c. plasma to give the dithiatriazine species $(XC_6H_4\overline{CNSNSN})_2$ (X=H[14b],Cl).

1.5 STRUCTURAL STUDIES

There have been five published X-ray analyses of dithiadiazolium salts, including $[CF_3CN_2S_2]_3Cl$ which may be said to consist of $(CF_3CN_2S_2)_2$+$[CF_3CN_2S_2]Cl$. An electron diffraction study has also been carried out on $CF_3CN_2S_2\cdot$. The results are presented in Tables 1.5 and 1.6. (The numbering scheme is based upon that given in Figure 1.1.).

TABLE 1.5

STRUCTURAL DATA (in Å AND °) FOR DITHIADIAZOLIUM CATIONS

COMPOUND	S_1-S_2	S_1-N_1	S_2-N_2	C-N_1	C-N_2	α	β	γ
$[CCl_3CN_2S_2]Cl$[3]	2.009 (5)	1.587 (10)	1.579 (10)	1.308 (15)	1.329 (13)	122.2 (11)	113.45 (10)	95.4 (5)
$[ClCN_2S_2]AsF_6$[8]	1.996 (2)	1.573 (5)	1.573 (5)	1.317 (8)	1.325 (8)	1.203 (5)	144.4 (4)	95.4 (2)
$[MeCN_2S_2]Cl$[10]	2.002 (1)	1.5945 (20)	1.5785 (30)	1.3335 (40)	1.334 (4)	118.6 (2)	115.4 (2)	95.25 (10)
$[MeCN_2S_2]_5[CoCl_4]Cl_3$[10]	2.006 (10)	1.592 (20)	1.562 (20)	1.368 (30)	1.354 (30)	118.0 (20)	116.0 (20)	95.69 (80)
$[CF_3CN_2S_2]_3Cl$[9]	1.989 (3)	1.605 (6)	1.573 (6)	1.333 (9)	1.313 (10)	118.6 (6)	115.5 (5)	95.15 (30)

TABLE 1.6

STRUCTURAL DATA (in Å and °) FOR DITHIADIAZOLES

COMPOUND	S_1-S_2	S_1-N_1	S_2-N_2	C-N_1	C-N_2	α	β	γ
$(PhCN_2S_2)_2$[18]	2.089	1.625	1.625	1.3375	1.330	121.0	115.5	94.1
$(CF_3CN_2S_2)_2$[9]	2.087 (2)	1.631 (5)	1.6285 (50)	1.3355 (80)	1.300 (8)	126.1 (6)	112.35 (40)	94.6 (2)
$CF_3CN_2S_2^{\cdot}$[9]	2.113 (6)	1.623 (3)		1.318 (6)		124.4 (11)	113.9 (6)	93.9 (5)
$[CF_3CN_2S_2]_3Cl$[9]	2.085 (2)	1.6475 (50)	1.6325 (50)	1.3205 (80)	1.3355 (80)	124.85 (50)	112.9 (5)	94.7 (2)

All of the rings are planar and comparison of the distances both within the rings themselves and with those listed in Table 1.7 shows that a strong degree of delocalisation occurs.

TABLE 1.7

SOME BOND LENGTHS IN LOCALISED AND DELOCALISED SPECIES

COMPOUND	BOND	BOND LENGTH	REF
$MeNH_2$	C-N	1.474(5)	36a
C_5H_5N	C-N	1.3402(10)	36b
$(Ph_2CN)_2S$	C=N	1.285(3)[a]	37
H_2NSO_3H	S-N	1.764(20)	38
$(4\text{-}CH_3C_6H_4N)_2S$	S=N	1.545(9)[a]	39
S_8	S-S	2.048(2)	40
S_4N_4	S-N	1.626(5)[a]	41
$[S_5N_5]Cl$	S-N	1.582(2)[a]	42
	S---Cl	3.237(2)[a]	
$[S_4N_3]Br_3$	S-S	2.088(5)	43
S_4N_3Cl	S---Cl	2.864	3

[a] average values

Another feature of these structures is the importance of secondary interactions. In the salts containing chloride ion, which is roughly equidistant from the two ring sulphur atoms, the S-Cl distances have the following average values: 2.8555Å in $[CCl_3CN_2S_2]Cl$[3], 2.844Å in $[CF_3CN_2S_2]_3Cl$[9] (for the cationic ring), 2.925Å in $[MeCN_2S_2]Cl$[10] and 2.969Å in $[MeCN_2S_2]_5[CoCl_4]Cl_3$.[10] The $[CoCl_4]^-$ anion in the last salt also has non-bonded contacts with the cation sulphur atoms at 3.395Å. There are also short S-F distances in $[ClCN_2S_2]AsF_6$[8] with one of the fluorine atoms an average distance of 2.799Å from the sulphur atoms; these values can be compared with the sum of the van der Waals radii[25] for the elements concerned: S-Cl = 3.55Å, S-F = 3.27Å. In $[MeCN_2S_2]Cl$ and $[MeCN_2S_2]_5[CoCl_4]Cl_3$ there are also interactions, in the range 3.17-3.51Å (one at 3.02Å) between the sulphur atoms of one ring and chloride ions associated with other rings. The structure of

$[CCl_3CN_2S_2]Cl$ is shown in Figure 1.1.

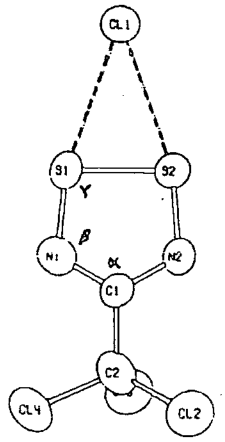


FIGURE 1.1

The neutral dithiadiazoles exist as weakly bonded dimers in the solid state as shown in Figures 1.2 and 1.3. In $(PhCN_2S_2)_2$ the rings are almost totally eclipsed and nearly parallel and the monomers are linked through S-S contacts in the range 3.038 - 3.186Å. There is some deviation from planarity in one monomer ring in each of the two dimers, $(PhCN_2S_2)_2$, in the assymetric unit, probably as a result of the secondary interactions shown as dotted lines in Figure 1.2. (Atoms N(12) and N(21) lie 0.81 and 0.54Å, respectively, out of the best least squares plane.)

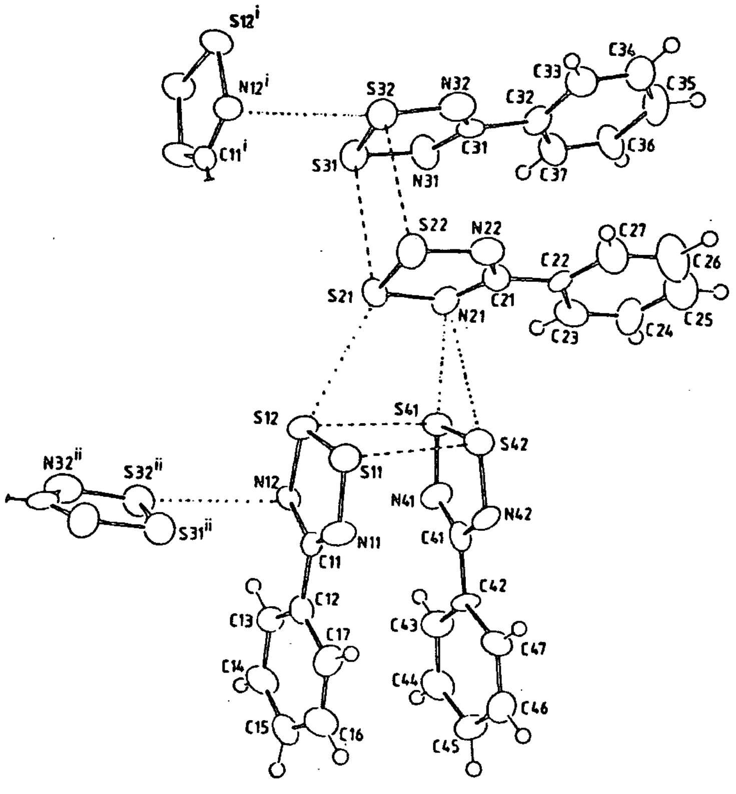


FIGURE 1.2

Starting from the staggered conformation, the structure of $(CF_3CN_2S_2)_2$ is obtained by rotating one of the rings through 95° about an S---S link so that an S---S bond lies above an S-N bond (see Figure 1.5). The S---S distances between rings are S(1)-S(5)=2.997Å and S(3)-S(7) =2.978Å. There are also weak S-N contacts: S(2)-N(3)=3.214Å, S(4)-N(6)=3.186Å, S(8)-S(7)=3.197Å, S(6)-N(1)=3.241Å (cf. sum of the van der Waals radii at 3.35Å[25]). Interactions between dimers also exist e.g. S(1)-N(6)=3.076Å, S(8)-N(6)=3.275Å, S(5)-S(7)=3.405Å, S(3)-N(7)=3.053Å.

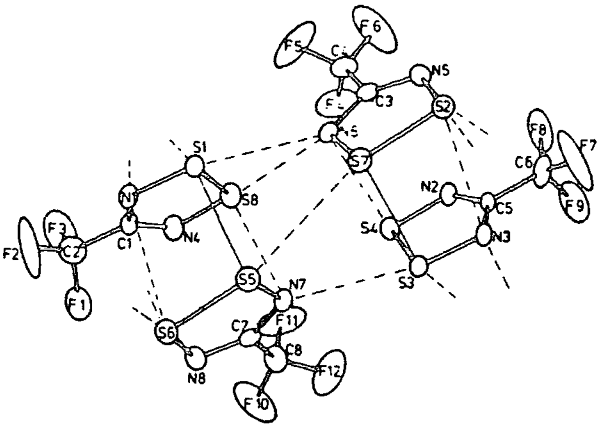


FIGURE 1.3

The rings are nearly parallel and form dihedral angles of ca. 9° within dimers. Gas phase electron diffraction showed the monomer ring to be planar and virtually unchanged structural parameters when compared to the dimer.

Finally, the dithiadiazole unit in $[CF_3CN_2S_2]_3Cl$ exists in the eclipsed form. Unfortunately, the S-S distances between monomers are not given but the average S-Cl distance is 3.167Å (cf. sum of van der Waals radii at 3.55Å[25]). Interestingly, each sulphur atom of the cation lies relatively close to a nitrogen atom of a radical belonging to a neighbouring unit: e.g. N(1)-S(6)=3.247Å, resulting in a chain of alternating radicals and cations as shown in Figure 1.4.

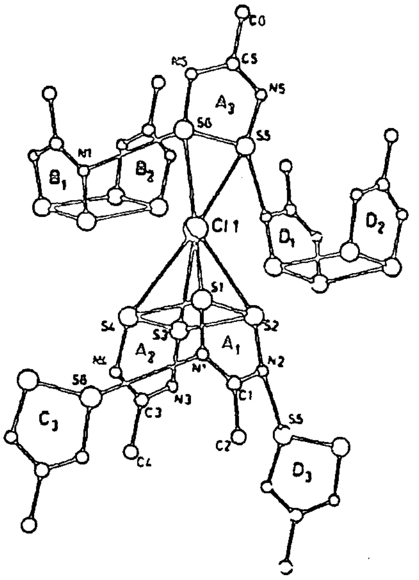


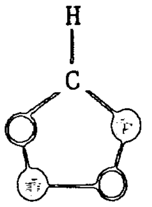
FIGURE 1.4

Addendum: The crystal structure[44] of $[PhCN_2S_2]Cl.1/6C_7H_8$ has been published very recently. The average bond lengths and angles are: S-S,1.990; S-N,1.590; C-N,1.340Å; SSN, 95.75; SNC, 114.7; NCN,119.0°. The average S-Cl distance is 2.906Å. There are also weaker S--Cl interactions, in the range 3.1 - 3.5Å, cf. $[MeCN_2S_2]Cl$ and $[MeCN_2S_2]_5[CoCl_4]Cl_3$.

1.6 THEORETICAL STUDIES AND BONDING

The earliest efforts[6,18] to describe the bonding in this compound drew attention to the similarity between $PhCN_2S_2\cdot$ and $S_3N_2^{+\cdot}$ since both possess 7π electrons, two electrons being supplied by each sulphur atom and one electron from the carbon and nitrogen atoms. The odd electrons in these species are used to form weak S---S links in a four-centre two-electron bond between two formally 6π species ($PhCN_2S_2^+$ and $S_3N_2^{2+}$).

The most complete theoretical study is that of Mews[9] who has carried out MNDO (Modified Neglect of Differential Overlap) calculations on a variety of dithiadiazole systems[9] both as monomers and dimers. The SOMO (Singly Occupied Molecular Orbital) in HCN_2S_2, was found to be of the following symmetry with atomic coefficients of -0.4 and +0.58 at nitrogen and sulphur, respectively.



This explains the decrease in S-S and S-N bond lengths observed on oxidation of the radical species (See Tables 1.5 and 1.6). The difference in energy between the eclipsed and staggered conformations was found to be very small (the staggered geometry was found to be 3.4KJmol^{-1} more stable in a model which allowed the S---S inter-ring distances to optimise at 2.97Å). The effect of the rotation of one ring with respect to the other in the dimer unit was also studied (see Figure 1.3) and again the energy changes were found to be very small. For the eclipsed conformation an energy minimum was achieved after rotation through 95.6° and for the staggered conformation, after rotation through 93.5° (see Figure 1.5).

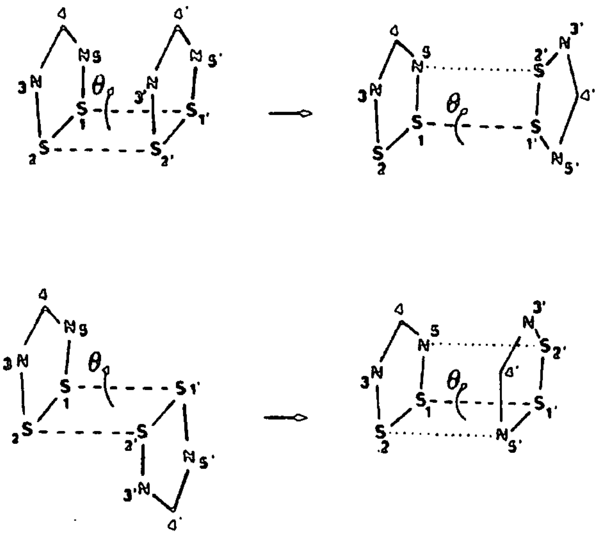


FIGURE 1.5

The rotated version of the eclipsed form was more stable by 8.4KJmol^{-1} whereas the rotated version of the staggered form was less stable by 7.0KJmol^{-1}. All of these energy differences lie within the experimental error inherent in the MNDO method (ca. 20KJmol^{-1}) suggesting that the actual conformation adopted may depend on very subtle effects such as secondary interactions and packing forces. The variation in the total energy of $(HCN_2S_2)_2$ as a function of inter-ring distance is shown in Figure 1.6.

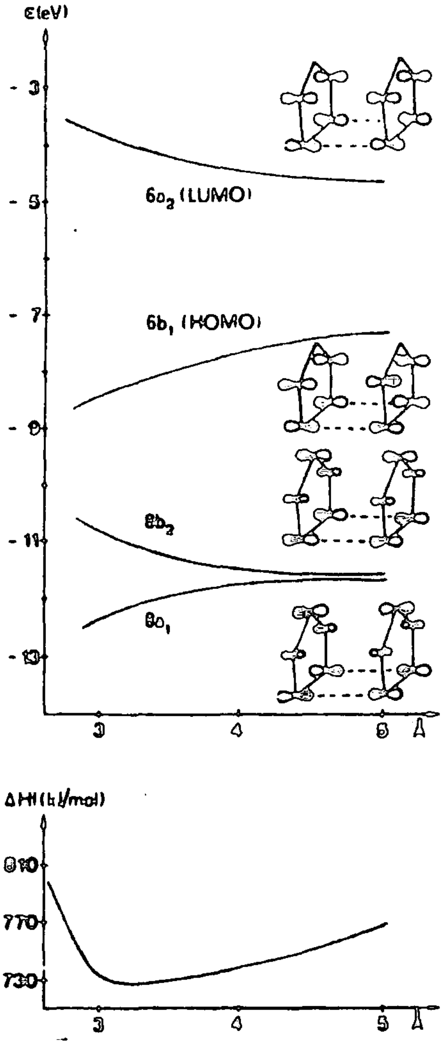


FIGURE 1.6

The effect of dimerisation on the calculated atomic changes was found to be minimal.

	C	N	S
$HCN_2S_2{}^9$	0.05	-0.24	0.13
$(HCN_2S_2)_2{}^9$	0.09	-0.30	0.17

An ab initio HFS (Hartree Fock Slater) study[26] has been made of $XCN_2S_2^+$ (X=H,Cl,NH_2). The atomic changes are listed below:

	C	N	S
X = H	0.61	-0.37	0.51
Cl	0.23	-0.33	0.50
NH_2	0.62	-0.31	0.42

The orbital energy diagram for X = H and NH_2 is shown below (taken from Ref.11):

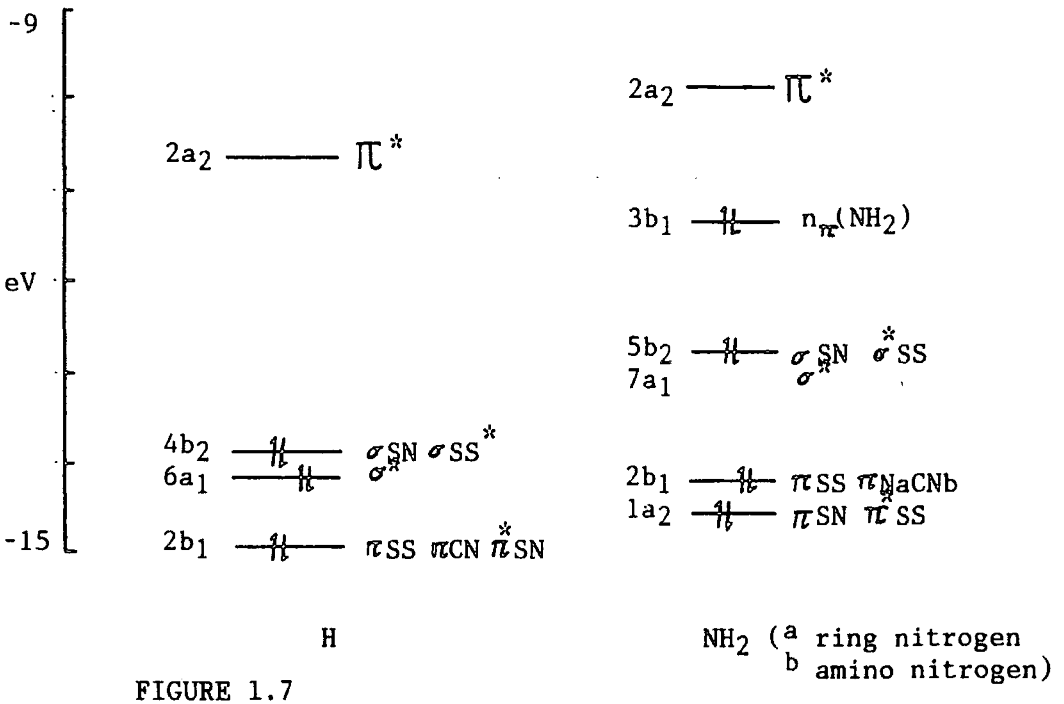


FIGURE 1.7

Substitution of H by Cl or NH_2 has a negligible effect on the bonding within the ring. For X = Cl, the C-N σ-bonding is slightly weakened while for X = NH_2 the S-N and S-S σ-bonds are strengthened and weakened, respectively.

1.7 PHYSICAL MEASUREMENTS

1.7.1 E.S.R. Spectra:

The first solid state e.s.r. study[6] on $(PhCN_2S_2)_2$ reported a broad line with a calculated splitting factor of 2.00, which is characteristic of one unpaired electron. This indicates that some dissociation into monomers occurs even in the solid state. Solid samples of the compounds $(XCN_2S_2)_2$ (X=CF_3,F,Cl,Br) were found to be diamagnetic but e.s.r. signals were obtained[9] from solutions in liquid sulphur dioxide. The signal from $(CF_3CN_2S_2)_2$ showed a clear quintet expected from an unpaired spin coupling to two equivalent nitrogen atoms (coupling constant a^N =0.51mT). The coupling constants obtained from other dithiadiazoles were found to be almost identical (a^N(mT) 0.49(R=Ph)[19], 0.49(R=CCl_3)[19], 0.51(R=F)[9], 0.53(R=Cl)[9], 0.58(R=Br)[9]) suggesting that the ligand has little influence on bonding within the ring (Section 1.6). The low values observed (cf. a^N(ArNSR) 9mT[27]) are in agreement with significant localisation of spin density onto sulphur (spin density in $(PhCN_2S_2)_2$, S:N $\approx$ 6:5)[28].

The most complete e.s.r. study is that of Sutcliffe[20] who obtained both isotropic and anisotropic data on $(MeCN_2S_2)_2$ and $(PhCN_2S_2)_2$. Spectra of $(MeCN_2S_2)_2$ showed well-resolved coupling to the methyl protons indicating free rotation, at -161°C. It was found that no $(PhCN_2S_2)_2$ was present above ca. -23°C (in toluene solution) and hence the thermodynamic parameters for dimerisation could be calculated:

$\Delta H=-35 KJmol^{-1}$, $\Delta G_{200}=12 KJmol^{-1}$, $\Delta S_{200}=-120 KJmol^{-1}$.

Ab initio and MNDO calculations were performed on the radical species and the minimum energy structures thus obtained used to obtain binding energies and hyperfine coupling constants using an INDO (Intermediate Neglect of Differential Overlap) programme. The agreement with the experimental coupling constants was poor.

1.7.2 UV-Visible Spectra: These studies[11] were prompted by the dark colour of $[Et_2NCN_2S_2]Cl$ when compared to that of other dithiadiazolium salts (except those with a polarisable anion). The band giving rise to the dark colour at 530nm, was assigned to an $n \longrightarrow \pi^*$ transition (see Figure 1.7). Band maxima and extinction coefficients have been reported for $[RCN_2S_2]Cl$; R=Ph[5,11], ^tBu[11], CCl_3[5] and Et_2N[11].

1.7.3 Other Studies: The ^1H n.m.r. signal for $[MeCN_2S_2]Cl$ has been reported[6] to appear at 1.05ppm, so that these protons are more strongly deshielded than the methyl protons in methyl cyclohexane. The substituent groups CN, CO_2H and NO_2 were however, reported to be more strongly deshielding than $CN_2S_2^+$. Although signals have been reported[17] for $(PhCN_2S_2)_2$ occurring between 7.24 (in pentane) and 7.80ppm. in monoglyme, no signal was observed by the present author in d_2-dichloromethane and it is probable that the signals observed earlier are due to hydrolysis products. The presence of paramagnetic species in N.M.R. samples can cause excessive line-broadening due to a decrease in the relaxation time.[29]

Cyclic voltammetry studies have also been made on $(PhCN_2S_2)_2$. The measured half-wave potentials were found to be +0.60V for oxidation and -0.70V for reduction (with respect to a standard Calomel electrode). Only the oxidation process, to $[PhCN_2S_2]^+$, was found to be reversible. The reduction was found to be a two-stage process; presumably $(PhCN_2S_2)_2^-$ is formed in the first step followed by further reduction to give $2[PhCN_2S_2]^-$. This work has received more detailed attention elsewhere.[30]

1.8 AN OVERVIEW OF THIS THESIS

This thesis represents the first systematic investigation of the chemistry of a member of this unusual class of stable free-radicals, the dithiadiazoles. The phenyl derivative of the 1,2 isomer was selected for study since it is readily prepared (Section 7.6.2) and easily handled under inert-atmosphere conditions. There is also a long-standing interest in this molecule in Durham.

As a consequence of the unusual nature of this species (free-radical with low enthalpy of dimerisation), there is no closely related compound with extensive chemistry which can be used for comparative purposes. However, in order to provide some basis for discussion of the reactivity of $(PhCN_2S_2)_2$ within the wider context of sulphur-nitrogen chemistry, S_4N_4 (like $PhCN_2S_2$, a non-Hückel species) which undergoes a wide variety of reactions[31], was chosen as a model.

At the present moment sulphur nitrogen chemistry appears to be diversifying along two main routes. The first is the introduction of a third element, especially carbon[32] and phosphorus[33], (both with substituent groups) into cyclic thiazene systems in order to confer more interesting structural or electronic properties, and greater stability. The second route leads into transition metal chemistry[34] where again, a great variety of structural and electronic effects can be investigated. Both of these routes are part of the current expansion of interest in sulphur nitrogen chemistry which began in 1975 when it was discovered that the polymer $(SN)_x$[35] is a quasi-one dimensional metal which becomes superconducting below 0.3K. Considerable effort has been devoted to the synthesis of suitable precursors to novel polymers which might exhibit superior physical properties to those of $(SN)_x$.

In this work a start along both routes is made in that the reactivity of a carbon-sulphur-nitrogen system toward a variety of electrophilic, nucleophilic and free-radical species has been investigated (Chapters 5 and 6). The action of several different transition metal systems has also been studied (Chapters 2 to 4) and it is anticipated that others will continue in this fascinating area of chemistry.

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43. J J Mayerle, G Wolmershäuser and G B Street, Inorg.Chem., 1979,18,1161.

44. A. Hazell and R.G. Hazell, Acta Crystallogr., Sect. C, 1988, 44,1807.

CHAPTER 2

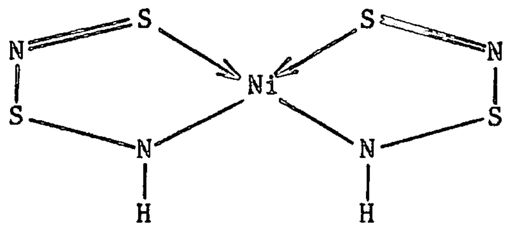
A STUDY OF THE REACTIONS OF PHENYL DITHIADIAZOLE WITH SOME BINARY TRANSITION METAL CARBONYL COMPOUNDS

2.1 GENERAL INTRODUCTION

The introduction reviews the reactions of binary transition metal carbonyls, or their derivatives containing very labile substituents such as MeCN or thf, with sulphur-nitrogen species. Only those reactions giving products in which the metal centre has a low formal oxidation state are described, so that, for instance, reactions involving $(NSCl)_3$ are excluded.[1] The first section discusses the work reported on reactions between metal carbonyls and S_4N_4 which usually give polymers from which mononuclear complexes can be extracted. The remaining two sections describe the sulphur-nitrogen chemistry of some iron and chromium group carbonyls, usually involving sulphur diimides. It is hoped that this section will help to place what follows in perspective. Reactions involving organic sulphur-nitrogen compounds, apart from RNSO and $(RN)_2S$, are not discussed.

2.1.1. Reactions involving S_4N_4

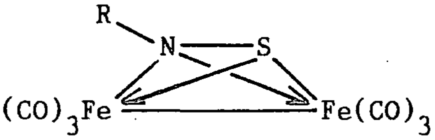
The first such reaction was reported in 1953 when $Ni(CO)_4$ and S_4N_4, in benzene solution, were found to give[2] a black, amorphous solid originally thought to approximate to $[Ni(NS)_4]_x$, also obtained from the reaction[3] of $Ni(CO)_4$ with S_2N_2. Extraction with methanol gave a complex formulated as $Ni(NS)_4$. However, later work[4] indicated $Ni(S_2N_2H)_2$ to be the correct formula with the nickel centre in a +2 oxidation state and a square planar environment with the hydrogens bonded to nitrogen. This was subsequently confirmed by X-ray crystallography[5]:



Cobalt forms analogous complexes.[2b,6] It should be noted that these complexes are best prepared from the metal halides.[7] The situation for iron complexes is less clear-cut. Although $Fe(CO)_5$ reacts with S_4N_4 in benzene to give species[2b,8] formulated as $Fe(SN)_4$, these have not been structurally characterised. The amorphous intermediates, which yield the soluble final products after solvent extraction, have been re-investigated[9a] for the reactions involving cobalt and iron carbonyls, and polymeric species of formulae $[Co_2(CO)S_4N_4]_y$ and $[Fe(CO)S_4N_4]_z$ proposed. Solvent extraction of the cobalt compound gave $Co(S_2N_2H)_2$ whereas the iron compound gave no soluble products. Later work[9b] led to the isolation of a highly unstable species, suggested to be $Fe(S_2N_2)_2$. A black amorphous solid of composition $Mo(CO)S_5N_5$ was obtained from the reaction[10] of $Mo(CO)_6$ with S_4N_4 in benzene. It was insoluble in all common organic solvents, and presumably polymeric.

2.1.2 Reactions involving the Iron Group Carbonyls

Sunlight irradiation of a mixture of $Fe(CO)_5$ and $(^tBuN)_2S$ in hexane gave $Fe_2(CO)_6$ (^tBuNS) while reaction of PhNSO with $Fe_2(CO)_9$ in benzene gave $Fe_2(CO)_6(PhNS)$. Spectroscopic data indicated that both compounds adopt the structure shown below $(R={}^tBu,Ph)$[11]:



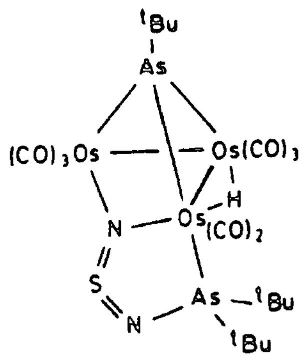
Later[12], $(^tBuN)_2S$ was found to react with $Fe_2(CO)_9$ to give the above derivative, 1, $(R={}^tBu)$, as well as $Fe_3(CO)_9(^tBuNS)(S)$, 2, $Fe_2(CO)_6S_2$

$Fe_3(CO)_9S_2$, $Fe_2(CO)_7(^tBuNS)$, 3, and $Fe_2(CO)_6(^tBuNC(O)S)$, 4. The tolyl derivatives of 1, 3 and 4 were obtained using $(4\text{-}MeC_6H_4N)_2S$ as well as $(4\text{-}MeC_6H_4N)_2$ and $Fe_3(CO)_9(4\text{-}MeC_6H_4N)(S)$. Yields were low (<7%). However the parent compound, $Fe_2(CO)_6(HNS)$, was prepared[13] in 51% yield by passing the trimethylsilyl derivative, made from $(Me_3SiS)_2N$ and $Fe_3(CO)_{12}$, down a silica column (i.e. via hydrolysis). The methyl derivative was obtained by reacting the parent compound with CH_2N_2.

A number of sulphinylanilines, ArNSO, (Ar=$4\text{-}MeOC_6H_4$, $4\text{-}MeC_6H_4$, $4\text{-}FC_6H_4$, Ph, $4\text{-}ClC_6H_4$, $4\text{-}BrC_6H_4$, $4\text{-}NO_2C_6H_4$) have been found[14] to react with $Fe_2(CO)_9$ to give red oils tentatively formulated as $Fe(CO)_4(\eta^1\text{-}(N)\text{-}ArNSO)$. These react wih phosphines, PR_3(R=Ph, $PhCH_2$, $4\text{-}MeOC_6H_4$, $4\text{-}MeC_6H_4$, $4\text{-}ClC_6H_4$) to form complexes of general formula $Fe(PR_3)_2(CO)_2(ArNSO)$. Infrared data suggest the structure of the complexes to be trigonal bipyramidal with the N-S bond lying along an equatorial edge.

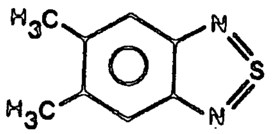
The ruthenium analogue of 1[15a] and the cluster shown below[15b] have also been prepared.

The osmium cluster compound, $Os_3(CO)_{12}$, reacted with $S(NSiMe_3)_2$[16a] to give $Os_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}NSiMe_3)$ and with $S(NAs^tBu_2)_2$[16b] to give the following:



2.1.3. Reactions involving the Chromium Group Carbonyls

The complexes $M(CO)_{6-n}L_n$ (n=2,3; M=Cr,Mo,W; L=MeCN[17],thf[18]) were found to react with $(^tBuN)_2S$ to give the octahedral complexes $[(^tBuN)_2S]M(CO)_4$, in which the sulphur diimide coordination is bidentate through its nitrogen atoms. The iso-propyl derivative of the chromium complex has also been prepared.[18] The compounds $M(CO)_5[(RN)_2S]$ (M=Cr[18],Mo[19a],W[18], R=Me,Et,^iPr) have also been prepared from $M(CO)_5$thf and $(RN)_2S$, the latter adopting monodentate coordination, through nitrogen.[18-20] Complexes of 5,6 - dimethyl-2,1,3-benzothiadiazole[19a](DMB), $M(CO)_{6-n}(DMB)_n$ (M=W, n=1,2; M=Cr, n=1, M=Mo, n=2) and the radical anion of the unsubstituted ring[19b], L, $M(CO)_5L$ and $[M(CO)_5]_2L$(M=Cr,Mo,W) have also been prepared, and these species and also $M(CO)_5\ S(NMe)_2$[18] appear to form sulphur- as well as nitrogen-metal bonded species. R_2NNS (R=Me,[21,22] Ph[22]) also formed metal-sulphur bonds when reacted with $Cr(CO)_5$thf.



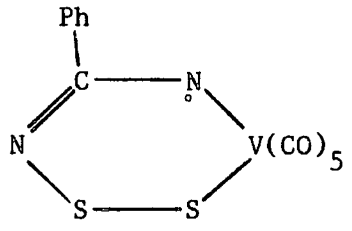
(DMB)

Tetrasulphur tetraimide, $S_4(NH)_4$, reacted with $M(CO)_5$thf (M=Cr,W) to form compounds of the type $S_4(NH)_4M(CO)_5$ and $[S_4(NH)_4][M(CO)_5]_2$ in which the metal was co-ordinated to a sulphur atom.[23]

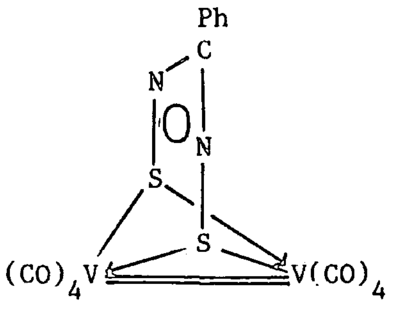
2.2 REACTION OF $(PhCN_2S_2)$ WITH $V(CO)_6$

2.2.1 Introduction

This reaction was of interest due to the existence of the redox couples $PhCN_2S_2^+$ - $PhCN_2S_2$ (Chapter 1) and $V(CO)_6$ - $V(CO)_6^-$ and to the fact that $V(CO)_6$ is the only stable paramagnetic, binary transition metal carbonyl.[24] Such properties might, in the absence of carbonyl substitution, lead to a system exhibiting interesting charge transfer effects, perhaps involving segregated stacks of partially oxidised anions and partially reduced cations.[25] The latter have been identified as potential molecular metals.[26] Alternatively, carbonyl substitution might occur to give complexes such as I or II:



[I]



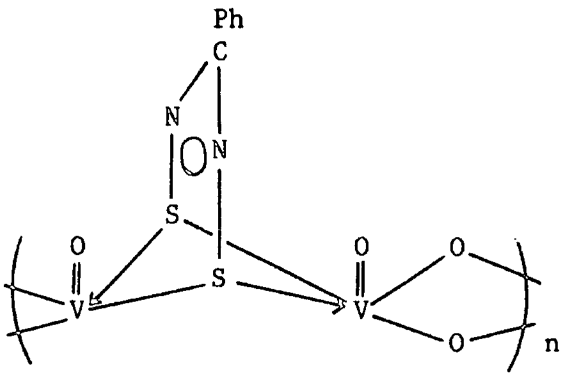
[II]

The vanadium atom in I is shown as having inserted into the S-N bond, since vanadium will probably bond to nitrogen, a harder centre. Although the odd electron is located on nitrogen in I, some spin pairing with vanadium may occur. Related species such as $VMe(CO)_4(diars)$[27] (diars = $C_6H_4(AsMe_2)_2$) and $[V(CO)_4(EPh_2)]_2$(E=P,As)[28] have been prepared previously, although, interestingly, none involving sulphur donors.

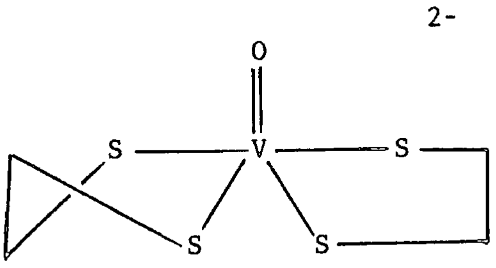
Finally, a complex in which the $PhCN_2S_2$ ring is bonded in a pentahapto-manner is an exciting, though remote, possibility. Vanadium complexes containing heteroatom π-ligands have not yet been prepared.

2.2.2. Results and Discussion

The 1:2 reaction of $(PhCN_2S_2)_2$ with $V(CO)_6$ in dichloromethane ($V(CO)_6$ disproportionates in donor solvents, L, to give $[VL_6][V(CO)_6]_2$[24]) gave a black, insoluble, presumably polymeric solid containing no carbonyl groups (Section 2.9.1). The mass spectra indicated that the dithiadiazole ring remained intact and the analyses suggested $C_7H_9N_2O_4S_2V_2$ as an empirical formula, so that III may be suggested as a possible structure. Mononuclear species such as IV have been prepared previously.[29]



[III]



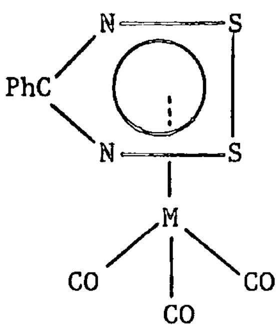
[IV]

Although oxygen was not analysed for directly, the only other oxidising agent present in the system, chlorine, in the form of dichloromethane, was not detected. The source of the oxygen (18%) is a matter for speculation. Solvents were dried and deoxygenated and care was taken to exclude air and moisture from the apparatus in use (Section 7.1). However, $V(CO)_6$ is very air-sensitive and atmospheric oxidation cannot be entirely ruled out. The other possible source of oxygen is carbonyl oxygen and reductive dissociation of CO has been observed previously in niobium and tantalum chemistry.[30] However, this process has usually been found to occur in the presence of strongly nucleophilic transition metal hydride species and seems unlikely in the system under discussion here. Further work may shed light on the reaction. The broad infrared band near $1000cm^{-1}$ may be due to V=O vibrations[29] but the poor quality of the spectra make definite assignment impossible.

2.3 REACTION OF $(PhCN_2S_2)_2$ WITH $M(CO)_3(RCN)_3$ (M=Mo,R=Me;M=W,R=^{i}Pr)

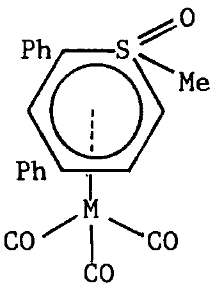
2.3.1. Introduction.

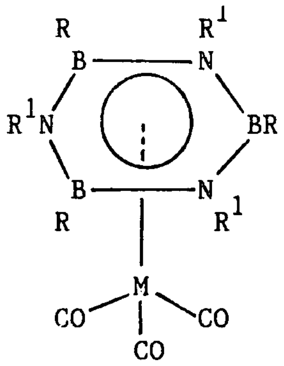
Unlike vanadium, the elements of the chromium group do form heterocyclic π-complexes and so one possibility, for the reactions described here, is the formation of the radical species shown below:

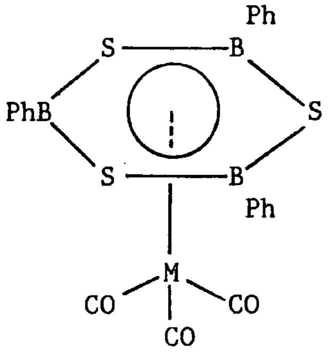


[V]

Heterocyclic π-complexes of molybdenum and tungsten containing sulphur or nitrogen (none include both) include VI[31] and VII[32] (M=Mo, R=Me, R'=Et; R=Et, R'=Me) and VIII.$^{3}/2C_4H_8O_2$.[33]



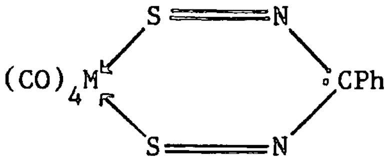




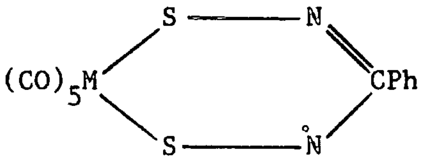
[VI] [VII] [VIII]

An X-ray analysis of the chromium analogue[31] of VI showed that the ring was non-planar but there was no evidence of metal co-ordination to the sulphur atom. The borathiin ring in VIII is best regarded as a η^3-trithia ligand with the boron atoms bonded to the oxygen atoms of dioxane. These complexes are prepared by reacting the appropriate ligand with either $M(CO)_6$ or $M(CO)_3(CH_3CN)_3$.

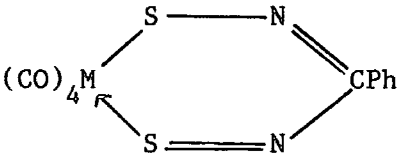
An alternative possible product is the paramagnetic system shown as IX, X or XI (M=Mo,W):



[IX]

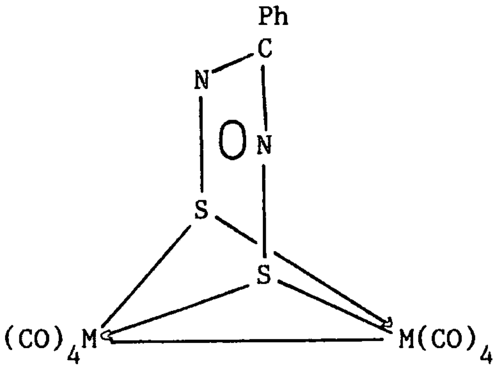


[X]



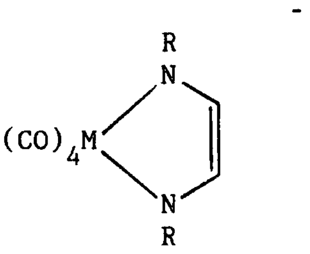
[XI]

or the binuclear bridged structure shown in XII (M=Mo,W):



[XII]

Anionic radical complexes containing the ligand glyoxaldimine have been prepared[34] (R=^{i}Pr,^{i}Bu,^{t}Bu):



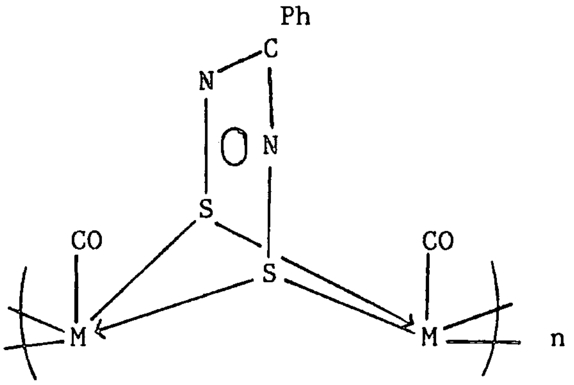
[XIII]

and several analogous neutral diamagnetic species containing sulphur donors are known.[35] Complexes analogous to XII, $[W(CO)_4(SR)]_2$

(R=Me, Et, ^{i}Pr, ^{t}Bu, Ph, 4-BrC$_6$H$_4$, 4-MeOC$_6$H$_4$)[36] and $[M(CO)_4SCF_3]_2$ (M=Mo, W)[42a] are also known.

2.3.2. Results and Discussion

The 1:2 reaction of $(PhCN_2S_2)_2$ with $M(CO)_3$ $(RCN)_3$ (M=Mo,W; R=Me, ^{i}Pr respectively) or with $Mo(CO)_6$ gave black, insoluble, presumably polymeric solids which gave analyses very close to those required for $PhCN_2S_2M(CO)$. The frequencies of the infrared bands, at 2160 and $2170m^{-1}$, in the molybdenum and tungsten - containing solids, respectively, are in good agreement with those observed for $FeS_4N_4(CO)$[9], $Co_2S_4N_4(CO)$[9] and $MoS_5N_5(CO)$[10] at $2180cm^{-1}$. All of these frequencies lie above that of CO itself at $2142cm^{-1}$, which is difficult to rationalise since co-ordination to a metal would be expected to lower the CO frequency due to off-loading of metal electron density into π^* CO orbitals. This effect makes the major contribution to the strength of the metal-carbon bond, outweighing the σ-donation from carbon to metal.[37] A previous explanation[9] of the high CO frequencies implied the S_4N_4 ligand to be a better π-acceptor (probably through S) than CO. The preparation of perfluoroalkylsulphur complexes containing carbonyl groups[41] which do not exhibit this high frequency mode suggests that a different explanation may be necessary. One possibility would be the formation of an isocyanate species (νas (NCO):2155-2284cm-1)[38a] and indeed such a reaction has previously been observed[38b] between $CpM(CO)_3H$ (M=Mo,W) and $Ph_2S{=}NH$, which gave $CpM(CO)_2(NH_3)NCO$ and Ph_2S. The reaction involving $(PhCN_2S_2)_2$ would presumably give $PhCNS_2M(NCO)$. However, the mass spectra, especially the appearance of $PhCN_2S^+$ for M=Mo, do not support this proposal. Another possibility would be that the σ-donation mentioned above, which involves an orbital which is slightly antibonding in character, is now dominating the metal-carbon bonding. This proposal implies an increase in the metal's oxidation state (to rule out substantial back-bonding) and further work is needed before definite conclusions can be drawn. A possible structure for the materials under discussion is given in XIV:



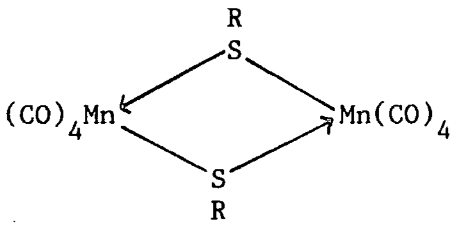
[XIV]

The molybdenum containing material did not conduct electricity and was found to be paramagnetic (see Appendix 3). UV photolysis of a solution of $Mo(CO)_6$ and $(PhCN_2S_2)$ in thf did not lead to reaction.

2.4 REACTION OF $(PhCN_2S_2)_2$ WITH $Mn_2(CO)_{10}$ AND $Re_2(CO)_{10}$: PREPARATION OF $Mn_2(CO)_8PhCN_2S_2$

2.4.1 Introduction

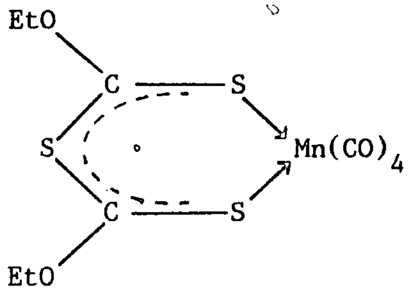
Although many dinuclear sulphur complexes of manganese are known[39], most are prepared from mononuclear starting materials such as $Mn(CO)_5X$ (X=Br,Cl,H). Those that have been prepared from $Mn_2(CO)_{10}$ include $[Mn(CO)_4S]_2$[40], $[Mn(CO)_4SR]_2$ ($R=CF_3$[41,42] CH_2Ph[43] Me[44], Ph[44]) and $Mn_2(CO)_8$ $(SCH_3)(SCF_3)$[41] and the structure shown as XVI was proposed on the basis of i.r. data.



[XVI]

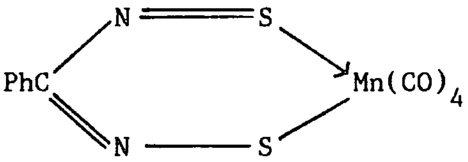
The X-ray structure of the analogous selenium derivative ($R=CF_3$) supports the above proposal.[45]

A mononuclear, paramagnetic (19-electron) species shown as XVII has also been prepared[46a] by photolysis of a mixture of $Mn_2(CO)_{10}$ and $(EtOCS)_2S$.



[XVII]

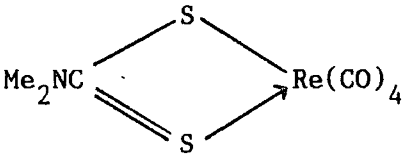
If $(PhCN_2S_2)_2$ reacted similarly then a diamagnetic (18-electron) species would be expected, as shown in XVIII.



[XVIII]

Dinuclear sulphur complexes of rhenium are also known[44,47] and are usually prepared from $Re(CO)_5X$ (X=Br,Cl,I,H).

The photochemical reaction[44] between $Re_2(CO)_{10}$ and tetramethylthiuram disulphide $[Me_2NC(S)S]_2$, gave the mononuclear complex shown as XIX.



[XIX]

A similar reaction[46b] involving $[R_2P(S)S]_2$ (R=Et,Ph) gave the R_2P (rather than Me_2NC) analogue of XIX.

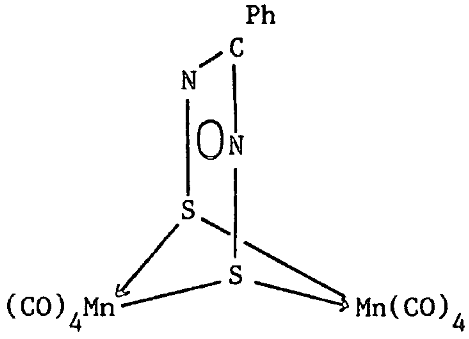
It should be noted that some dinuclear complexes of manganese and rhenium, where the substituent on sulphur is not highly electronegative, are susceptible to loss of CO with the formation of tetranuclear, cubane clusters.[48] However, this reaction only occurs at higher temperatures[49] (130°C) or under certain photolytic conditions.[44,50]

2.4.2 Results and Discussion

$(PhCN_2S_2)_2$ did not react with $Mn_2(CO)_{10}$ under UV photolysis conditions ($Mn_2(CO)_{10}$ is known[51] to give $Mn(CO)_5^-$ on irradiation in thf) and gave only decomposition products at high temperatures in the solid state and in toluene. The decomposition reaction given below represents the most likely pathway, although there was evidence for a very low concentration of carbonyl-containing material in the toluene reaction products (Section 2.9.5(c)).

$$(PhCN_2S_2)_2 + Mn_2(CO)_{10} \longrightarrow MnS + Mn(NCO)_2 + 2PhCN + 3/8\ S_8 + 8CO$$

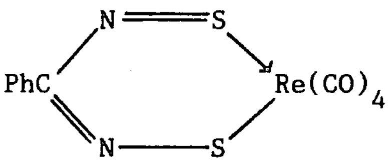
However, reaction to give a carbonyl species did occur in the presence of Me_3NO, which gave $Mn_2(CO)_8PhCN_2S_2$ in good yield. The reagent Me_3NO (with which $(PhCN_2S_2)_2$ does not react, Section 5.5) has been used previously to decarbonylate a variety of transition metal carbonyl species,[52] including $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. The manganese complex was found to be insoluble in hydrocarbon solvents, ethers and acetonitrile and only slightly soluble in dichloromethane. All attempts at crystal growth via temperature rippling and extraction failed (Section 2.9.5(d)), and so the structure was inferred from i.r. data. The number and frequency of the bands in the carbonyl region agree fairly well with those reported[53a] for $Mn_2(CO)_8(SR)_2$ (R=Me,Et,Bu) and so the following structure is proposed:



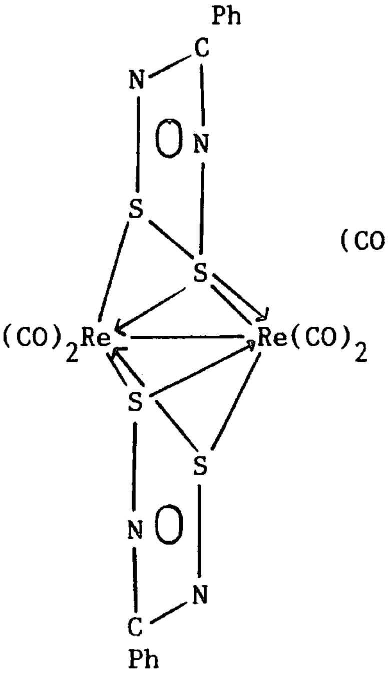
[XX]

The compound is paramagnetic with a magnetic susceptibility of $0.375\text{JT}^{-2}\text{Kg}^{-1}$ (see Appendix 3)

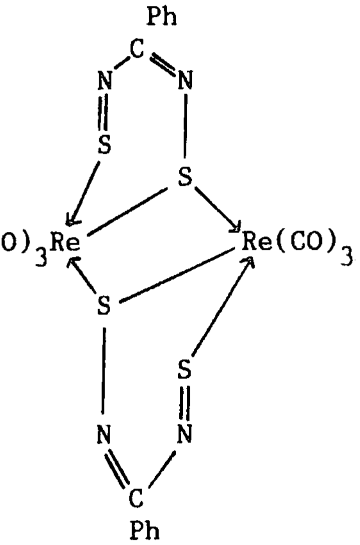
The results for the rhenium reaction are less easy to explain. The similarity in the i.r. spectra, in the carbonyl region, between the manganese and rhenium-containing products suggests a similar structure for both. However, the analyses for the latter do not support this. In fact, the analytical results (see Table 2.1) are much closer to those expected from the three other complexes, the structures of which are shown as XXI-XXIII.



[XXI]



[XXII]



[XXIII]

Table 2.1 Analytical Data (%) for the Rhenium Compound

Compound	C	H	N	Re	S
$Re_2(CO)_8PhCN_2S_2$	23.2	0.6	3.6	47.9	8.2
$Re(CO)_4PhCN_2S_2$	27.6	1.0	5.8	38.8	13.4
$Re_2(CO)_4(PhCN_2S_2)_2$	25.5	1.2	6.6	44.0	15.1
$Re_2(CO)_6(PhCN_2S_2)_2$	26.6	1.1	6.2	41.3	14.2
Actual	25.9	2.2	6.3	35.8	12.2

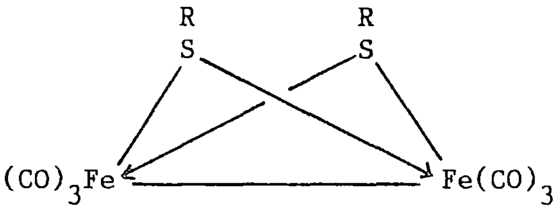
Unfortunately, neither the i.r. spectra (Section 2.9.6(b)) nor the analyses allow definite elucidation of the structure of the compound. The magnetic data (see Appendix 3) show that the compound is paramagnetic, with a susceptibility of $0.014JT^{-2}Kg^{-1}$ and indicate a structure different to that of the manganese complex. Rhenium complexes such as XXII have not yet been prepared and i.r. spectra, especially the appearance of a band near $2100cm^{-1}$ suggest that the compound under discussion here adopts structure XXI rather than XXIII. This is supported by the usual preparation of the latter at higher temperatures.[53b]

The rhenium compound is slightly more soluble in dichloromethane than the manganese compound and so it may be possible to obtain crystals for X-ray analysis.

2.5 REACTION OF $(PhCN_2S_2)_2$ WITH $Fe_2(CO)_9$ AND $Fe_3(CO)_{12}$: PREPARATION OF $Fe_2(CO)_6PhCN_2S_2$

2.5.1 Introduction

Many dinuclear, sulphur bridged complexes of iron, prepared from $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ are known[54a] and a wealth of spectroscopic and structural information is available. Thiols, sulphides, and disulphides usually react to give species of general formula $Fe_2(CO)_6(SR)_2$ the structure of which is given as XXIV



[XXIV]

Elemental sulphur and H_2S react to give $Fe_2(CO)_6S_2$ and $Fe_3(CO)_9S_2$, the structure of which is based on an open triangle of $Fe(CO)_3$ groups with triply bridging sulphur atoms above and below the plane. Other trinuclear species are known[54b] but these are less common.

2.5.2 Results and Discussion

The reaction of $(PhCN_2S_2)_2$ with both $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ gave the new compound $Fe_2(CO)_6$ $PhCN_2S_2$, the structure of which is given in Figure 2.1. Structural data are given in Tables 2.2 - 2.5.

The structure is based on the well-known Fe_2S_2 'butterfly' core which possesses idealised C_{2v} symmetry. The first noteworthy feature is the S---S distance at 2.930(2)Å which is the same as that observed in $Fe_2(CO)_6(SR)_2$ (R=Et[55],Ph[56]) (latter distance calculated from atomic coordinates). Although this distance is below the sum of the van der

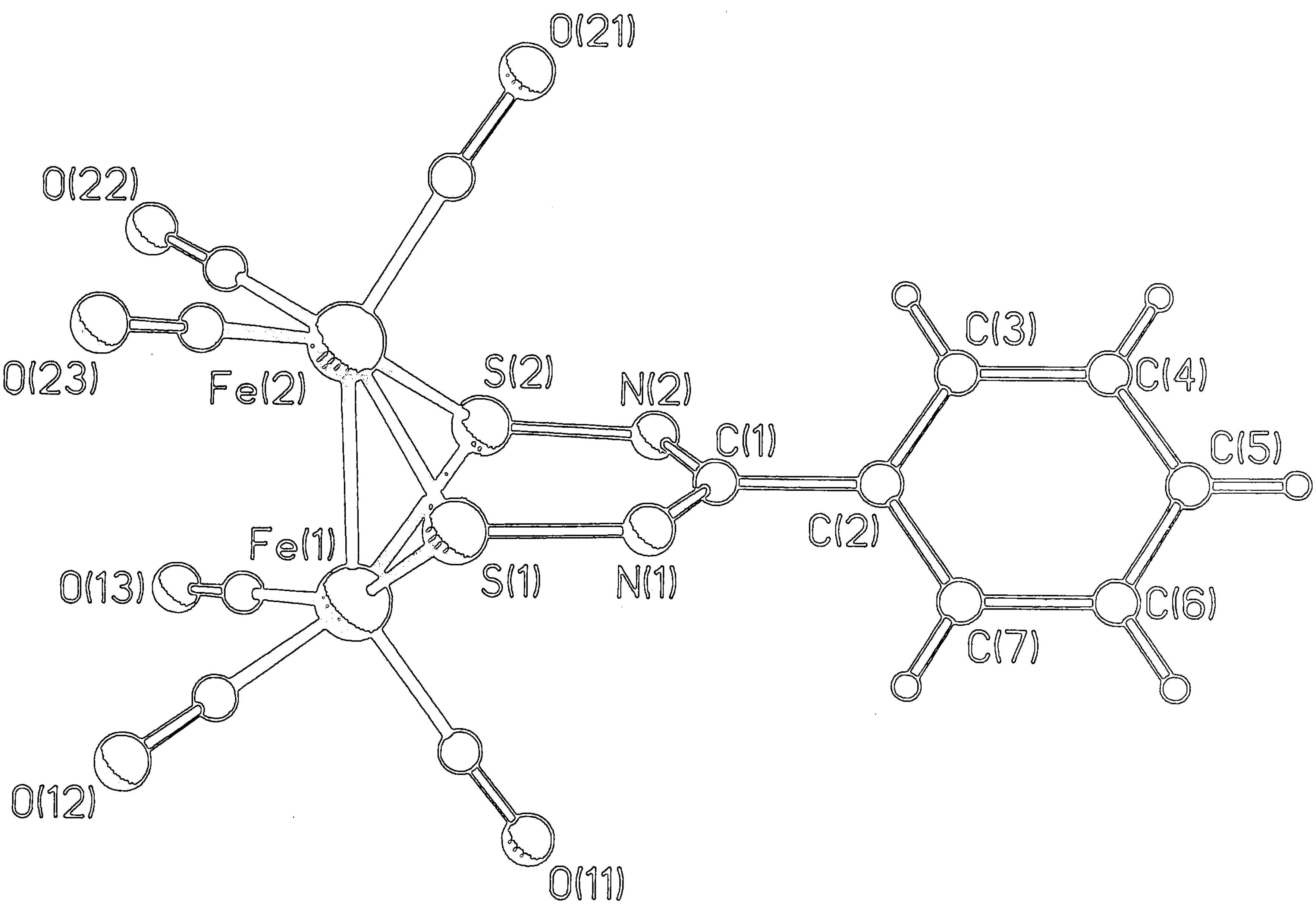
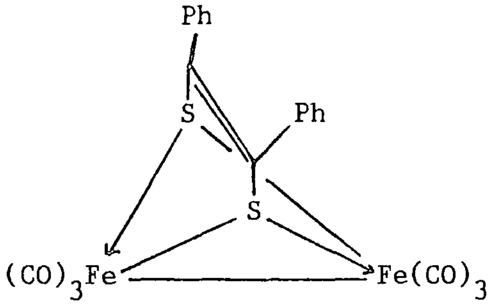


Figure 2.1. X-Ray Structure of $Fe_2(CO)_6PhCN_2S_2$

Waals radii[57] for sulphur at 3.6Å, at best a very weak bond is assumed to be present. Perhaps a more direct comparison can be made with the ethane[58] or diphenylethenethiolate[59] derivatives, XXV, where the sulphurs are bridged in the ligand (via CC as opposed to NCN).



[XXV]

In these compounds the S---S distances are 2.887(1) and 2.866(7)Å, respectively. These values contrast with that for $Fe_2(CO)_6S_2$[60] which is also based on the Fe_2S_2 core but possesses an S—S bond; d_{ss} = 2.007(5)pm. The S - S distance in the free ligand[61] is 2.09Å. The Fe-Fe and Fe-S distances are representative, as shown in Table 2.6 as are the structural parameters of the carbonyl groups.

Table 2.2

Bond lengths (Å) and angles (°)

Fe(1)-Fe(2)	2.533(2)	Fe(1)-S(1)	2.232(2)
Fe(1)-S(2)	2.220(2)	Fe(1)-C(11)	1.800(7)
Fe(1)-C(12)	1.786(8)	Fe(1)-C(13)	1.807(6)
Fe(2)-S(1)	2.235(2)	Fe(2)-S(2)	2.211(2)
Fe(2)-C(21)	1.774(7)	Fe(2)-C(22)	1.800(7)
Fe(2)-C(23)	1.805(8)	S(1)-S(2)	2.930(2)
S(1)-N(1)	1.694(5)	S(2)-N(2)	1.716(5)
N(1)-C(1)	1.295(8)	N(2)-C(1)	1.348(7)
C(1)-C(2)	1.494(8)	C(2)-C(3)	1.376(10)
C(2)-C(7)	1.387(9)	C(3)-C(4)	1.387(10)
C(4)-C(5)	1.371(12)	C(5)-C(6)	1.361(13)
C(6)-C(7)	1.366(10)	C(11)-O(11)	1.131(9)
C(12)-O(12)	1.142(10)	C(13)-O(13)	1.126(8)
C(21)-O(21)	1.152(9)	C(22)-O(22)	1.136(9)
C(23)-O(23)	1.137(10)		

Fe(2)-Fe(1)-S(1)	55.5(1)	Fe(2)-Fe(1)-S(2)	55.0(1)
S(1)-Fe(1)-S(2)	82.3(1)	Fe(2)-Fe(1)-C(11)	147.5(2)
S(1)-Fe(1)-C(11)	103.5(2)	S(2)-Fe(1)-C(11)	101.7(2)
Fe(2)-Fe(1)-C(12)	102.6(2)	S(1)-Fe(1)-C(12)	85.3(2)
S(2)-Fe(1)-C(12)	157.5(2)	C(11)-Fe(1)-C(12)	99.4(3)
Fe(2)-Fe(1)-C(13)	102.9(2)	S(1)-Fe(1)-C(13)	157.1(3)
S(2)-Fe(1)-C(13)	91.0(2)	C(11)-Fe(1)-C(13)	99.3(3)
C(12)-Fe(1)-C(13)	93.3(3)	Fe(1)-Fe(2)-S(1)	55.4(1)
Fe(1)-Fe(2)-S(2)	55.3(1)	S(1)-Fe(2)-S(2)	82.4(1)
Fe(1)-Fe(2)-C(21)	146.4(2)	S(1)-Fe(2)-C(21)	106.5(2)
S(2)-Fe(2)-C(21)	97.5(2)	Fe(1)-Fe(2)-C(22)	100.7(2)
S(1)-Fe(2)-C(22)	154.5(3)	S(2)-Fe(2)-C(22)	90.8(3)
C(21)-Fe(2)-C(22)	98.8(3)	Fe(1)-Fe(2)-C(23)	106.7(3)
S(1)-Fe(2)-C(23)	87.5(3)	S(2)-Fe(2)-C(23)	162.0(3)
C(21)-Fe(2)-C(23)	99.7(3)	C(22)-Fe(2)-C(23)	91.9(3)
Fe(1)-S(1)-Fe(2)	69.1(1)	Fe(1)-S(1)-S(2)	48.7(1)
Fe(2)-S(1)-S(2)	48.4(1)	Fe(1)-S(1)-N(1)	113.1(2)
Fe(2)-S(1)-N(1)	114.7(2)	S(2)-S(1)-N(1)	83.0(2)
Fe(1)-S(2)-Fe(2)	69.7(1)	Fe(1)-S(2)-S(1)	49.0(1)
Fe(2)-S(2)-S(1)	49.1(1)	Fe(1)-S(2)-N(2)	111.2(2)
Fe(2)-S(2)-N(2)	109.8(2)	S(1)-S(2)-N(2)	78.3(2)
S(1)-N(1)-C(1)	123.6(4)	S(2)-N(2)-C(1)	127.2(4)
N(1)-C(1)-N(2)	127.8(5)	N(1)-C(1)-C(2)	116.9(5)
N(2)-C(1)-C(2)	115.3(5)	C(1)-C(2)-C(3)	121.8(6)
C(1)-C(2)-C(7)	119.5(6)	C(3)-C(2)-C(7)	118.6(6)
C(2)-C(3)-C(4)	120.0(7)	C(3)-C(4)-C(5)	120.0(8)
C(4)-C(5)-C(6)	120.5(7)	C(5)-C(6)-C(7)	119.7(7)
C(2)-C(7)-C(6)	121.3(7)	Fe(1)-C(11)-O(11)	177.6(7)
Fe(1)-C(12)-O(12)	177.2(6)	Fe(1)-C(13)-O(13)	178.9(7)
Fe(2)-C(21)-O(21)	174.9(6)	Fe(2)-C(22)-O(22)	178.4(7)
Fe(2)-C(23)-O(23)	178.0(7)		

Table 2.3

Anisotropic thermal parameters (Å^{2}x10^4)

The anisotropic temperature factor exponent takes the form
$-2\ ^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe(1)	287(5)	386(6)	330(5)	-1(5)	60(4)	19(5)
Fe(2)	341(5)	354(6)	374(5)	25(5)	96(4)	25(5)
S(1)	308(9)	406(10)	266(8)	-40(8)	89(7)	20(8)
S(2)	348(9)	415(11)	248(8)	19(8)	55(7)	56(8)
N(1)	276(27)	373(32)	247(27)	-11(26)	74(21)	28(26)
N(2)	366(31)	403(35)	249(28)	20(26)	52(24)	53(27)
C(1)	261(33)	211(36)	294(34)	-4(27)	40(28)	0(28)
C(2)	374(39)	346(40)	262(34)	-25(31)	42(29)	-47(32)
C(3)	432(42)	468(47)	494(43)	49(36)	164(35)	51(36)
C(4)	446(46)	823(69)	885(64)	-237(52)	262(44)	142(46)
C(5)	523(53)	765(65)	708(60)	-85(50)	-111(46)	379(49)
C(6)	685(57)	700(62)	432(49)	-28(42)	46(43)	359(49)
C(7)	521(45)	448(45)	311(39)	-71(35)	90(33)	130(37)
C(11)	386(39)	476(48)	382(40)	-6(36)	17(31)	72(36)
O(11)	939(44)	396(33)	870(43)	-27(32)	57(35)	-22(32)
C(12)	314(40)	460(50)	597(50)	70(39)	67(38)	39(36)
O(12)	555(35)	963(47)	694(38)	32(35)	362(31)	266(34)
C(13)	406(42)	613(53)	475(44)	-48(41)	73(35)	23(40)
O(13)	535(33)	1267(57)	618(37)	90(37)	-154(28)	113(36)
C(21)	545(47)	310(42)	572(48)	-12(36)	76(38)	10(37)
O(21)	598(37)	883(47)	1244(53)	-235(40)	408(36)	-283(34)
C(22)	435(47)	528(53)	546(52)	-10(43)	109(40)	35(41)
O(22)	784(43)	927(49)	651(40)	367(36)	36(33)	234(37)
C(23)	457(46)	438(50)	554(51)	63(42)	30(39)	77(40)
O(23)	976(47)	753(47)	849(44)	-309(37)	304(37)	211(38)

Table 2.4

Atomic coordinates (x10^{4})

Atom	*x*	*y*	*z*
Fe(1)	6373(1)	3309(1)	4158(1)
Fe(2)	7426(1)	4948(1)	4075(1)
S(1)	7652(1)	3785(1)	5800(2)
S(2)	7471(1)	3477(1)	2874(1)
N(1)	8636(3)	2970(4)	5911(5)
N(2)	8521(3)	2769(4)	3538(5)
C(1)	8931(4)	2606(5)	4863(5)
C(2)	9828(4)	1918(5)	5137(6)
C(3)	10550(4)	2024(6)	4407(7)
C(4)	11403(5)	1421(7)	4754(8)
C(5)	11531(6)	727(7)	5831(8)
C(6)	10818(6)	610(6)	6552(8)
C(7)	9976(5)	1200(5)	6211(6)
C(11)	6320(5)	1880(5)	4342(6)
O(11)	6305(4)	979(4)	4422(6)
C(12)	5641(5)	3703(6)	5325(8)
O(12)	5206(4)	3972(5)	6103(6)
C(13)	5376(5)	3483(6)	2692(7)
O(13)	4748(4)	3600(5)	1790(5)
C(21)	8607(5)	5442(5)	4004(7)
O(21)	9377(4)	5703(5)	3890(7)
C(22)	6716(5)	5620(6)	2606(8)
O(22)	6248(4)	6036(5)	1687(6)
C(23)	7083(5)	5920(6)	5211(8)
O(23)	6847(4)	6511(5)	5936(6)

H atoms: atomic coordinates (x10^{4}) and isotropic thermal parameters (Å^{2}x10^{4})

	x	*y*	*z*	*U*
H(3)	10463	2516	3659	543
H(4)	11903	1488	4238	833
H(5)	12128	321	6080	838
H(6)	10907	116	7298	736
H(7)	9475	1116	6723	507

Table 2.5

Crystallographic data for $Fe_2(CO)_6PhCN_2S_2$

Crystal System	Monoclinic
Space Group	$P2_1/c$
Unit Cell Measurements	
a (Å)	13.941(1)
b (Å)	12.508(1)
c (Å)	10.077(1)
ß (°)	102.61(1)
U (A^3)	1714.8
Dc(gcm^{-3})	1.785
Z	4
F(000)	916 electrons
T(°C)	25
No.Unique Reflections	2992
No.Observed Reflections	1815
R	0.0516
Rw	0.0387
μ(Mo-K)(mm^{-1})	1.956

Table 2.6 Structure Data (in Å and °) of some Iron-Sulphur Compounds

Compound	Fe-S[a]	Fe-Fe	S-S	Fe-S-Fe[a]	S-Fe-S[a]
$Fe_2(CO)_6(SEt)_2$	2.259(7)	2.537(10)	2.932(14)	68.3(3)	81.0(3)
$Fe_2(CO)_6(SPh)_2$	2.270(2)	2.516(2)		67.3(1)	79.8(1)
$Fe_2(CO)_6(SCH_2)_2$	2.240(1)	2.502(1)	2.887(1)	68.0(3)	80.3(4)
$Fe_2(CO)_6(SCPh)_2$	2.259(3)	2.507(5)	2.886(7)	67.4(1)	78.7(1)
$Fe_2(CO)_6S_2$	2.228(2)	2.552(2)	2.007(5)	69.9(1)	53.5(1)

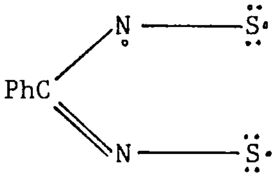
a average values.

The geometry of related species has previously been described in terms of two distorted square-based pyramids joined along a common edge defined by the S - S vector, the other corners of the square being carbonyl carbon atoms. In $Fe_2(CO)_6PhCN_2S_2$, Fe(1) and Fe(2) are displaced 0.373 and 0.362Å respectively, from their basal planes in the direction of the axial carbonyl group. The dihedral angle between these planes is 73.0°. The idealised C_{2v} symmetry manifests itself in the angle of 89.8 between the Fe-Fe vector and the S-S vector. Again, these values are typical.[55]

The average S-N distance (1.705(5)Å) is 0.085Å longer than in the free ligand and approaches that of an S-N single bond (cf. 1.73Å in S_7NH)[62] whereas there is no significant change in the average C-N distance. The average angles at carbon and nitrogen increase by 6.8° and 9.9° respectively, but those at sulphur decrease by 13.5°. The latter changes are a natural consequence of the ring opening at the S-S bond and of the decrease in S-N bond order which allows the angles at N to expand.[63]

The molecule, $Fe_2(CO)_6PhCN_2S_2$, is paramagnetic with a magnetic susceptibility of $0.058JT^{-2}Kg^{-1}$ (see Appendix 3). Extended Huckel calculations[64] place the odd electron in an orbital located mainly on the ligand which is antibonding with respect to S-S and S-N, in accord with the changes in bond length given above (cf. free ligand[65]). There are intermolecular contacts between adjacent nitrogen atoms, of neighbouring $PhCN_2S_2$ rings, at 2.842Å (cf. sum of the van der Waals radii for nitrogen[57] at 3.1Å and a typical N-N single bond length[66] at 1.453(5)Å). The contacts (see Figure 2.2) may be the result of some degree of spin pairing (see Appendix 3). The phenyl ring is twisted 40° out of the dithiadiazole plane.

The bonding description of $Fe_2(CO)_6PhCN_2S_2$ can be considered in an analogous manner to that invoked for other $Fe_2(CO)_6(SR)_2$-type complexes in which each sulphur atom formally contributes three electrons for bonding[67] to iron. These, together with six electrons from the carbonyl groups, one from the other iron atom and the eight from irons valence shell make eighteen electrons in all, as required. Thus, the dithiadiazole ring appears to be acting as an acyclic donor as shown below:



[XXVI]

Each sulphur atom carries a formal charge of -1, in contrast to the small positive charge (+0.85) found by the Extended Huckel calculations.[64] Such differences have been noted previously.[68]

The insoluble residues formed in these reactions are most probably polymeric. The solid obtained from the $Fe_2(CO)_9$ reaction does not contain carbonyl groups whereas that obtained from $Fe_3(CO)_{12}$ did show bands in the carbonyl region of the infrared spectrum. Interestingly, a band at $2190cm^{-1}$ was observed (Section 2.3.2).

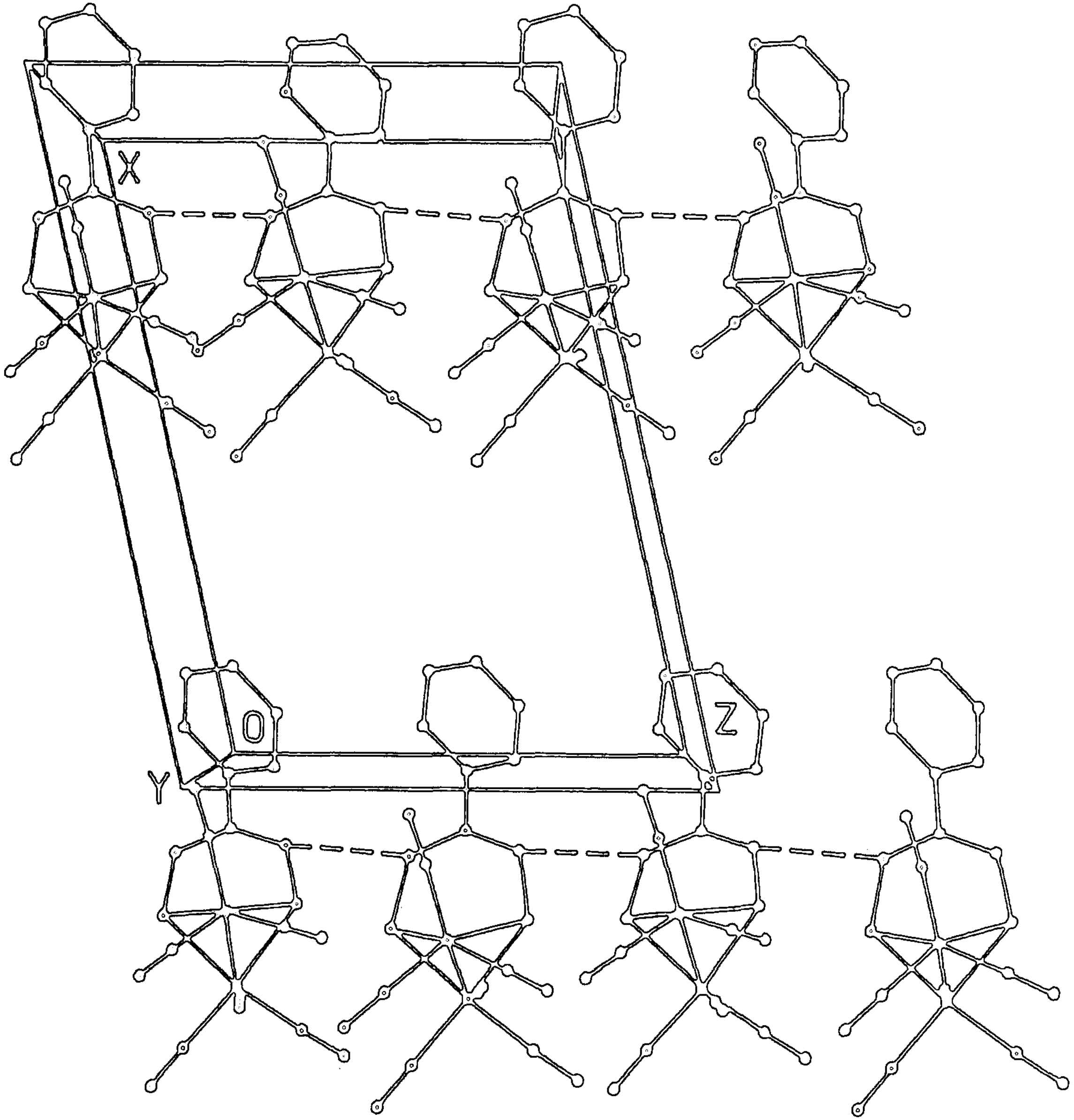
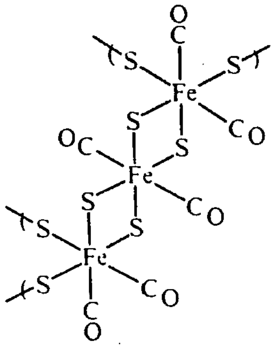


Figure 2.2. Packing Diagram (showing N--N interactions) of $Fe_2(CO)_6PhCN_2S_2$

2.6 REACTION OF $(PhCN_2S_2)_2$ WITH $Fe(CO)_5$

2.6.1 Introduction

Iron pentacarbonyl is the most inert of the binary carbonyls of iron, and this is borne out by its low reactivity toward a range of disulphides and thiols. However, bis (trifluoromethyl) dithietene and 3,4 toluenedithiol do react under mild conditions[69], to give $Fe_2(CO)_6S_2E$ ($E=MeC_6H_3,C_2(CF_3)_2$). Later $Fe(CO)_5$ was found to give $Fe_2(CO)_6(SMe)_2$ with Me_2S_2 at 130° under high CO pressure.[70] In the absence of additional CO, an insoluble polymer, $[Fe(CO)_2(SMe)_2]_n$ was formed as the major product together with a little $Fe_2(CO)_6(SMe)_2$. The proposed structure of the polymer, with cis carbonyl groups is shown below (Me groups omitted):



[XXVII]

The reactivity of the iron carbonyls towards sulphides, disulphides and thiols has been placed on a quantitative footing and the following orders of reactivity deduced:[71] $Fe(CO)_5 < Fe_2(CO)_9 < Fe_3(CO)_{12}$ and $RSR < RSSR < RSH$.

2.6.2 Results and Discussion

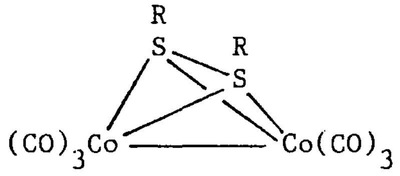
Iron pentacarbonyl did not react with $(PhCN_2S_2)_2$ in toluene at 100°C but in the presence of Me_3NO (Section 2.9.9(b)) at 21°C gave $Fe_2(CO)_6PhCN_2S_2$ (10% based on $Fe(CO)_5$) and an insoluble, presumably polymeric solid which still contained carbonyl groups and is possibly based on the structure shown in XXVII.

2.7 REACTION OF $(PhCN_2S_2)_2$ WITH $Co_2(CO)_8$

2.7.1 Introduction

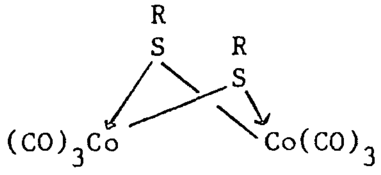
Most reactions of $Co_2(CO)_8$ with sulphur-containing species lead to the isolation of polynuclear cobalt compounds[72], often with at least one vertex occupied by a naked sulphur atom. This is not surprising in view of the effectiveness of $Co_2(CO)_8$ as a desulphurisation reagent.[73] Reaction of $Co_2(CO)_8$ with tetrathionapthalene (TTN)[74] gave a polymeric amorphous powder of composition $[Co_2(CO)_2TTN]_n$.

Although early evidence[75] for dinuclear derivatives of the type $[(RS)Co(CO)_3]_2$ (R=Et) with bridging RS and terminal CO groups and possessing no Co-Co bond has since been disproved,[76] such compounds have been reported using perhalogeno-organosulphur species.[77] The high electronegativity of these ligands was thought to decrease the tendency of sulphur to form multiple bridges. The following structure was suggested in which the sulphur atoms act as two-electron donors ($R=C_6F_5,C_6Cl_5$):



[XXVIII]

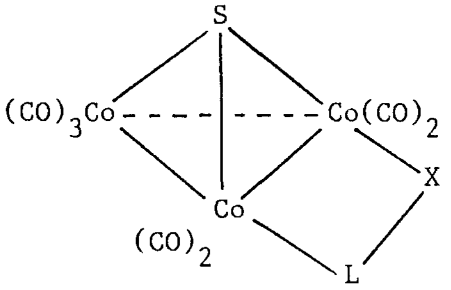
However, the evidence for the above, in particular the assertion, in support of the Co-Co bond, that 'no binuclear metal carbonyl derivatives containing non-planar briding ligands are known without metal-metal bonds' is open to question (Section 2.4.1). The experimental data can be equally well explained by the structure shown below in which the sulphur atoms each donate three electrons to the metal.



[XXIX]

Interestingly, the reaction between bis(trifluoromethyl) dithietene and $Co_2(CO)_8$ gave a trinuclear cobalt compound.[78]

Finally, the reaction of $Co_2(CO)_8$ with $R^1C(S)NHR^2$ (R^1=Me,Ph; $R^2=C_6H_{11}$),[79a] $Me_2NC(S)X$ (X=H,Cl)[79b] and $RC(S)NH_2$ (R=Me,Ph,4-$MeOC_6H_4$)[79c] gave species with a structure based on that shown below, where the LX fragment acts as a three-electron donor:



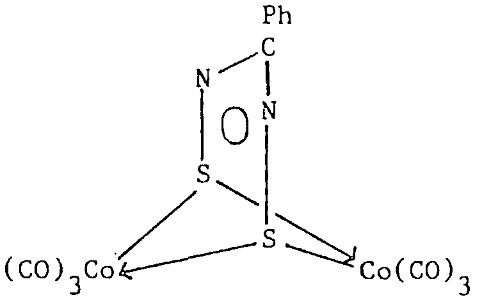
[XXX]

From the above discussion it is evident that the products of the reaction between $(PhCN_2S_2)_2$ and $Co_2(CO)_8$ will probably be polynuclear and that characterisation will be 'difficult without the aid of X-ray crystallography'.[72]

2.7.2 Results and Discussion

The 2:1, 1:1 and 1:2 reactions between $Co_2(CO)_8$ and $(PhCN_2S_2)_2$ in toluene or dichloromethane gave black, air-stable, amorphous solids of variable composition.

The 2:1 reaction (Section2.9.10(a)) gave a material, the analysis of which suggested a structure as shown in XXXI (Calc. for XXXI: Co,25.3,N,6.0; S,13.7% Found: Co,26.6; N,6.4; S,14.8%).



[XXXI]

These data are supported by the solution phase i.r. spectra (Figure 2.3) which show three bands in the terminal carbonyl region at 2058, 2078 and 2110cm^{-1} (cf. ν max $Co_2(CO)_6(SC_6F_5)_2$[77]: 2059, 2066, 2081, 2111cm^{-1}). However, the mass spectrometry results do not show any evidence for the above structure.

The solution phase infrared spectra of the 1:1 reaction in the carbonyl region (Figure 2.4) again show three bands at 2060, 2075 and 2095cm^{-1}. After 24h, both the 2:1 and 1:1 reaction spectra are dominated by a broad band centred at 2060cm^{-1} with a shoulder at 2090cm^{-1}. The nujol spectra of the 2:1 reaction product in the region below 800cm^{-1} show two bands, at 773 and 798cm^{-1}, in addition to those also observed in the 1:1 reaction spectra, at 695 and 735cm^{-1}. Also, the main carbonyl band is relatively more intense in the 2:1 spectra.

The analyses of the 1:1 reaction product suggested a structure based on the $PhCN_2S_2Co(CO)$ unit perhaps as a dimer (Calc.: Co,22.0; N,10.4; S,23.9%. Found: Co,19.6; N,9.5; 21.1%) and there is some mass spectral evidence to support this with weak peaks at 296, 268, 264 and 226. The appearance of peaks[80] due to $(PhCN_2S)_2$ is interesting since this could arise via desulphurisation of $(PhCN_2S_2)_2$. However, this compound could not be sublimed out (Section 2.9.10(g)).

The solution phase infrared spectra of the 1:2 reaction (Section 2.9.10(c)) now show a very weak carbonyl band at 2060cm^{-1}. The new bands in the low frequency region have increased in intensity with respect to those originally present in the 2:1 reaction, at 695 and 735cm^{-1} while the former has increased its intensity relative to the latter. The analyses of these materials are not informative.

The nujol spectra of the product from the reaction involving a fourfold excess (Section 2.9.10(d)) of $(PhCN_2S_2)_2$ now show bands due

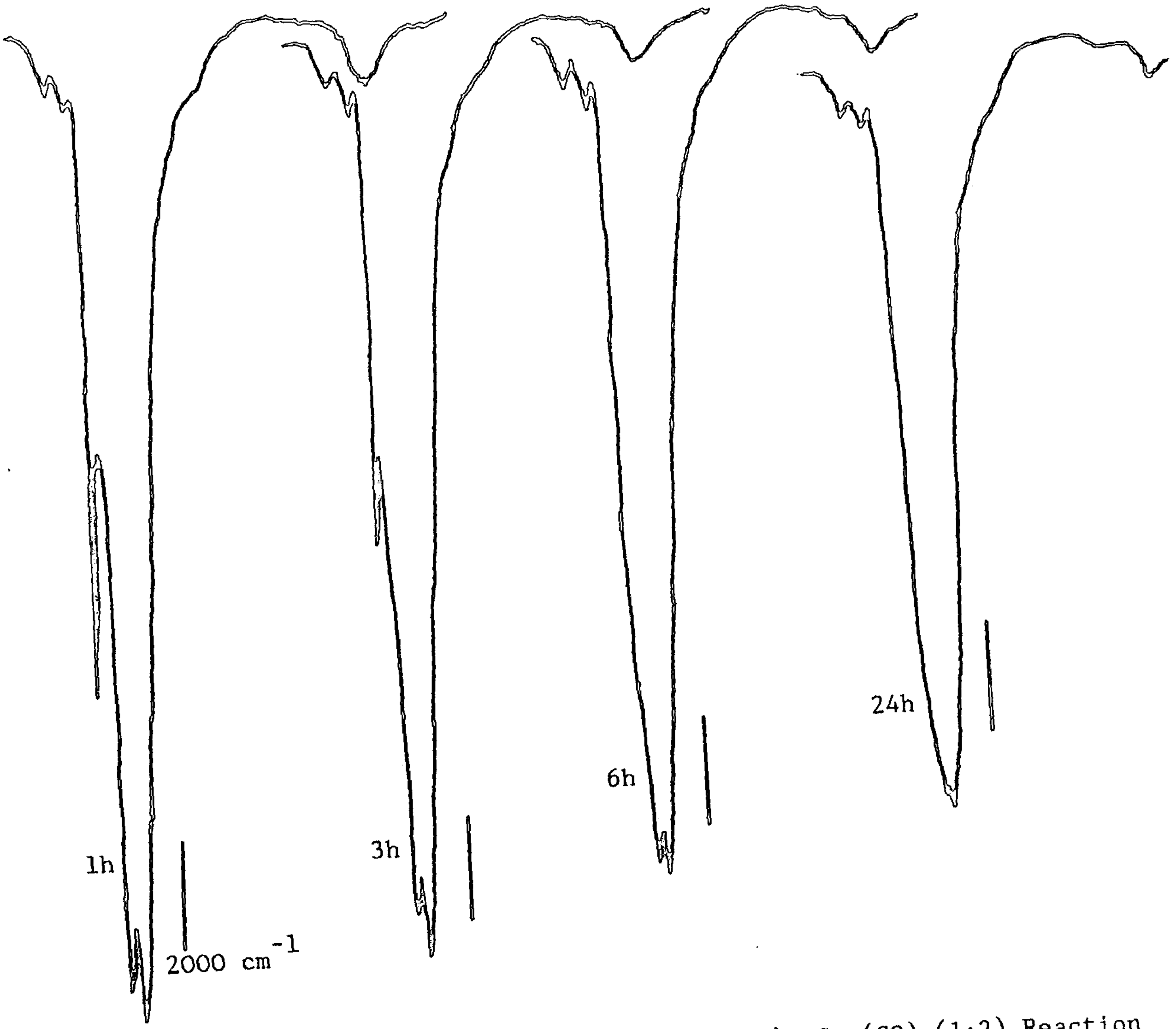


Figure 2.3 Solution Phase I.R. Spectra of $(PhCN_2S_2)_2$-$Co_2(CO)_8$(1:2) Reaction

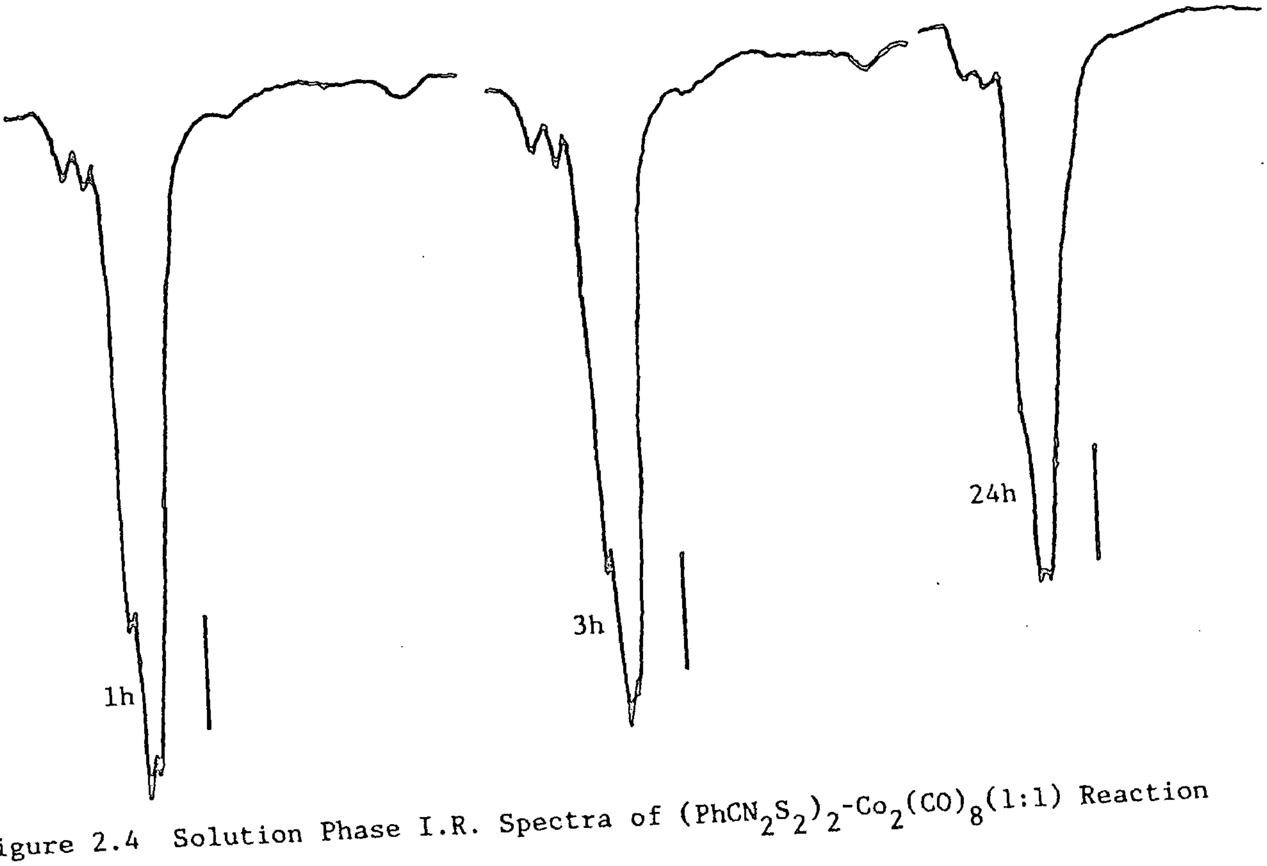
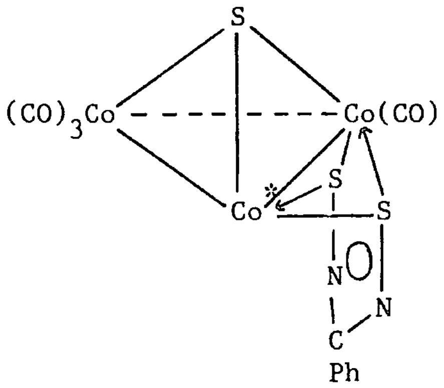


Figure 2.4 Solution Phase I.R. Spectra of $(PhCN_2S_2)_2$-$Co_2(CO)_8$(1:1) Reaction

to this starting material. The band in the carbonyl region is still very weak and the bands at 695 and 735cm^{-1} have almost disappeared.

The mass spectra of the above reaction products are complicated. The peak at 391 which appears in all spectra may be due to $SCo_3PhCN_2S_2$ which suggests the following structure, based on that of $SCo_3(CO)_9$[81] and shown in XXXII. This compound contains a 17 electron cobalt atom (Co*) and would therefore possess two unpaired spins.



[XXXII]

Unfortunately, the isotope distribution for the peak does not support this proposal (Calc.: 390(100.0), 391(11.1), 392(12.85) Obs.: 390(100.0), 391(28.4), 392(4.5)).

Attempts at solvent extraction on these solids led to the isolation of materials, the analytical and spectroscopic data for which indicate mixtures still to be present.

The infrared spectra of the products from reactions carried out at 50°C (Section 2.9.10(e)) did not differ from those obtained from products obtained at 20°C. The analyses, however, show a decrease in sulphur content of the former.

2.7.3 Conclusion

The reaction between $(PhCN_2S_2)_2$ and $Co_2(CO)_8$ gives rise to a complicated mixture of products, arising in part, no doubt, from the effectiveness of $Co_2(CO)_8$ as a desulphurisation agent.[73] Attempts to understand this system would be greatly aided by a separation procedure, such as chromatography which has been very important in the investigation of the $Co_2(CO)_8$-CS_2 reaction.[82] Unfortunately, in this work column chromatography on silica or Bio-Beads columns only led to decomposition (dichloromethane does not form a gel with Bio-Beads and cannot be used on these columns).

2.8 CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

It is clear that full characterisation of the vanadium, molybdenum and tungsten containing materials is made difficult by their insolubility in organic solvents. Further characterisation, for example by EXAFS[83a], ESCA[83b] and or Mossbauer spectroscopy[83c] (for the tungsten materials) will probably only be worthwhile if their magnetic behaviour (observed for the molybdenum materials - see Appendix 3) proves to be of sufficient interest.

It may be possible to obtain mono- or dinuclear species if these reactions are carried out in the presence of a coordinating ligand such as pyridine. This will hopefully result in the occupation of coordination sites, by pyridine, made vacant by CO loss, and not occupied by $PhCN_2S_2$, thereby eliminating the tendency for polymer formation.

The manganese and rhenium compounds are more soluble in organic solvents, the latter more so than the former, and so crystal growth for X-ray analysis may be possible. The reactions involving dicobalt octacarbonyl only merit further investigation if a suitable separation procedure can be found for the mixtures obtained.

The iron carbonyls, $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ gave $Fe_2(CO)_6PhCN_2S_2$ which was fully characterised. The one-electron redox chemistry[84] of this species should be interesting and also its reactions with activated alkynes.[85]

Finally, reaction with $Os_3(CO)_{10}(MeCN)_2$ may give a compound in which the metal triangle is retained. Such species have been previously obtained with disulphides.[86]

2.9 EXPERIMENTAL

2.9.1 Reaction of $(PhCN_2S_2)_2$ with $V(CO)_6$

A solution of $(PhCN_2S_2)_2$ (0.36g, 1mmol) in dichloromethane ($25cm^3$) was added to $V(CO)_6$ (0.4g, 1.8mmol) via syringe. The resulting solution was stirred for 4h during which time a black solid was precipitated. This was filtered off, washed with acetonitrile for 25h, then with liquid sulphur dioxide for 12h in an extractor (Figure 7.1). Yield 0.32g. Found C,21.8; H,2.4; N,8.1; S,20.4; V,27.5%. $C_7H_5N_2O_4S_2V_2$ requires C,24.2; H,1.4; N,8.1; S,18.5; V,29.3. ν max 1675w, 1635w, 1154w, 1000w, bd, 693w cm^{-1}. m/z (C.I.(+)NH_3). 181 ($PhCN_2S_2^+$,12%), 103($PhCN^+$),25), 77(Ph^+,4), 64(S_2^+,55), 46(SN^+,7), 32(S^+,6). The D.S.C. trace showed a broad decomposition profile, 80-140°C. Only $(PhCN_2S_2)_2$ was recovered from the filtrate as shown by i.r. spectroscopy.[87] ν max 832m, 806m, 779s, 770s, 692s, 655m, 509m cm^{-1}.

2.9.2 Reaction of $(PhCN_2S_2)_2$ with $Mo(CO)_3(CH_3CN)_3$

A solution of $Mo(CO)_3(CH_3CN)_3$ (Section 7.6.3) (1.2g, 3.96mmol) in tetrahydrofuran ($30cm^3$) was added to $(PhCN_2S_2)_2$ (0.71g, 1.96mmol) and the solution heated to 60°C for 3h. A black solid was precipitated and this was filtered off and washed with acetonitrile in an extractor (Figure 7.1) for 24h. Yield 0.624g. Found C,29.0; H,2.7;

N,10.2; Mo,32.3; S,20.5%. $C_8H_5N_2MoO_2S_2$ requires C,31.5; H,1.6; N,9.2; Mo,31.4; S,21.0%. V max 2160w.bd, 1260w.bd, 1170w, 1115w, 1068w, 1022w, 940w.bd, 914w, 765sh, 754m, 692m, 510w, 460w.bd cm^{-1}. m/z (E.I.) 181($PhCN_2S_2^+$,4%), 135($PhCNS^+$,93), 103($PhNC^+$,93), 95(Mo^+,1), 89(PhC^+,2), 77(Ph^+,92), 64(S_2^+,94), 46(SN^+,5), 32(S^+,13). The D.S.C. trace showed a broad decomposition profile 185-290°C. Only unreacted starting materials[87,88a] were recovered from the filtrate. V max 1940vs(CO), 832m, 800s, 774s, 718m, 693s, 650s, 587s, (CO) 503m cm^{-1}. The carbonyl bands are, in fact, due to unreacted $Mo(CO)_6$.

2.9.3 Reaction of $(PhCN_2S_2)_2$ with $Mo(CO)_6$

a) A solution of $(PhCN_2S_2)_2$ (0.38g, 1.05mmol) in thf ($30cm^3$) was added to $Mo(CO)_6$ (0.56g, 2.1mmol) via syringe and the mixture heated to 60°C for 3h. After cooling to 21°C a black solid was filtered off, washed with thf (3 x $5cm^3$) and pumped dry. It was then washed with acetonitrile in an extractor for 24h. Yield 0.32g. Found: C,28.0; H,1.6; N,9.5; Mo,30.0; S,21.6%. $C_8H_5N_2MoOS_2$ requires C,31.5; H,1.6; N,9.2; Mo,31.4; S,21.0% V max 2160m.bd, 1260m,bd, 1165w, 1150w, 1113w, 1068w, 1022m, 995w, 930m.bd, 850vw, 755m, 690s, 510vw, 465w cm^{-1}. m/z (E.I.) 181 ($PhCN_2S_2^+$,1) 149 ($PhCN_2S^+$,98), 128 (MoS^+,5), 103 ($PhCN^+$,100), 95 (Mo^+,8), 89 (PhC^+,3), 77 (Ph^+,13), 64 (S_2^+,94), 46 (SN^+,1), 32 (S_2^+,32). Infrared spectra of the filtrate residue showed only starting materials to be present. V max 1980vs, 1222w, 1135w, 1064w, 1020w, 930w, 843m, 800m, 778m, 769m, 730m, 685m, 650m, 588s, 367s cm^{-1}. See below for assignments.

A little of the material was placed in the middle of an open ended capillary and platinum electrodes were placed in each end and pressed into the material. The resistance was measured on a Thandar TM 351 digital multimeter and was found to be greater than 20MΩ.

b) A solution of $(PhCN_2S_2)_2$ (0.36g, 1mmol) and $Mo(CO)_6$ (0.53g, 2mmol) in thf ($30cm^3$) was irradiated with 350nm light for 5h. However, solution i.r. in the carbonyl region ($2400-1600cm^{-1}$) showed only $Mo(CO)_6$, ν max 1975vs cm^{-1}. No solid was observed and removal of the solvent by pumping only gave a mixture of starting materials.

ν max 1972vs, 1221w, 1137m, 1070w, 1020w, 921w, 898w, 846m, 800s, 778s, 770s, 720m, 683s, 652s, 590vs, 508s, 365vs cm^{-1}. Underlined bands[88a] are due to $Mo(CO)_6$, the remainder[87] to $(PhCN_2S_2)_2$.

2.9.4 Reaction of $(PhCN_2S_2)_2$ with $W(CO)_3(^iPrCN)_3$

A solution of $(PhCN_2S_2)_2$ (0.64g, 1.8mmol) in thf ($20cm^3$) was added via syringe to a solution of $W(CO)_3(^iPrCN)_3$ (Section 7.6.3) (0.845g, 1.8mmol) in thf ($25cm^3$). The mixture was heated at 60°C for 6h and the black solid precipitated was filtered off at 21°C and washed in an extractor (Figure 7.1) with liquid sulphur dioxide for 36h. Yield 0.28g. Found: C,21.1; H,1.2; N,6.6; S,14.7; W,48.0%. $C_8H_5N_2O_2SW$ requires C,24.4; H,1.3; N,7.1; S,16.3; W,46.8%. ν max 2170w.bd, 1880m.bd, 1176w, 1150w, 1070vw, 1024m, 960m.bd, 692s, 520w.bd cm^{-1}. The band at $1880cm^{-1}$ is assigned[89] to $W(CO)_3(^iPrCN)_3$. m/z (C.I.(+),NH_3), 103 ($PhCN^+$,100), 89 (PhC^+,2), 77 (Ph^+,3), 64 (S_2^+,2).

2.9.5 Reaction of $(PhCN_2S_2)_2$ with $Mn_2(CO)_{10}$

a) $(PhCN_2S_2)_2$ (0.36g, 1mmol) and $Mn_2(CO)_{10}$ (0.39g, 1mmol) were sealed in a pyrex tube ($100cm^3$) under nitrogen and heated to 134°C for 17h. Visual inspection showed unreacted starting material so heating was continued at 160°C for 5h. The tube was then cooled to -196°C, opened (by hot-spotting) and a nitrogen inlet immediately inserted. The tube was then allowed to warm to room temperature (21°C) and toluene ($20cm^3$) added. The resulting mixture was then filtered under nitrogen to give a buff-coloured solid, 0.16g, ν max 2200vs(NCO)[38a], 302s cm^{-1}. Analyses: C,17.1; N,10.6; Mn,41.9; S,18.0%. The solvent was pumped off from the filtrate to give a sticky red solid. ν max $\underline{\text{2220w}}$, 1218w, 1070w, 1020m, 920w, 835m, 802s, 778s, 765s, $\underline{\text{755s}}$, 720m, 685s, 652s, $\underline{\text{540m}}$, 504s cm^{-1}. Underlined bands are due[90] to PhCN, the remainder[87] to $(PhCN_2S_2)_2$.

b) $(PhCN_2S_2)_2$ (0.36g, 1mmol) and $Mn_2(CO)_{10}$ (0.39g, 1mmol) dissolved in thf (25cm^3) were irradiated with light at 350nm for 11h. Solution i.r. in the carbonyl region (2400-1600cm^{-1}) showed bands due to $Mn_2(CO)_{10}$[88b] and $Mn(CO)_5^-$, ν max 2050vs, 2015vs, 1978vs, 1900sh. The last band[51] is due to $Mn(CO)_5^-$. Removal of the solvent *in vacuo* from the solution gave a dark red solid. ν max 2080w, 2010vs, 1985vs, 1900s (CO), 1025m, 835w, 805m, 780s, 770m, 720w, 690m, 652s, 620m (CO), 508 cm^{-1}. The carbonyl bands are all due to $Mn_2(CO)_{10}$ apart from that at 1900cm^{-1} due to $Mn(CO)_5^-$. The remaining bands are due to $(PhCN_2S_2)_2$.

c) $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) and $Mn_2(CO)_{10}$ (0.195g, 0.5mmol) were dissolved in toluene (25cm^3) and stirred at 100°C for 4h. A beige coloured solid was observed and this was filtered off, washed with toluene (2 x 5cm^3) and hexane (5cm^3) and pumped dry, 0.11g. ν max 2190w, 2010w, 1920w.bd, 1150m.bd, 1030w, 700m cm^{-1}. Analyses: Mn,37.4; N,6.2; S,48.1%. The filtrate was pumped dry to give a mixture of starting materials.[87,88b] ν max 2050m, 2020m, 1982w (CO), 1242w, 1228w, 1188w, 1180w, 1140m, 1079m, 1027m, 925w, 903w, 839w, 808s, 780s, 772s, 691s, 657s, 511s cm^{-1}. See above for assignments.

d) A solution of Me_3NO (0.3g, 4mmol) in dichloromethane (10cm^3) was added dropwise to a vigorously stirred solution of $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) and $Mn_2(CO)_{10}$ (0.195g, 0.5mmol) in toluene (25cm^3) at 21°C. A yellow solid was slowly precipitated and after 26h this was filtered off, washed with toluene (2 x 5cm^3) and diethyl ether (5cm^3) and pumped dry. Yield 0.18g, 69.2%. Found: N,5.4; Mn,21.1; S,12.2%. $Mn_2(CO)_8PhCN_2S_2$ requires N,5.4; Mn,21.3; S,12.45%. νmax 2082w, 2040sh, 2016vs, 1995sh, 1945sh, 1910vs,bd (CO), 1640w, 1319w, 1238m, 1138m, 1112m, 1035sh, 1025m, 960sh, 946m, 835m, 766s, 732s, 694s, 668sh, 662s, 628sh, 620s, 547sh, 527s, 485m, 475sh cm^{-1}. A mass spectrum of this compound could not be recorded since it did not volatilise in the spectrometer below its decomposition temperature. The D.S.C. trace showed a fairly broad decomposition profile (100-190°C) with a peak at ~145°C and a shoulder at ~165°C. Only starting materials[87,88b] could be recovered from the solid filtrate residue as shown by i.r. spectroscopy. νmax 2055s, 2022s, 1972s, 1142w, 1070w, 1028m, 928w, 904w, 841m, 808s, 782s, 773s, 690s, 654sh, 648vs, 625sh, 512m, 470m cm^{-1}. See above for assignments.

Crystal growth was attempted using the method described in Section 2.9.8.

2.9.6 Reaction of $(PhCN_2S_2)_2$ with $Re_2(CO)_{10}$

a) A solution of $(PhCN_2S_2)_2$ (0.2g, 0.55mmol) and $Re_2(CO)_{10}$ (0.36g, 0.55mmol) in toluene (30cm^3) was heated to 60°C for 3h and then to 110°C for 4h. Solution i.r. spectra showed no reaction to have occurred.[88b] νmax 2078s, 2019vs, 1967s cm^{-1}.

b) A solution of Me_3NO (0.15g, 2mmol) in dichloromethane (10cm^3) was added dropwise to a vigorously stirred solution of $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) and $Re_2(CO)_{10}$ (0.32g, 0.5mmol) in toluene (25cm^3) at 21°C. Stirring was continued for 26h during which time a yellow solid was deposited. This was filtered off, washed with toluene (2 x 2cm^3) and pentane (2cm^3) and pumped dry. Yield 0.06g. A further 0.08g was recovered from the filtrate residue after extraction with toluene (identical i.r.). Analysis: C,25.9; H,2.2; N,6.3; Re,35.8; S,12.2%. νmax 2100m, 2025vs, 1900vs.bd (CO), 1162m, 1020m, 988w, 828m, 760sh, 698m, 614m, 587m, 523w cm^{-1}. A mass spectrum of this material could not be recorded since it did not volatilise below its decomposition temperature. The D.S.C. trace showed a broad decomposition profile (90-210°C) reaching a maximum at ~160°C. Only starting materials were recovered from the final filtrate residue. ν max ~2000vs,v bd, 804m, 779m, 758m, 735w, 692s, 653m, 590vs, 540m, 512w, 475w, 438w, 400w cm^{-1}. Underlined frequencies are due[87] to $(PhCN_2S_2)_2$, the remainder[88b] to $Re_2(CO)_{10}$.

2.9.7 Reaction of $(PhCN_2S_2)_2$ with $Fe_2(CO)_9$

A solution of $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) and $Fe_2(CO)_9$ (0.36g, 1mmol) was stirred in thf (25cm^3) at 45°C for 4h, to give a deep orange-brown solution. The solvent was then pumped off and the residue extracted with toluene (4 x 5cm^3). Recrystallisation of the extracted material from toluene gave orange $Fe_2(CO)_6PhCN_2S_2$. Yield 0.08g, 17%. m.p. (from D.S.C.) 167.2°C followed by decomposition. Analysis: C,32.3; H,1.3; N,6.0; Fe,24.2; S,14.1%. $Fe_2(CO)_6PhCN_2S_2$ requires C,33.8; H,1.1; N,6.1; Fe,24.2; S,13.9%. ν max (IR) 2081vs, 2070vs, 2047sh, 2035vs, 2001vs, 1988vs, 1973vs (CO)[91] 1584vw, 1533m, 1522w, 1498w, 1412s, 1290m, 1285m, 1158w, 1138m, 1128w, 970vw, 925vw, 906w, 847vw, 764m, 739s, 696s, 677m, 643m, 618s, 602s, 584vs, 563vs, 494m, 461vw, 441w cm^{-1}; (Raman) 378s, 224m (Fe-Fe)[92], 180w, 117sh, 98s, 61vs, 43s cm^{-1}. $\delta_H(CD_2Cl_2)$ 7.50ppm (multiplet). m/z (NH_3,C.I.-) 461 (M^+,2%) 377 (M-3CO,85), 349 (M-4CO,100), 321 (M-5CO,53), 293 (M-6CO,12). m/z(NH_3,C.I.+) 181 ($PhCN_2S_2^+$,100%), 149 ($PhCN_2S^+$,1), 135 ($PhCNS^+$,8), 103 ($PhCN^+$,53), 77 (Ph^+,52), 64 (S_2^+,2), 46 (SN^+,9), 32 (S^+,2).

The residue left after extraction was a black solid, 0.02g. Found: Fe,15.7; N,2.9; S,15.3%. νmax 1150sh, 1115sh, 1050s,bd, 700w cm^{-1}. m/z (E.I.) 256 (S_8^+,13), 224 (S_7^+,6), 192 (S_6^+,21), 181 ($PhCN_2S_2^+$,20), 160 (S_5^+,24), 135 ($PhCNS^+$,5), 128 (S_4^+,11), 103 ($PhCN^+$,61), 96 (S_3^+,11), 89 (PhC^+,7), 77(Ph^+,5), 64 (S_2^+,100).

2.9.8 Reaction of $(PhCN_2S_2)_2$ with $Fe_3(CO)_{12}$

A solution of $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) and $Fe_3(CO)_{12}$ (0.34g, 0.68mmol) were stirred in toluene at 45°C for 6h. After allowing to cool to 21°C, the mixture was filtered to give a brown solid (0.21g). This was extracted with boiling dichloromethane (4 x 30cm^3) and recrystallised from this solvent to give 0.11g product. A further 0.06g was extracted from the filtrate residue to give a total yield of $Fe_2(CO)_6PhCN_2S_2$, 0.17g, 37%. νmax 2080vs, 2070vs, 2048sh, 2036vs, 1998vs, 1988vs, 1978vs (CO)[91] 1588vw, 1533w, 1521w, 1501w, 1406m, 1294m, 1284m, 1158w, 1136w, 1130w, 1027vw, 968vw, 929vw, 906w, 851vw, 764m, 738m, 695m, 677w, 647w, 612m, 603m, 581s, 561s, 493w cm^{-1}. m/z (NH_3,C.I.-) 461 (M^+,1%), 377 (M-3CO,2), 349 (M-4CO,2), 321 (M-5CO,3), 293 (M-6CO,8).

The residue left after extraction was a black powder, 0.04g. νmax 2190w, 2070m, 2038s, 1990s,bd, 1630w, 1025w, 920w, 760m, 582vw, 568vw cm^{-1}. m/z (E.I.) 256 (S_8^+,58%), 224 (S_7^+,12), 192 (S_6^+,69), 181 ($PhCN_2S_2^+$,10), 160 (S_5^+,84), 149 ($PhCN_2S^+$,7), 135 ($PhCNS^+$,9), 128 (S_4^+,80), 103 ($PhCN^+$,42), 96 (S_3^+,54), 89 (PhC^+,5), 77 (Ph^+,11), 64 (S_2^+,100), 56 (Fe^+,5), 32, (S^+,100).

Crystals were grown by cycling the temperature of a saturated dichloromethane solution, immersed in a low temperature bath (Section 7.3) between -10 and 0°C for 10d.

2.9.9 Reaction between $(PhCN_2S_2)_2$ and $Fe(CO)_5$

a) A solution of $(PhCN_2S_2)_2$ (0.2g, 0.55mmol) and $Fe(CO)_5$ (0.3cm^3, 0.43g, 2.7mmol) in toluene (10cm^3) was stirred at 21°C for 1h, then at 45°C for 3h, then at 70°C for 2h, then at 90°C for 1h, the reaction being monitored by solution i.r. spectroscopy in the carbonyl region (2400-1600cm^{-1}). The spectrum remained constant throughout the experiment. νmax 2022vs, 1992vs cm^{-1}; showing no reaction to have occurred. νmax $(Fe(CO)_5)$[88c] 2034, 2013cm $^{-1}$.

b) A solution of Me_3NO (0.45g, 6.0mmol) in dichloromethane was added dropwise to a vigorously stirred solution of $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) and $Fe(CO)_5$ (0.15cm^3, 1.35mmol) in toluene (25cm^3) at 21°C. Stirring was continued for 1h when an orange-brown solid was filtered off, washed with toluene (2 x 5cm^3) and pentane (5cm^3) and pumped dry. Yield 0.25g. This was extracted with dichloromethane (2 x 5cm^3) to give a red solution from which a waxy orange-red solid was recovered. Yield 0.03g. ν max 3300s,vbd (NH), 2065w, 2020m, 1970m,bd (CO) cm^{-1}. The residue was pumped dry to give a brown powder. Yield 0.2g.

νmax 3300s,vbd (NH), 2020s, 1969m,bd (CO), 1665sh, 1635sh, 1660m, 1555s,bd, 1400sh, 1240m,bd, 1178w, 1153w, 1108w, 1019m, 938m,bd, 840w, 825w, 784m, 700s, 525sh, 604m, 520w, 463w,bd cm^{-1}. The filtrate was pumped dry and the solid extracted with toluene (2 x 5cm^3) leaving an orange-brown solid. Yield 0.03g. νmax 3300m,vbd(NH), 2080m, 2070m, 2050sh, 2038s, 2002s, 1983s, 1970m (CO) cm^{-1}. See below for assignments. The toluene solution was pumped dry to give a purple solid. Yield 0.07g. νmax 2080m, 2070m, 2050sh, 2038s, 2000s, 1983s, 1970m, $\underline{872w}$, $\underline{802s}$, $\underline{778s}$, $\underline{767m}$, $\underline{686s}$, $\underline{652m}$, 582m, 560m, $\underline{508m}$ cm^{-1}. Underlined bands[87] are due to $(PhCN_2S_2)_2$, the remainder to $Fe_2(CO)_6PhCN_2S_2$ (Section 2.9.7).

2.9.10 Reaction between $(PhCN_2S_2)_2$ and $Co_2(CO)_8$

a) A solution of $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) in toluene (20cm^3) was slowly added (via syringe) to a stirred solution of $Co_2(CO)_8$ (0.34g, 1mmol) in toluene (20cm^3) at 20°C. The solution immediately darkened and gas was evolved. Stirring was continued for 24h, the reaction being monitored by solution phase i.r. spectroscopy in the range 2300-1800cm^{-1}. At this stage the solution was filtered to give a black solid. Yield 0.045g. νmax 2070sh, 2030s, 1345s, 1335sh, 1278w, 1030w, 738s, 698s cm^{-1} and a deep orange solution from which the solvent was pumped off to give a black shiny solid. Yield 0.26g. Analysis; Co,26.6; N,6.4; S,14.8%. νmax 2090sh, 2060vs, 1860w (CO), 1346m, 1332sh, 1177m, 1160vw, 742s, 697s, 680w, 500m cm^{-1}. m/z (C.I.(+),NH_3), 390 ($Co_3S.PhCN_2S_2$,16%), 167 ($PhCNS_2^+$,5), 149 ($PhCN_2S^+$,4), 103 ($PhCN^+$,52), 91 (86), 89 (PhC^+,4), 77 (Ph^+,1), 64 (S_2^+,4). (E.I.) 149(3), 103(98), 91(72), 77(7), 64(3). X-ray powder diffraction showed this material to be amorphous. The solid was transferred to a 'dog' of the type shown in Figure 7.2 where it was washed with toluene until the washings were colourless. The solvent was then pumped off leaving two solids, one soluble (A), 0.05g, and one insoluble (B), 0.09g, in toluene.
Analyses: (A) Co,26.6; N,6.6; S,7.5% (B) Co,28.2; N,7.2; S,13.3.%.
m/z (D.C.I., iso-C_4H_{10}) (A) 390(58%), 167(21), 149(62), 103(99).
(B) 103(97)

The solution phase i.r. spectra observed in dichloromethane were very similar to those obtained using toluene, except that the former enabled observation of the bridging carbonyl region, and for this reason they are given in Figure 2.3. The weak band at 1860cm^{-1} is assigned to $Co_2(CO)_8$, present in very low concentration.[88d]

b) A solution of $(PhCN_2S_2)_2$ (0.36g, 1mmol) in toluene (30cm^3) was slowly added, via syringe, to a stirred solution of $Co_2(CO)_8$ (0.34g, 1mmol) in toluene (20cm^3) at 20°C. The solution immediately darkened and gas was evolved. The reaction was monitored by solution phase i.r. spectroscopy for 14h when it was filtered to give a black solid. 0.02g, max 2050s, (CO), 1345, 1330sh, 1268w, 1247w, 795m, 772w, 735s, 696s, 675w cm^{-1}. The dark orange-brown filtrate was pumped dry to give a black, shiny, air-stable solid, 0.45g. Analysis: Co,19.3; N,9.5; S,21.1%. νmax 2062s (CO), 1342m, 1330sh, 1176m, 1147w, 928vv, 917vw, 844vw, 798s, 773m, 735s, 694s, 678m, 618w, 500w cm^{-1}. m/z (D.C.I., NH_3) 446 ($Co_3(CO)_2S.PhCN_2S_2^+$,1%) 390 ($Co_3S.PhCN_2S_2^+$,1) 299 ($Co_2PhCN_2S_2^+$,2), 298 ($[PhCN_2S]_2^+$,2), 296 ($Co(CO)_3PhCN_2S_2^+$,1), 268 ($Co(CO)PhCN_2S_2^+$,5), 226 ($[PhCN_2]_2S^+$,8), 264 ($Co(CO)_2PhCN_2S^+$,2), $\underline{253}$ (11), $\underline{252}$ ($PhCN_2SNCPh^+$,3), 236 ($Co(CO)PhCN_2S^+$,7), 208 ($CoPhCN_2S^+$,3), $\underline{195}$ ($PhCN_2S_2N^+$,2), $\underline{181}$ ($PhCN_2S_2^+$,1), $\underline{167}$ ($PhCNS_2^+$,3) $\underline{149}$ ($PhCN_2S^+$,22), $\underline{135}$ ($PhCNS^+$,23), $\underline{103}$ ($PhCN^+$,9), 89 (PhC^+,7), $\underline{77}$ (Ph^+,2), $\underline{64}$ (S_2^+,100), $\underline{46}$ (SN^+,2). Underlined peaks also appear in the spectrum of $(PhCN_2S)_2$.[87] X-ray powder diffraction showed the material to be amorphous.

The solid was transferred to one limb of a 'dog' (Figure 7.2) where it was washed with toluene until the washings were colourless. The solvent was then pumped off leaving two black solids, one soluble (A) and the other insoluble (B) in toluene. Analysis (A) Co,11.3; N,11.3; S,14.2% (B) Co,10.5; N,8.8; S,13.5%.
m/z (D.C.I., NH_3) (A) 446(1%), 390(3), 208(9), 181(98), 103(38), 77(32), 46(10) (B) 390(6), 253(2), 252(1), 181(13), 149(20), 103(100), 77(2).

Identical solution phase spectra were obtained using dichloromethane as solvent and since these also show the bridging carbonyl region they are given in Figure 2.4. The spectra are also very similar to those observed for the 2:1 reaction, except that after 24h $Co_2(CO)_8$ is no longer evident.

c) A solution of $(PhCN_2S_2)_2$ (0.36g, 1mmol) in toluene (25cm^3) was slowly added to a solution of $Co_2(CO)_8$ (0.17g, 0.5mmol) in toluene (15cm^3) at 21°C. The reaction was monitored by solution phase i.r. spectroscopy which only showed a weak band at 2060cm^{-1}. The solution was filtered but no solid was obtained so the solvent was removed *in vacuo* to give a black solid. Yield 0.43g. Analysis:Co,12.8; N,11.0; S,23.2%; νmax 2050w, 1340w, 1175m, 1145m, 1072w, 1030m, 929vw, 908w, 840w, 795s, 772m, 730m, 692s, 673m, $\underline{\text{655w}}$, 615w, $\underline{\text{508w}}$ cm^{-1}. Underlined bands are due to $(PhCN_2S_2)_2$. m/z (D.C.I., iso-C_4H_{10}) 390 ($Co_3S.PhCN_2S_2^+$,5%), 181 ($PhCN_2S_2^+$,62), 167 ($PhCNS_2^+$,7), 149 ($PhCN_2S^+$,18), 103 ($PhCN^+$,81), 91(24).

The solid was transferred to a 'dog' (Figure 7.2) where it was washed with toluene until the washings were colourless. The solvent was pumped off to give two solids, one soluble (A) and one insoluble (B) in toluene. Analyses: (A) Co,14.2; N,6.5; S,13.5%; (B) Co,14.9; N,7.7; S,14.1%. m/z (C.I., iso-C_4H_{10}) (A) 103(11), 91(11), (B) 103(100), 91(16), 77(Ph^+,4), 64(S_2^+,6).

d) A solution of $(PhCN_2S_2)_2$ (0.36g, 1mmol) in dichloromethane (20cm^3) was added, via syringe, to a solution of $Co_2(CO)_8$ (0.1g, 0.29mmol) in dichloromethane (5cm^3) at 20°C. The solution was stirred for 24h, the reaction being monitored by i.r. spectroscopy which only showed a weak band at 2060m^{-1}. The solvent was pumped off to give a black solid. Yield 0.31g. νmax 2050w, 1325m, $\underline{\text{1240vw}}$, $\underline{\text{1227vw}}$, 1170w, $\underline{\text{1140m}}$, $\underline{\text{1079w}}$, $\underline{\text{1030m}}$, $\underline{\text{924w}}$, $\underline{\text{905w}}$, $\underline{\text{840m}}$, $\underline{\text{832sh}}$, $\underline{\text{808m}}$, 800m, $\underline{\text{780s}}$, $\underline{\text{773s}}$, 730m, $\underline{\text{690s}}$, 672w, $\underline{\text{658s}}$, $\underline{\text{512s}}$ cm^{-1}. Underlined peaks[87] are due to $(PhCN_2S_2)_2$. The bands at 690 and 773cm^{-1} are also present in the spectrum of the cobalt-containing material.

e) A solution of $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) in toluene ($10cm^3$) was added to a stirred solution of $Co_2(CO)_8$ (0.34g, 1mmol) in toluene ($15cm^3$) at 21°C. The mixture was then heated to 50°C for 16h, the reaction being monitored by solution phase i.r. spectroscopy. A single band, initially present at $2060cm^{-1}$, gradually disappeared. A black solid was filtered off from a very pale orange-brown solution, washed with toluene (2 x $5cm^3$), hexane ($5cm^3$) and pumped dry. Yield 0.31g. Analysis: Co,27.9; N,7.0; S,8.0%. νmax 2060sh, 2030m, 1340m, 1175m, 1029w, 755sh, 735s, 698s, 500w cm^{-1}.
m/z (D.C.I., iso-C_4H_{10}) 144(1), 103 (PhCN,44).

f) A solution of $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) in toluene ($20cm^3$) was added to $Co_2(CO)_8$ (0.17g, 0.5mmol) and the solution heated to 50°C for 10h. The reaction was monitored by solution phase i.r. spectroscopy; after 6h a very weak band at $2070cm^{-1}$ was observed and after 10h this had completely disappeared. A black solid was filtered off, washed with pentane (2 x $5cm^3$) and dried in vacuo. Yield 0.23g. Analysis: Co,21.1; N,9.7; S,14.8%. νmax 2050s, 1340m, 1285sh, 1175m, 1145w, 925vw, 907vw, 798m, 770m, 738s, 697s, 678m, 618w cm^{-1}.

g) A sample of the material (0.2g) recovered from the experiment described in a) was heated to 180°C in a sublimation apparatus under vacuum with water cooling. No sublimation occurred but the solid lost mass; final weight 0.13g. Analysis: Co,30.2%, N,10.9; S,18.8%.
νmax 755m, 697m cm^{-1}.

Fast-atom-bombardment (F.A.B.) mass spectra were recorded for several of the above materials but the results were no different to those given using more conventional techniques.

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CHAPTER 3

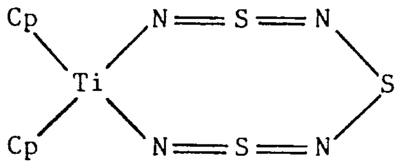
A STUDY OF THE REACTIONS OF PHENYL DITHIADIAZOLE WITH SOME TRANSITION METAL CYCLOPENTADIENYL CARBONYL COMPOUNDS

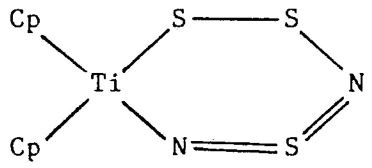
3.1 GENERAL INTRODUCTION

Since several of the reactions of $(PhCN_2S_2)_2$ with binary transition metal carbonyls (Chapter 2) had given non-carbonyl containing polymeric products (V,Mo,W) or complicated mixtures (Co), it was hoped that the introduction of a cyclopentadienyl group, much less easily lost than CO and formally occupying three coordination sites[1], might lead to simpler mono- or dinuclear products. Moreover, such products should be more soluble in organic solvents, making the growth of single crystals, for X-ray studies, easier to achieve.

Cyclopentadienyl transition metal carbonyl species have received little attention in sulphur-nitrogen chemistry and, so as not to make the account too fragmentary, these are mentioned in the relevant Introduction to each section on individual reactions. However, as in Chapter 2, most of the Introductions are concerned with the chemistry of organic sulphur compounds.

Cyclopentadienyl titanium complexes are discussed in Chapter 4, as it was decided to use the more readily available Cp_2TiCl_2, rather than $Cp_2Ti(CO)_2$. However, it may be noted here that $Cp_2Ti(CO)_2$ reacts with S_4N_4 to give $Cp_2TiS_3N_4$ and $Cp_2TiS_3N_2$. The structures[2] of these complexes, depicted below, show that titanium bonds preferentially to nitrogen, perhaps because it is the harder centre.

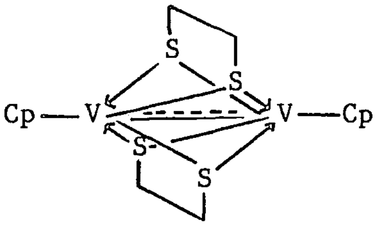




3.2 REACTION OF $(PhCN_2S_2)_2$ WITH $CpV(CO)_4$: PREPARATION OF $[CpV(PhCN_2S_2)]_2$

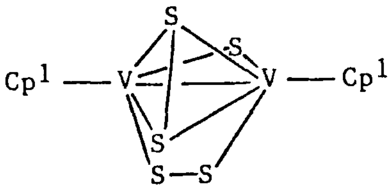
3.2.1 Introduction

The carbonyl groups of $CpV(CO)_4$ can be substituted using either thermal or photolytic methods.[3] Thermal reaction with Me_2S_2 or MeSH yielded $[CpV(SMe)_2]_2$ [4] and with $F_2C(S)=C(S)CF_3$ gave $Cp_2V_2[(CF_3)_2C_2S_2]_2$.[5,29] Both of these products were found to be weakly paramagnetic suggesting a partial vanadium-vanadium double bond. Unpublished X-ray work supported this[6], and further evidence was provided by the structure determination[7] of $[CpVSC_2H_4S]_2$ which is shown in I.



[I]

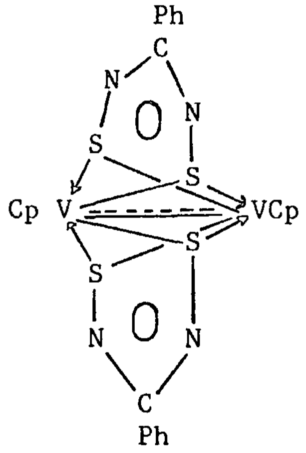
Other work[8] found the phenyl derivative (prepared from PhSH) to be diamagnetic and although this has been questioned[9], it is thought likely that the material '$[CpV(SPh)_2]_2$', prepared in the latter work, contained a paramagnetic impurity[8b], perhaps Cp_2VCl_2. Photolysis of a solution of $CpV(CO)_4$ and Me_2S_2 in thf led to the isolation of an intermediate[10] formulated as $Cp_2V_2(\mu\text{-}SMe)_2(CO)_4$. The other product was $CpV(SMe_2)_2$. Reaction[11] of $CpV(CO)_4$ with S_8 and with cyclohexene sulphide in refluxing toluene gave air-stable, diamagnetic $[Cp_2V_2S_5]_n$. Later X-ray work[12] indicated n likely to be 1 or 2, and the former was confirmed when the structure of $(C_5H_4Me)_2V_2S_5$ was published.[13] This is shown in II (Cp^1=C_5H_4Me).



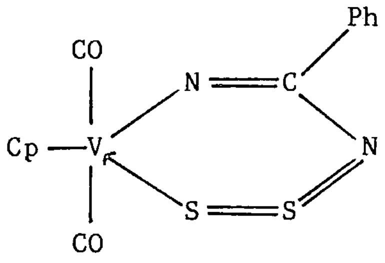
[II]

A compound of composition [CpVS]$_n$ has also been isolated from reaction^{14a} of CpV(CO)$_4$ with S$_8$. Photolysis of Cp*V(CO)$_4$ and S$_8$ in thf gave^{14b} Cp*V$_2$S$_4$ as well as Cp*V$_2$S$_5$ and oxo-species

On the basis of the work discussed in the previous paragraph it was thought that the new species III would be the likely product of the reaction between CpV(CO)$_4$ and (PhCN$_2$S$_2$)$_2$. However, an early transition metal such as vanadium, may prefer to bond to the harder nitrogen centre so that species such as IV cannot be ruled out.



[III]



[IV]

3.2.2. <u>Results and Discussion</u>

The proton n.m.r. spectrum of a d$_8$-toluene solution of a 2:1 mixture of CpV(CO)$_4$ and (PhCN$_2$S$_2$)$_2$ displayed, after 18h thermolysis at 100°C, a weak resonance (<10% CpV(CO)$_4$ peak) at 6.10ppm. due to π-bonded Cp (Section 3.9.1(a)). The signal was much more intense in a d$_6$-benzene solution which had been photolysed for 20h.

In order to fully characterise this species, a larger-scale photolysis experiment was performed, which resulted in the isolation of a black crystalline solid (Section 3.9.1(b)). The i.r. spectrum of this material showed all of the carbonyl groups to have been displaced, and also exhibited bands due to Cp and dithiadiazole rings. These data, together with the singlet observed in the proton n.m.r.

indicating η^5-Cp to be present, and the formula indicated by the mass spectrum and analytical results, are all consistent with a species of structure III. Unfortunately, crystals suitable for X-ray analysis were not obtained. The appearance of $Cp_2V_2S_5$ in the mass spectrum is surprising and may be due to decomposition occurring in the spectrometer probe.

The magnetic properties of this compound were investigated and the results, while highly interesting, were not straightforward and are discussed in Appendix 3.

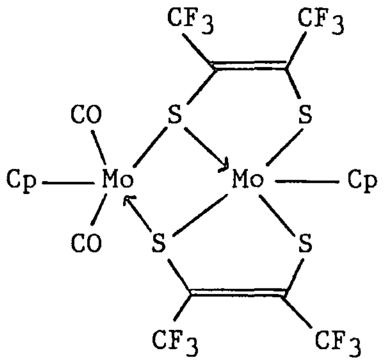
A small quantity (30mg) of an insoluble material with a V:S ratio of 3:4 was also isolated. The i.r. spectrum showed that it did not contain carbonyl groups and it was not investigated further.

Although Me_3NO does not seem to have been used previously to decarbonylate $CpV(CO)_4$, the latter's carbonyl stretching frequencies, at 1933 and 2030cm^{-1} suggest the process to be feasible.[15] (A comparatively high carbonyl frequency indicates relatively weak metal-carbon bonding due to the less pronounced metal-CO π^* back-bonding.) However, in this work no reaction between $(PhCN_2S_2)_2$ and $CpV(CO)_4$ in the presence of Me_3NO at 60°C was observed (Section 3.9.1(a)).

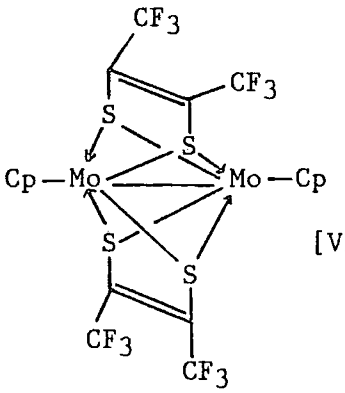
3.3 REACTION OF $(PhCN_2S_2)_2$ WITH $[CpMo(CO)_3]_2$

3.3.1 Introduction

Early work[5] reported the reactions of $[CpMo(CO)_3]_2$ with Me_2S_2 and with $CF_3C(\overset{\frown}{S)=C(S})CF_3$, which were found to give $[CpMo(SMe)_2]_2$ and $[CpMo(C_4F_6S_2)]_2$, respectively. These compounds have analogues in vanadium chemistry (Section 3.2.1) but are diamagnetic with a Mo-Mo single bond. Cyclohexene sulphide reacted[11] with $[CpMo(CO)_3]$ to give a product first formulated as $[CpMo(S_2C_6H_{11})]_n$ but parallel work[16] identified at least ten different products including $[CpMo(CO)_2SC_6H_{11}]_2$, $CpMo(CO)_3SC_6H_{11}$ and two isomers of $[CpMoS_2C_6H_{10}]_2$. The reaction involving Ph_2S_2 has been followed using i.r. spectroscopy[17a] and $CpMo(CO)_3SPh$ observed as an intermediate. However, only $[CpMo(SPh)_2]_x$ could be isolated. A later study[17b] obtained $CpMo(CO)_2SC_6H_4$-2-SPh. Photolysis[18] of a mixture of $[CpMo(CO)_3]_2$ and $(CF_3)_2S_2$ gave $CpMo(CO)_3SCF_3$ which could be decarbonylated at 90°C to give $[CpMo(CO)_2SCF_3]_2$. Ethylene and propylene sulphides reacted[19] to give complexes of general formula $[CpMoSC_nH_{2n}S]_2$ (n=2,3). It has also been reported[20] that $[CpMo(CO)_3]_2$ reacts with 3,4 dimercaptotoluene to give $[CpMo(CO)S_2C_6H_3Me]_2$, photolysis of which gave $[CpMoS_2C_6H_3Me]_2$. Very recent work[21] has also resulted in two dinuclear products being isolated from the reaction involving $CF_3C(S)=C(S)CF_3$. These are shown in V and VI.

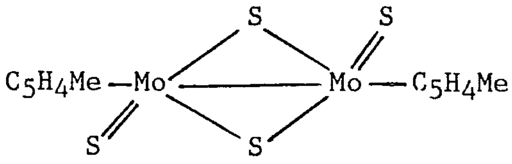


[V]

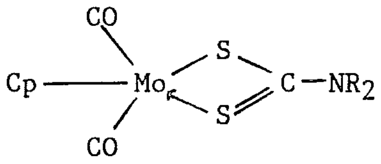


[VI]

Photolysis of V gave VI, which is isostructural with $[CpMoS_2C_6H_3Me]_2$; $[CpMo(CO)S_2C_6H_3Me_2]_2$ was thought to be isostructural with V. Reaction of $[CpMo(CO)_3]_2$ with elemental sulphur was first reported[5] to give non-carbonyl containing species of indeterminate composition. A later, more detailed study[22] of this system, with a methyl substituent on the Cp ring identified $[MeC_5H_4MoS_2]_2$, (VII), as the soluble product. In addition, insoluble polymeric products, $[MeC_5H_4MoS_x]_y$ were also formed.



[VII]



[VIII]

Finally, it may be noted that $[CpMo(CO)_3]_2$ reacted with tetramethyldithiuram disulphide[23a], $[Me_2NC(S)S]_2$ or with an Et_2NH-CS_2 mixture[23b] to give the mononuclear species $CpMo(CO)_2(\eta^2\text{-}S_2CNR_2)$ (R=Me,Et), (VIII).

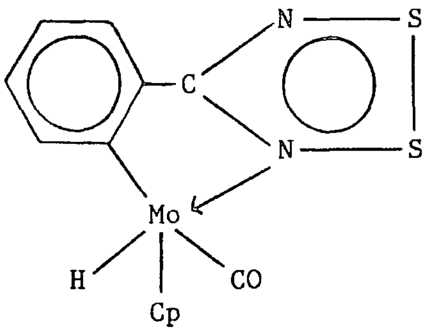
Although a species such as $CpMo(\eta^5\text{-}S_2N_2CPh)$, in which the dithiadiazole ring functions as a seven-electron donor, would be a very interesting species to isolate, the above discussion suggests complex reactions are quite likely but that a doubly-bridged complex, analogous to III, may be isolable.

3.3.2. Results and Discussion

The proton n.m.r. spectrum of a d_8-toluene solution of a 2:1 mixture of $[CpMo(CO)_3]_2$ and $(PhCN_2S_2)_2$ exhibited several new resonances in the phenyl and cyclopentadienyl regions after 18h at 100°C. However, a line due to $[CpMo(CO)_3]_2$ remained. Interestingly, the lines also sharpened up suggesting the concentration of paramagnetic species in solution to be reduced. Photolysis of an identical solution in d_6-benzene for 26h produced no observable change in the n.m.r., although a black solid was precipitated. When the above thermolysis reaction was repeated on a 1:1 scale, only very broad, uninformative lines were observed in the proton n.m.r. and much black solid was precipitated (Section 3. 9 .2a).

The monitoring of a preparative-scale 1:1 thermolysis experiment by solution phase i.r. spectroscopy in the carbonyl region (1800-$2150cm^{-1}$) showed gradual loss of bands due to $[CpMo(CO_3]_2$ and the appearance of a band at $2020cm^{-1}$. After brief growth this band remained constant in intensity (w.r.t. solvent bands). However, when the reaction mixture was worked-up, this band was not present in the spectra of any of the solid materials isolated. The spectrum of the insoluble black material (filtered off) was dominated by a strong band at $2205cm^{-1}$, whereas the solid recovered from the filtrate contained mainly starting materials (Section 3.9 .2b).

The origin of the band at $2205cm^{-1}$ is difficult to explain. It is unlikely to be a carbonyl band for the reasons given in Section 2.3.2 and might possibly be due to an isocyanate[24a] group or to a hydride[24b] (see below). The proton n.m.r. spectrum of this solid in toluene solution was very similar to the preliminary spectrum recorded from the 2:1 reaction mixture; both spectra indicated the presence of a low concentration of $[CpMo(CO)_2]_2$ as well as several other, as yet uncharacterised, cyclopentadienyl-containing species. The phenyl region also gave evidence for several products. The triplets at 6.66 and 6.82ppm. are assigned to the meta and para protons respectively, of a normal phenyl group. The signals due to the ortho protons (doublets) are most probably hidden under the toluene resonance. The remaining assignments are more tentative. The triplet at 7.97ppm. together with the doublet at 8.51ppm. are suggestive of a 1,2 disubstituted benzene ring. One way this could come about is via an ortho-metallation reaction[24c] to give a species of the type shown below:

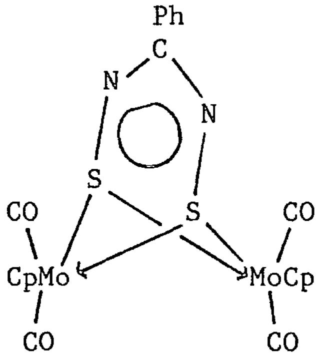


[IX]

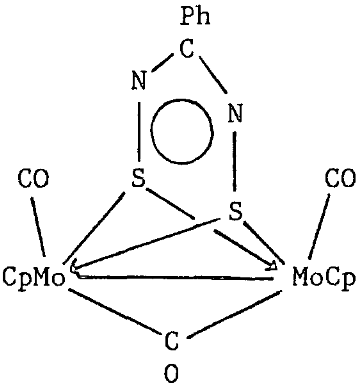
The observed signals would then be due to protons, meta and ortho, respectively to the carbon-metal bond. The other set of signals was presumably hidden under the solvent resonance. The i.r. band at 2205cm^{-1} might then be assigned to the metal-hydrogen stretch. However, there is no evidence for such species in the proton n.m.r. (no signal up to -60ppm.)^{24d} and replacement of H by CO would give a more stable 18 electron complex.

Finally, the analyses suggest that $[CpMo(PhCN_2S_2)]_2$ may, in fact, be the major species present (Analyses: Calc - Mo,28.0; S,18.8; N,8.1; C,42.2; H,2.9%. Found - Mo,27.9; S,18.8; N,5.9; C,38.4; H,2.8%) with the n.m.r. spectrum only showing signals due to minor, more soluble side-products. The magnetic properties of this material are discussed in Appendix 3.

The photolysis experiments proceeded differently. The 2:1 and 1:1 reaction $((CpMo(CO)_3)_2:(PhCN_2S_2)_2)$ both gave shiny, black solids which were shown by i.r. spectrosocopy to be mixtures of the thermolysis product (containing no carbonyl groups) and carbonyl containing species. The infrared spectra in the carbonyl region were very similar with bands at or near 1818, 1910, 1960 and 2025cm^{-1}, but the 1:1 product showed an additional band at 2070cm^{-1}. The band at 1818cm^{-1} is typical of bridging CO whereas the other bands can all be assigned to terminal carbonyl groups. The following species are tentatively proposed as possible products, in addition to the PhCN$_2$S$_2$ analogues of V and VI.



[X]



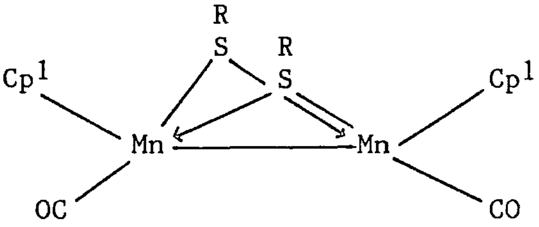
[XI]

The ^{1}H n.m.r. spectrum of this material exhibited two intense sets of lines in the cyclopentadienyl region (5.33 and 6.08ppm.) and two multiplets in the phenyl region (7.37 and 7.50ppm.). A possible follow-up to this work would be to repeat the reactions on a larger scale and try and separate the different species obtained using column chromatography. Such an approach has previously proved useful in this area.[21]

3.4 ATTEMPTED REACTION OF (PhCN$_2$S$_2$)$_2$ WITH CpMn(CO)$_3$

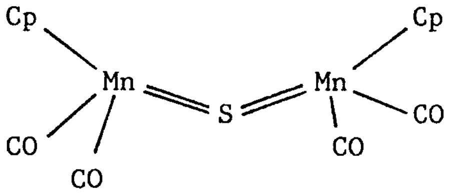
3.4.1. Introduction

Substitution of the carbonyl groups in CpMn(CO)$_3$ requires u.v. photolysis (no reaction occurs between CpMn(CO)$_3$ and Ph$_3$P in decalin at 140°C) and a large number of monosubstituted derivatives have been prepared.[25a] Dinuclear complexes, resulting from displacement of two carbonyl groups, are less common and generally contain phosophorus donors. Indeed, attempts to prepare a sulphur complex of the type shown in XII were unsuccessful[26] (R=Et,CH$_2$Ph; Cp^1=C$_5$H$_4$Me) as were attempts[29] to prepare [CpMnS$_2$C$_2$(CF$_3$)$_2$]$_2$ from CpMn(CO)$_3$ and $CF_3C(\overline{S)=C(S})CF_3$.

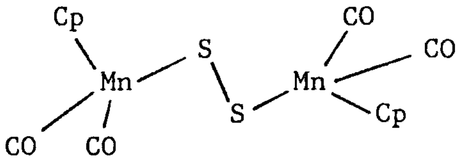


[XII]

The reagent Me_3NO has been used to carry out carbonyl substitution reactions^{15a} on $(C_5H_4Me)Mn(CO)_3$ at 60-80°C, though only monosubstituted products were prepared. Interestingly, $CpMn(CO)_2$thf reacts^{27a} with both S_8 and $SR_2{}^1$ (R^1=NR_2,SiR_3,SnR_3) in thf to give XIII whereas reaction^{27b} with COS, under similar circumstances, gave XIV.



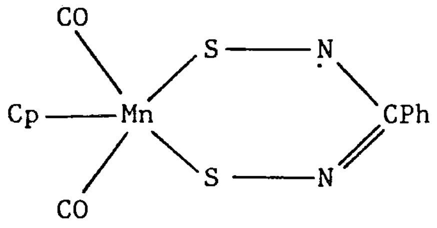
[XIII]



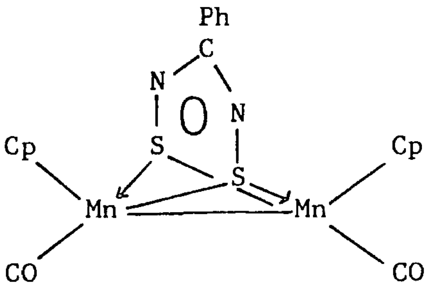
[XIV]

Both of the above complexes as well as $CpMn(CO)_2(S_2)$ were later isolated^{27c} from the reaction of $CpMn(CO)_2$thf with S_8. Reaction^{27a} of $SO(NEt_2)_2$ with $CpMn(CO)_2$thf gave $CpMn(CO)_2SO(NEt_2)_2$. The radical complexes $Cp^1Mn(CO)_2SR$ (Cp^1=C_5Me_5,C_5H_5, R=^{t}Bu,2-adamantyl) have also been prepared^{28}, via the thiols RSH.

In the light of this work it was thought that reaction between $CpMn(CO)_3$ and $(PhCN_2S_2)_2$ may occur to give species such as:



[XV]



[XVI]

3.4.2 Results and Discussion

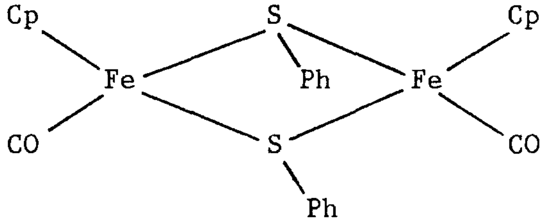
Proton n.m.r. spectroscopy revealed that $CpMn(CO)_3$ did not react with $(PhCN_2S_2)_2$ in toluene at 100°C, or in the presence of Me_3NO at 60°C or under photolysis conditions (Section 3. 9 .3). The first of these results is not surprising. The other results require further comment. The formation of compound XV may be precluded simply for steric reasons since it involves an expansion of coordination number for manganese to seven, usually only observed in hydride complexes.[25b] In reactions where photolysis has resulted in the loss of a second carbonyl group, it is noteworthy that the new ligand is a relatively good π-acceptor (e.g. PR_3, RNC).[25a] The use of such ligands does not entail an increase in the strength of the remaining metal-carbonyl bonds which usually follows substitution by a less efficient π-acceptor (poorer acceptors lead to a build-up of electron density on the metal which can only be off-loaded into the remaining carbonyl π^* orbitals). The efficiency of the $PhCN_2S_2$ unit as a π-acceptor is probably low since the acceptor orbital is relatively high in energy (Figure 1.6). Sulphur is usually only a good π-acceptor with highly electronegative ligands attached.

The results discussed above further support the statement[25a] that 'these compounds $(Mn(CO)_3(\eta^5\text{-}C_5H_4R)$ (R=H,Me) must be among the most inert, if they are not the most inert, of metal carbonyl species'.

3.5 REACTION BETWEEN $[CpFe(CO)_2]_2$ AND $(PhCN_2S_2)_2$

3.5.1 Introduction

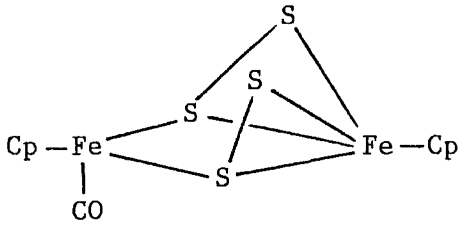
Early work[30] reported the thermal reaction between $[CpFe(CO)_2]_2$ and Me_2S_2 to give $[CpFe(CO)(\mu\text{-}SMe)]_2$(1). This was later extended when an improved yield of 1,[31,32] and the t-butyl,[31] the ethyl[32], phenyl[32] and tolyl[33] analogues, together with the corresponding photolysis reaction which gave $CpFe(CO)_2SR$ ($R=Me^{31}, CF_3{}^{18}$) was published. Pyrolysis of $CpFe(CO)_2SR$ gave $[CpFe(CO)(\mu\text{-}SR)]_2$ ($R=Me^{31}$, $CF_3{}^{34}$). The reaction between $[CpFe(CO)_2]_2$ and bis (trifluoromethyl) dithetene, $CF_3C(\overline{S)=C(S})CF_3$, gave black involatile materials of uncertain composition.[29] The stereochemistry of the above complexes has aroused interest[32,33] and an X-ray structure of the most stable form, with R=Ph, has been determined.[35] The phenyl and the carbonyl groups are both cis, as shown in [XVII].



[XVII]

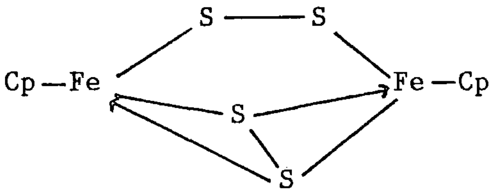
In addition to the usual dinuclear products, trinuclear compounds, $[Cp_3Fe_3(CO)_2(S)SR]$, have been produced[36] from the thermolysis reaction between $[CpFe(CO)_2]_2$ and R_2S_2 ($R=Me,Et,{}^iPr,{}^tBu,Bz,Ph$). Recent work has included photolysis of Ph_2S_2 with $[C_5Me_5Fe(CO)_2]_2$ to give $C_5Me_5Fe(CO)_2SPh$[37], and with $[CpFe(CO)_2]_2$, to give $CpF\overline{e(CO)SC_6H_2R\text{-}2\text{-}S}C_6H_4R$ and $CpFe(CO)_2SC_6H_3R\text{-}2\text{-}SC_6H_4R(R=H,Me)$.[17b] The preparation and crystal structure of $[CpFe(CO)(\mu\text{-}SC_5H_9NMe)]_2$ has also appeared.[38]

The reaction between $[CpFe(CO)_2]_2$ and S_8[11a] or cyclohexene sulphide[11b] in refluxing toluene led to the isolation of $[CpFeS]_4$ the structure of which is based on a tetrahedron of iron atoms each terminally bonded to a Cp ring and with sulphur atoms sitting above the faces of the tetrahedron. A red oil, also obtained[11a], was tentatively formulated as $[CpFe(CO)(\mu\text{-}S)]_2$. A red-brown solid of this composition was later isolated[39] from the products of the reaction between $[CpFe(CO)_2]_2$ and $2\text{-}C_6H_4\overline{C(S)S}S$. A black solid, containing no carbonyl groups, previously obtained from the reaction involving S_8, was also formed. Photolysis of $[C_5H_4RFe(CO)_2]_2$ (R=H,Me) in the presence of S_8 yielded[40] a mixture of compounds each containing four sulphur and two iron atoms. The structure of one, characterised[40a] by X-ray diffraction is shown in XVIII:



[XVIII]

Later, two more components were similarly characterised[41a,b] and one is shown as XIX (the structure of the C_5Me_5 derivative, prepared in boiling toluene, has also been determined[41c]):

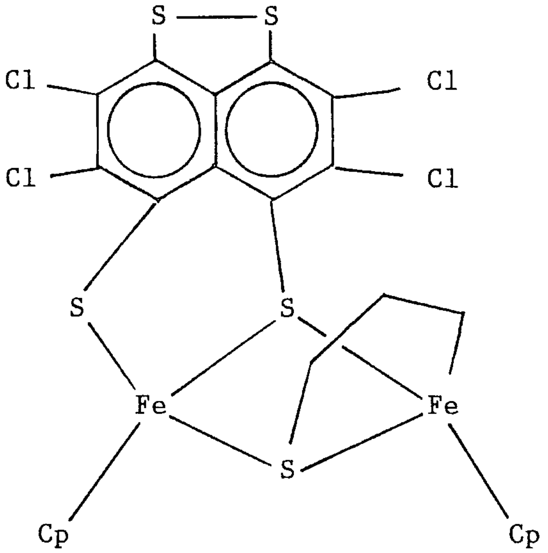


[XIX]

The other isomer contains two η^1, η^2-disulphide ligands in a syn arrangement.[41b] A trisulphide, $[CpFe(CO)_2]_2S_3$ has also been obtained[41d], on thermolysis of $[CpFe(CO)_2]_2$ and S_8 in thf. The reaction of $[CpFe(CO)_2]_2$ with ethyl polysulphide (a mixture of the tri- and tetrasulphides) gave a compound[42] based on XIX but with the doubly bridging sulphur atoms ethylated and no longer bonded to each other. The polynuclear species $Cp_3Fe_3S_2(SEt)$, $Cp_4Fe_4S_4$, $Cp_4Fe_4S_5$ and $Cp_4Fe_4S_6$ were later prepared[43] from ethyl polysulphides, the latter three also being obtained from S_8.

The mononuclear complexes $CpFe(CO)_2(\eta^1\text{-SC(S)NR}_2)$[23] (R=Me,Et) and $Cp^*Fe(CO)_2(\eta^1SP(S)(OR)_2)$[44] ($Cp^*=C_5H_5,C_5H_4Me$, C_5Me_5) have been characterised as the products from the reactions between $[Cp^*Fe(CO)_2]_2$ and $[Me_2NC(S)S]_2$[23a] or $NHEt_2\text{-}CS_2$[23b] and

$[SP(S)(OR)_2]_2$, respectively. Also $[Cp^1Fe(CO)_2]_2$ ($Cp^1=C_5H_5$ or C_5Me_5) and $(SC(S)OEt)_2$ gave $Cp^1Fe(CO)_2(\eta^1\text{-}SC(S)OEt)$.[23c] Finally[45], the tetrathiolene, $C_{10}Cl_4S_4$ reacted with $[Cp^*Fe(CO)_2]_2$ to give the desulphurised product $Cp_2Fe_2(C_{10}Cl_4S_4)(C_{10}Cl_4S_3)$, as shown in XX (only the $C_{10}Cl_4S_4$ ligand is shown).



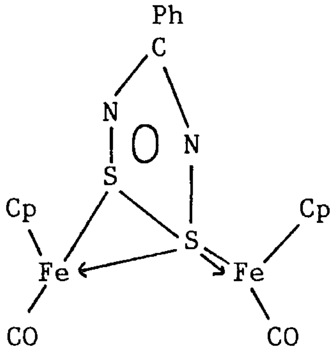
[XX]

3.5.2 Results and Discussion

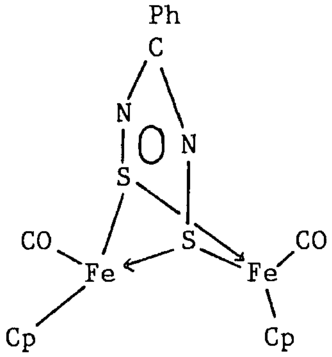
The proton n.m.r. spectrum of a 1:1 mixture of $[CpFe(CO)_2]_2$ and $(PhCN_2S_2)_2$, which had been heated to 60°C for 12h, gave two major new signals in the Cp region at 4.43 and 4.48ppm. with a minor signal also appearing at 4.33ppm. The relative intensity of the peak at 4.43ppm. decreased with time. Photolysis of a 2:1 mixture in d_6-benzene gave rise to only one major new Cp signal, at 4.43ppm, in the proton n.m.r., although a minor peak also appeared at 4.36ppm. These positive results were followed up by carrying out preparative-scale experiments. The thermolysis reaction on a 2:1 reaction mixture, resulted in the isolation of a black insoluble solid, the i.r. spectrum of which showed three carbonyl bands at 1940sh, 1974 and 2030cm^{-1} (Section 3.9.4).

Scale-up of the photolysis reaction again gave a black, insoluble solid with carbonyl i.r. bands at 1955sh, 1980 and 2030cm^{-1}. Although prolonged washing with toluene or dichloromethane did lead to a reduction in the intensity of the 1950cm^{-1} band, it was never completely removed. The mass spectrum and analytical data of the product were largely uninformative, although the latter did indicate the Fe:S ratio to be close to 1:1. Similar results were obtained with the solid isolated from the thermolysis reaction.

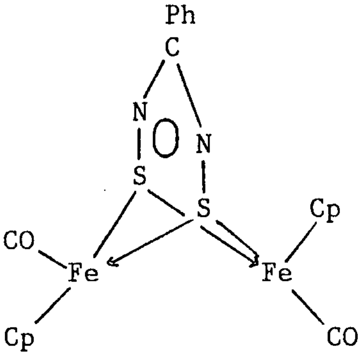
The initial n.m.r. data obtained in the study of this reaction, in which the observed chemical shifts all lie in the range (3.86 - 4.62ppm.)[32,33,36] previously reported for similar species, suggest that compound XXI is obtained as the major product in solution. There are three isomeric forms of this compound possible, as shown in XXI - XXIII:



[XXI]



[XXII]

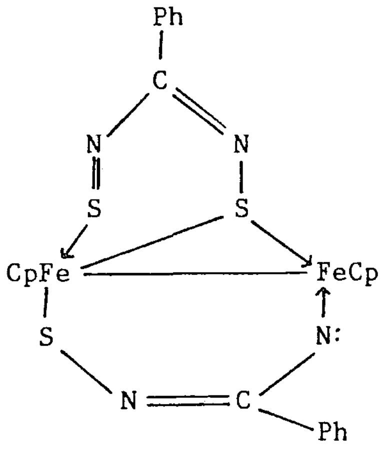


[XXIII]

These will give one, one and two signals in the Cp region of the proton n.m.r., respectively. This suggested that a mixture of XXI and and XXII are obtained in the thermolysis reaction (2 signals at 4.43 and 4.48ppm.) whereas only XXI <u>or</u> XXII is obtained on photolysis (1 signal at 4.43ppm.). No evidence for interconversion of these isomers was obtained. Although the spectroscopic data do not allow unequivocal assignment of signals to a particular isomer, previous work[32,33] on isomerism in [CpFe(CO)SR]$_2$ complexes has identified organosulphur derivatives of XXII as the most stable form. These species have lower chemical shifts than the less-stable isomers and so the signal at 4.43ppm. is assigned to this isomer while that at 4.48ppm. is assigned to XXI. These assignments are also in accord with the reduction in intensity of the signal at 4.48ppm. on prolonged thermolysis. Species XXI and XXII should each give one carbonyl i.r. band and so, in this work the band at 2030cm^{-1} is assigned[32,33] to XXII, while that at 1975/80 is assigned to XXI. The shoulder at 1940/50 is most probably due to $[CpFe(CO)_2]_2$ (Section 3.9.4).

The analyses indicate that other non-carbonyl containing material is present in these solids. However, the very low solubilities of the component compounds have not made extraction of any one component possible to date. It is hoped that column chromatography will achieve separation of at least the carbonyl species (which show slight solubility in toluene and dichloromethane). Preliminary work indicated this to be feasible (Section 3.9.4(b)). The n.m.r. signal at 4.33ppm. remains unassigned but may be due to a non-carbonyl containing product. The structure of such a species may be based on that of XXI, but with an iron-iron double bond replacing the two terminally bonded carbonyl groups. However, this complex will probably be highly reactive[45] and may well further react with $(PhCN_2S_2)_2$ to form desulphurised (e.g. XXIV) and/or polymeric products.

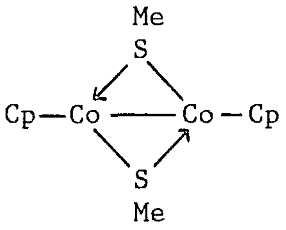
[XXIV]



3.6 REACTION OF $CpCo(Co)_2$ WITH $(PhCN_2S_2)_2$: PREPARATION OF $[CpCo(PhCN_2S)]_2$

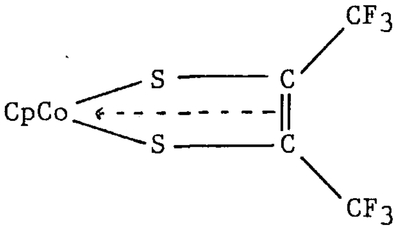
3.6.1 Introduction

The reaction between $CpCo(CO)_2$ and Me_2S_2 has been reported[30] to give a compound of composition $[CpCoSMe]_2$, thought to adopt structure XXV.

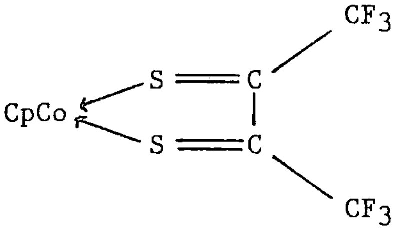


[XXV]

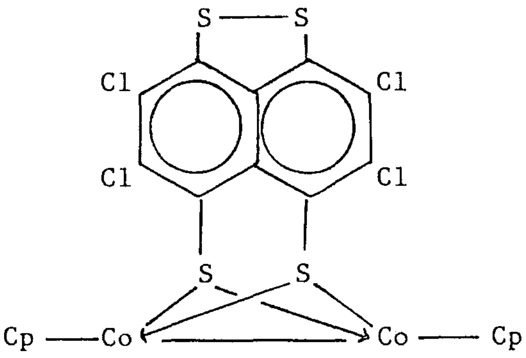
The proposed[5] structure, XXVI, of the product from $CpCo(CO)_2$ and $CF_3C(S)=C(S)CF_3$ was based on molecular weight determinations. However, the lack of reactivity toward Lewis bases[29] and a crystallographic study[46] (low R Value) favoured the structure shown as XXVII. The reaction between $CpCo(CO)_2$ and R_2S_2 ($R=CF_3,C_6F_5$) gave $[CpCo(SR)]_2$, $CpCo(CO)(SC_6F_5)_2$ or $CpCo_2(SC_6F_5)_3$ depending on the conditions.[47] The tetrathiolene, $C_{10}Cl_4S_4$, formed a dinuclear complex[45] shown as XXVIII.



[XXVI]



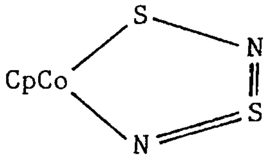
[XXVII]



[XXVIII]

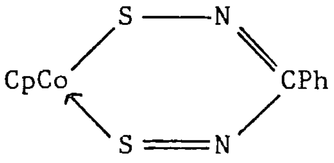
The reaction of S_8 with $CpCo(CO)_2$ resulted[48] in the synthesis of $Cp_4Co_4S_6$ in which a distorted tetrahedron of CpCo fragments were connected by two triply bridging S_2 units and two triply bridging S atoms located above the four triangular faces of the tetrahedron.

Finally, a few experiments involving sulphur-nitrogen species have been described. Reaction[49] of $CpCo(CO)_2$ with $(^tBuN)_2S$ gave $Cp_2Co_2(CO)(NBu^t)_2$, $Cp_3Co_3S_2$ and $Cp_3Co_3(CO)S$, while S_4N_4 gave[50] $CpCoS_2N_2$, the structure of which is shown in XXIX. The bonding[51] in this compound has been discussed and extensive π-delocalisation proposed in the metallocycle with lone-pair donation from the bonded sulphur and nitrogen atoms to cobalt.

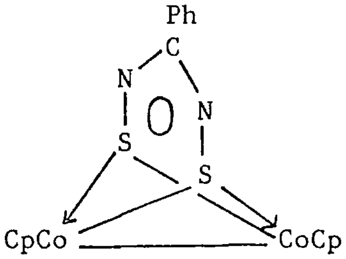


[XXIX]

These results suggest that the formally 17 electron compound XXX or the dinuclear species XXXI may be obtained from $CpCo(CO)_2$ and $(PhCN_2S_2)_2$.



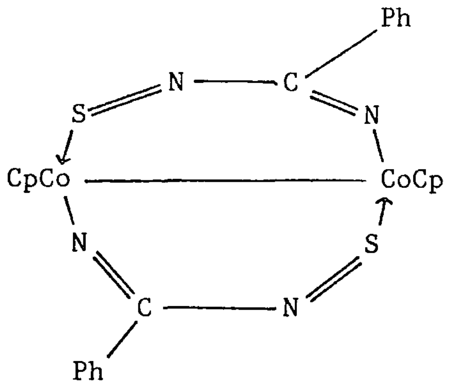
[XXX]



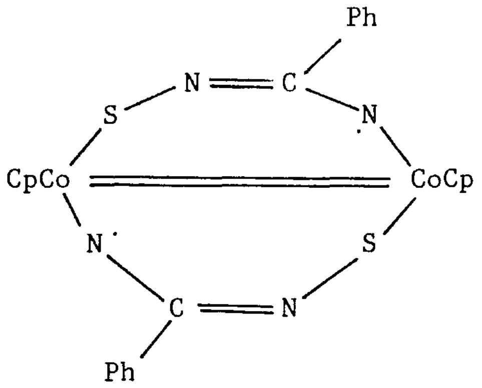
[XXXI]

3.6.2 Results and Discussion

In this reaction the product was precipitated immediately from toluene (Section 3. 9.5) and so good n.m.r. spectra could not be obtained. A solution phase i.r. study on a 2:1 $CpCo(CO)_2$-$(PhCN_2S_2)_2$ reaction revealed that no carbonyl species remained in solution after 21h stirring at 21°C. A similar study on a 4:1 reaction mixture showed $CpCo(CO)_2$ still to be present after 24h at 21°C, suggesting only one $PhCN_2S_2$ ring to react with each molecule of $CpCo(CO)_2$. The black solid filtered off after the latter reaction showed no carbonyl bands in the i.r. spectrum. The formula of the product was obtained after the observation of a molecular ion peak at 548 in the mass spectrum. This evidence together with the analytical data (the CHN data indicate slight contamination with a species such as XXX, Section 3.9.5) suggest the following bidentate bridged structures:

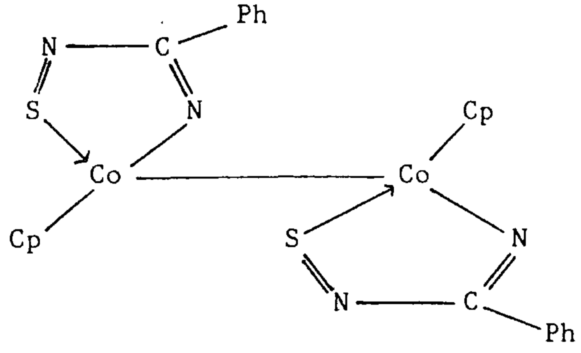


[XXXII]



[XXXIII]

The very weak paramagnetism observed from this material (Appendix 3) suggests that structure XXXII is adopted, in which the spins forming the cobalt-cobalt bond are not fully paired. Alternatively, a structure, XXXIV, could be adopted in which the $PhCN_2S$ unit acts in a non-bridging role:



[XXXIV]

Such a structure would explain the high intensity peak in the mass spectrum, at 274, corresponding to breaking of the cobalt-cobalt bond. The weak paramagnetism could then be due to a trace impurity or partial dissociation in the solid state.

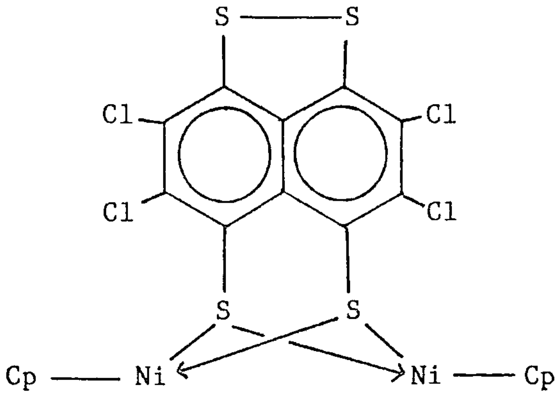
The desulphurisation of $PhCN_2S_2$ observed in this experiment has a precedent in the reaction[49] of $CpCo(CO)_2$ with $S(N^tBu)_2$, which gave $Cp_3Co_3S_2$ (22%) as the major sulphur-containing product. There is some evidence for this species in the mass spectrum of $CpCo(PhCN_2S)$ with peaks at 189 (Cp_2Co^+) and 436 ($Cp_3CoS_2^+$) but these may be present as a result of decomposition in the spectrometer probe.

3.7 REACTION OF $[CpNi(CO)]_2$ WITH $(PhCN_2S_2)_2$: PREPARATION OF $Cp_2Ni_2(PhCN_2S_2)$

3.7.1 Introduction

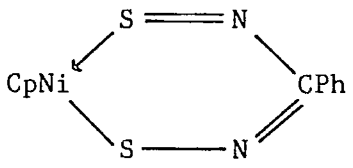
A black paramagnetic solid of composition $CpNiC_4F_6S_2$ was isolated[5] from the reaction between $[CpNi(CO)]_2$ and $CF_3C(\overline{S)=C(S})CF_3$. Although the structure was originally thought to be that adopted by the cobalt complex in XXVI, (though without Co-C π-bonding) a crystallographic study[46] found the complex to be isomorphous with XXVII. The action[11] of cyclohexene sulphide produced carbonyl-free black solids of undetermined composition. Photolysis[34] of $[CpNi(CO)]_2$ with R_2S_2 in a closed system ($R=CF_3,C_6F_5$) gave the monomeric species $CpNi(CO)SR$; in an open system $[CpNiSR]_n$ was obtained. The tetrathiolene, $C_{10}Cl_4S_4$, gave[45] $CpNi_2S_2C_{10}Cl_4S_2$, shown in XXXV.

[XXXV]

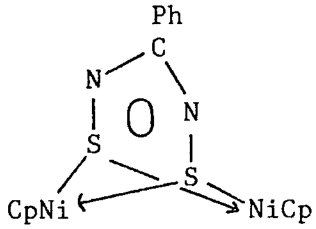


Reaction[52] of $[CpNi(CO)]_2$ with S_8 gave $CpNi_3S_2$ and, finally, the sulphur diimide, $S(NBu^t)_2$ reacted with $[CpNi(CO)]_2$ to give[49] $Cp_3Ni_3NBu^t$.

Although so little work had been done in organosulphur-nickel chemistry it was thought, on the basis of the above results and by analogy with the analogous chemistry of cobalt, that species such as XXXVI or XXXVII might result.



[XXXVI]



[XXXVII]

3.7.2 Results and Discussion

A considerable amount of black solid was precipitated immediately on mixing the $[CpNi(CO)]_2$ and $(PhCN_2S_2)_2$ in d_8-toluene and so n.m.r. spectra could not be obtained. The solution phase i.r. spectra recorded from a preparative scale 2:1 $[CpNi(CO)]_2$-$(PhCN_2S_2)_2$ solution mixture showed that no carbonyl species remained in solution after stirring for 14h at 21°C. A black solid was filtered off but was found to be highly insoluble in common organic solvents and the analytical data, although giving an Ni:S ratio close to 1:1 did not correspond to either XXXVI, XXXVII or the desulphurised derivative of

XXXVI. This solid is presumably polymeric and was not investigated further.

However, a dark red crystalline material was recovered from the filtrate and the analytical data on this compound together with its mass spectrum, with a parent ion at 427, indicated the formula to be that of XXXVII. The structure was determined by X-ray crystallography as shown in Figure 3.1. The relevant bond lengths and angles are given in Table 3.1 and the other crystallographic data in Tables 3.2 to 3.4.

The most interesting structural feature of the complex is the nickel-nickel distance at 2.440(1)Å. This value is rather longer than that observed in other CpNi species (See Table 3.5) but is shorter than previously reported "short" non-bonding Ni-Ni distances e.g. 2.880Å in $Cp_2Ni_2(C_{10}Cl_4S_4)$.[45]

Table 3.5 Ni-Ni Bond Lengths in Some CpNi Compounds

COMPOUND	D(Ni-Ni)(Å)	REF
$[CpNi(MeCN)]_2$	2.3217	53
$Cp_2Ni_2(PhC{\equiv}CPh)$	2.329(4)	54
$[CpNi(CO)]_2$	2.3569(9)#	55
$Cp^*CoNi_2Cp_2(\mu^3\text{-}CO)_2$	2.3260(23)	56

average value for 2 molecules in asymmetric unit.

If it is assumed that the $PhCN_2S_2$ fragment donates three electrons to each metal atom, as in $Fe_2(CO)_6PhCN_2S_2$ (Section 2.5.2) then each nickel centre in $Cp_2Ni_2PhCN_2S_2$ can adopt an 18-electron configuration without forming an Ni-Ni bond. However, the 18-electron rule (which is a consequence of a transition metal's tendency to use all of its valence orbitals) is not universally applicable, e.g. nickelocene is a

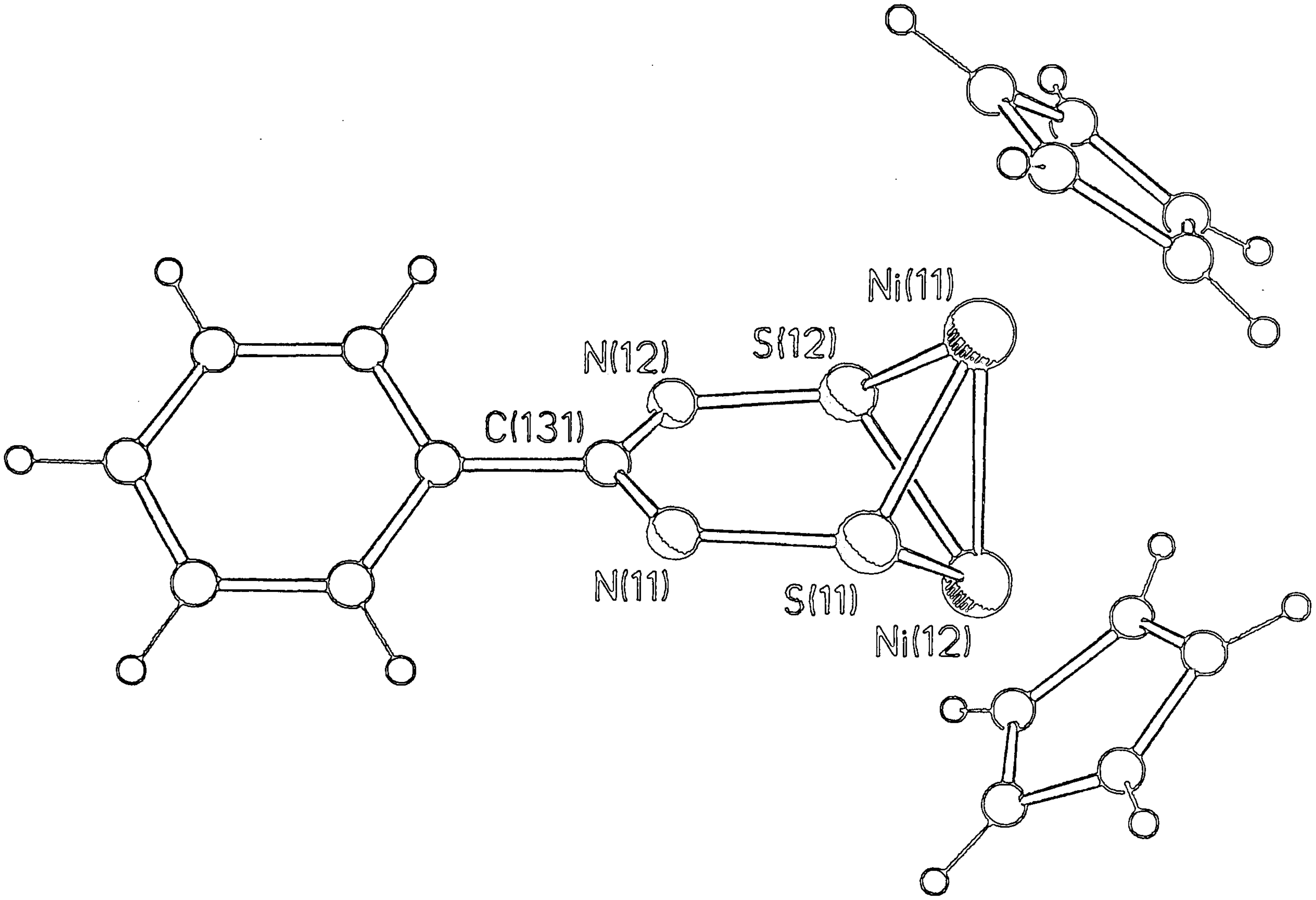


Figure 3.1. X-Ray Structure of $Cp_2Ni_2(PhCN_2S_2)$

Table 3.1

Bond lengths (Å) and angles (°)

Ni(11)-C(111)	2.101(5)	Ni(11)-C(112)	2.089(4)
Ni(11)-C(113)	2.062(6)	Ni(11)-C(114)	2.056(5)
Ni(11)-C(115)	2.080(4)	Ni(11)-Ni(12)	2.440(1)
Ni(11)-S(11)	2.175(1)	Ni(11)-S(12)	2.168(1)
C(111)-C(112)	1.298(7)	C(111)-C(115)	1.295(7)
C(112)-C(113)	1.417(8)	C(113)-C(114)	1.387(9)
C(114)-C(115)	1.290(8)	Ni(12)-C(121)	2.126(4)
Ni(12)-C(122)	2.102(4)	Ni(12)-C(123)	2.119(4)
Ni(12)-C(124)	2.105(4)	Ni(12)-C(125)	2.132(4)
Ni(12)-S(11)	2.174(1)	Ni(12)-S(12)	2.180(1)
C(121)-C(122)	1.423(6)	C(121)-C(125)	1.375(5)
C(122)-C(123)	1.414(6)	C(123)-C(124)	1.388(6)
C(124)-C(125)	1.401(5)	S(11)-N(11)	1.640(2)
S(12)-N(12)	1.634(3)	N(11)-C(131)	1.336(4)
N(12)-C(131)	1.324(4)	C(131)-C(132)	1.485(4)
C(132)-C(133)	1.384(5)	C(132)-C(137)	1.391(4)
C(133)-C(134)	1.358(6)	C(134)-C(135)	1.368(6)
C(135)-C(136)	1.346(7)	C(136)-C(137)	1.365(5)
Ni(21)-C(211)	2.121(4)	Ni(21)-C(212)	2.112(5)
Ni(21)-C(213)	2.103(4)	Ni(21)-C(214)	2.095(5)
Ni(21)-C(215)	2.121(4)	Ni(21)-Ni(22)	2.441(1)
Ni(21)-S(21)	2.171(1)	Ni(21)-S(22)	2.172(1)
C(211)-C(212)	1.403(6)	C(211)-C(215)	1.395(8)
C(212)-C(213)	1.376(8)	C(213)-C(214)	1.345(7)
C(214)-C(215)	1.387(8)	Ni(22)-C(221)	2.122(4)
Ni(22)-C(222)	2.109(4)	Ni(22)-C(223)	2.125(4)
Ni(22)-C(224)	2.098(4)	Ni(22)-C(225)	2.118(4)
Ni(22)-S(21)	2.169(1)	Ni(22)-S(22)	2.170(1)
C(221)-C(222)	1.414(6)	C(221)-C(225)	1.341(6)
C(222)-C(223)	1.391(6)	C(223)-C(224)	1.372(6)
C(224)-C(225)	1.424(6)	S(21)-N(21)	1.634(3)
S(22)-N(22)	1.627(3)	N(21)-C(231)	1.325(4)
N(22)-C(231)	1.327(4)	C(231)-C(232)	1.488(4)
C(232)-C(233)	1.377(4)	C(232)-C(237)	1.382(4)
C(233)-C(234)	1.405(5)	C(234)-C(235)	1.369(5)
C(235)-C(236)	1.346(6)	C(236)-C(237)	1.394(5)

C(111)-Ni(11)-C(112)	36.1(2)	C(111)-Ni(11)-C(113)	63.7(2)
C(112)-Ni(11)-C(113)	39.9(2)	C(111)-Ni(11)-C(114)	61.7(2)
C(112)-Ni(11)-C(114)	63.9(2)	C(113)-Ni(11)-C(114)	39.4(2)
C(111)-Ni(11)-C(115)	36.1(2)	C(112)-Ni(11)-C(115)	61.0(2)
C(113)-Ni(11)-C(115)	63.2(2)	C(114)-Ni(11)-C(115)	36.3(2)
C(111)-Ni(11)-Ni(12)	169.7(1)	C(112)-Ni(11)-Ni(12)	151.8(2)
C(113)-Ni(11)-Ni(12)	118.6(1)	C(114)-Ni(11)-Ni(12)	113.0(2)
C(115)-Ni(11)-Ni(12)	134.5(1)	C(111)-Ni(11)-S(11)	133.7(1)
C(112)-Ni(11)-S(11)	109.4(1)	C(113)-Ni(11)-S(11)	112.6(1)
C(114)-Ni(11)-S(11)	145.6(1)	C(115)-Ni(11)-S(11)	169.6(1)
Ni(12)-Ni(11)-S(11)	55.9(1)	C(111)-Ni(11)-S(12)	117.2(1)
C(112)-Ni(11)-S(12)	151.8(2)	C(113)-Ni(11)-S(12)	155.9(2)
C(114)-Ni(11)-S(12)	117.7(2)	C(115)-Ni(11)-S(12)	102.5(1)
Ni(12)-Ni(11)-S(12)	56.1(1)	S(11)-Ni(11)-S(12)	84.5(1)
Ni(11)-C(111)-C(112)	71.4(3)	Ni(11)-C(111)-C(115)	71.1(3)
C(112)-C(111)-C(115)	109.4(5)	Ni(11)-C(112)-C(111)	72.5(3)
Ni(11)-C(112)-C(113)	69.0(3)	C(111)-C(112)-C(113)	108.0(4)
Ni(11)-C(113)-C(112)	71.1(3)	Ni(11)-C(113)-C(114)	70.1(3)
C(112)-C(113)-C(114)	103.0(4)	Ni(11)-C(114)-C(113)	70.5(3)
Ni(11)-C(114)-C(115)	72.8(3)	C(113)-C(114)-C(115)	108.3(5)
Ni(11)-C(115)-C(111)	72.8(3)	Ni(11)-C(115)-C(114)	70.8(3)
C(111)-C(115)-C(114)	111.2(5)	Ni(11)-Ni(12)-C(121)	152.2(1)
Ni(11)-Ni(12)-C(122)	118.1(1)	C(121)-Ni(12)-C(122)	39.3(2)
Ni(11)-Ni(12)-C(123)	107.8(1)	C(121)-Ni(12)-C(123)	65.4(1)
C(122)-Ni(12)-C(123)	39.1(2)	Ni(11)-Ni(12)-C(124)	128.2(1)

121)-Ni(12)-C(124)	64.4(1)	C(122)-Ni(12)-C(124)	64.7(1)
123)-Ni(12)-C(124)	38.4(2)	Ni(11)-Ni(12)-C(125)	166.0(1)
121)-Ni(12)-C(125)	37.7(1)	C(122)-Ni(12)-C(125)	64.4(1)
123)-Ni(12)-C(125)	64.5(2)	C(124)-Ni(12)-C(125)	38.6(1)
(11)-Ni(12)-S(11)	55.9(1)	C(121)-Ni(12)-S(11)	151.3(1)
122)-Ni(12)-S(11)	161.3(1)	C(123)-Ni(12)-S(11)	122.8(1)
124)-Ni(12)-S(11)	104.0(1)	C(125)-Ni(12)-S(11)	116.9(1)
(11)-Ni(12)-S(12)	55.6(1)	C(121)-Ni(12)-S(12)	108.8(1)
122)-Ni(12)-S(12)	107.1(1)	C(123)-Ni(12)-S(12)	135.6(1)
124)-Ni(12)-S(12)	171.7(1)	C(125)-Ni(12)-S(12)	138.2(1)
11)-Ni(12)-S(12)	84.2(1)	Ni(12)-C(121)-C(122)	69.4(2)
(12)-C(121)-C(125)	71.4(2)	C(122)-C(121)-C(125)	107.4(3)
(12)-C(122)-C(121)	71.2(2)	Ni(12)-C(122)-C(123)	71.1(2)
121)-C(122)-C(123)	108.0(3)	Ni(12)-C(123)-C(122)	69.8(2)
(12)-C(123)-C(124)	70.3(2)	C(122)-C(123)-C(124)	106.9(3)
(12)-C(124)-C(123)	71.4(2)	Ni(12)-C(124)-C(125)	71.8(2)
123)-C(124)-C(125)	109.0(3)	Ni(12)-C(125)-C(121)	70.9(2)
(12)-C(125)-C(124)	69.7(2)	C(121)-C(125)-C(124)	108.8(3)
(11)-S(11)-Ni(12)	68.3(1)	Ni(11)-S(11)-N(11)	111.8(1)
(12)-S(11)-N(11)	112.1(1)	Ni(11)-S(12)-Ni(12)	68.3(1)
(11)-S(12)-N(12)	110.2(1)	Ni(12)-S(12)-N(12)	113.0(1)
11)-N(11)-C(131)	124.0(2)	S(12)-N(12)-C(131)	125.1(2)
11)-C(131)-N(12)	129.0(3)	N(11)-C(131)-C(132)	115.7(2)
12)-C(131)-C(132)	115.2(2)	C(131)-C(132)-C(133)	121.2(3)
131)-C(132)-C(137)	120.2(3)	C(133)-C(132)-C(137)	118.6(3)
132)-C(133)-C(134)	119.6(3)	C(133)-C(134)-C(135)	121.0(4)
134)-C(135)-C(136)	120.0(4)	C(135)-C(136)-C(137)	120.5(4)
132)-C(137)-C(136)	120.2(3)	C(211)-Ni(21)-C(212)	38.7(2)
211)-Ni(21)-C(213)	63.9(2)	C(212)-Ni(21)-C(213)	38.1(2)
211)-Ni(21)-C(214)	63.7(2)	C(212)-Ni(21)-C(214)	63.5(2)
213)-Ni(21)-C(214)	37.4(2)	C(211)-Ni(21)-C(215)	38.4(2)
212)-Ni(21)-C(215)	64.6(2)	C(213)-Ni(21)-C(215)	64.0(2)
214)-Ni(21)-C(215)	38.4(2)	C(211)-Ni(21)-Ni(22)	176.4(1)
212)-Ni(21)-Ni(22)	138.0(1)	C(213)-Ni(21)-Ni(22)	112.5(1)
214)-Ni(21)-Ni(22)	114.1(1)	C(215)-Ni(21)-Ni(22)	141.6(2)
211)-Ni(21)-S(21)	124.5(1)	C(212)-Ni(21)-S(21)	103.8(1)
213)-Ni(21)-S(21)	115.8(1)	C(214)-Ni(21)-S(21)	150.0(2)
215)-Ni(21)-S(21)	162.6(2)	Ni(22)-Ni(21)-S(21)	55.7(1)
211)-Ni(21)-S(22)	127.6(1)	C(212)-Ni(21)-S(22)	166.2(1)
213)-Ni(21)-S(22)	148.1(2)	C(214)-Ni(21)-S(22)	115.4(2)
215)-Ni(21)-S(22)	105.5(1)	Ni(22)-Ni(21)-S(22)	55.7(1)
21)-Ni(21)-S(22)	83.4(1)	Ni(21)-C(211)-C(212)	70.3(3)
(21)-C(211)-C(215)	70.8(3)	C(212)-C(211)-C(215)	107.8(4)
(21)-C(212)-C(211)	71.0(3)	Ni(21)-C(212)-C(213)	70.6(3)
211)-C(212)-C(213)	107.2(4)	Ni(21)-C(213)-C(212)	71.3(3)
(21)-C(213)-C(214)	71.0(3)	C(212)-C(213)-C(214)	108.8(4)
(21)-C(214)-C(213)	71.7(3)	Ni(21)-C(214)-C(215)	71.8(3)
213)-C(214)-C(215)	109.9(5)	Ni(21)-C(215)-C(211)	70.8(3)
(21)-C(215)-C(214)	69.8(3)	C(211)-C(215)-C(214)	106.3(4)
(21)-Ni(22)-C(221)	165.7(1)	Ni(21)-Ni(22)-C(222)	127.5(1)
221)-Ni(22)-C(222)	39.0(2)	Ni(21)-Ni(22)-C(223)	108.2(1)
221)-Ni(22)-C(223)	64.4(2)	C(222)-Ni(22)-C(223)	38.4(2)
(21)-Ni(22)-C(224)	118.5(1)	C(221)-Ni(22)-C(224)	64.1(2)
222)-Ni(22)-C(224)	64.1(2)	C(223)-Ni(22)-C(224)	37.9(2)
(21)-Ni(22)-C(225)	153.2(1)	C(221)-Ni(22)-C(225)	36.9(2)
222)-Ni(22)-C(225)	63.9(2)	C(223)-Ni(22)-C(225)	64.4(2)
224)-Ni(22)-C(225)	39.5(2)	Ni(21)-Ni(22)-S(21)	55.8(1)
221)-Ni(22)-S(21)	138.4(1)	C(222)-Ni(22)-S(21)	170.2(1)
223)-Ni(22)-S(21)	133.4(1)	C(224)-Ni(22)-S(21)	106.1(1)
225)-Ni(22)-S(21)	108.9(1)	Ni(21)-Ni(22)-S(22)	55.8(1)
221)-Ni(22)-S(22)	117.3(1)	C(222)-Ni(22)-S(22)	106.0(1)
223)-Ni(22)-S(22)	126.4(1)	C(224)-Ni(22)-S(22)	163.7(1)
225)-Ni(22)-S(22)	150.1(1)	S(21)-Ni(22)-S(22)	83.5(1)
(22)-C(221)-C(222)	70.0(2)	Ni(22)-C(221)-C(225)	71.4(3)
222)-C(221)-C(225)	108.6(4)	Ni(22)-C(222)-C(221)	71.0(2)
(22)-C(222)-C(223)	71.4(2)	C(221)-C(222)-C(223)	107.5(4)

)-C(223)-C(222)	70.2(2)	Ni(22)-C(223)-C(224)	70.0(3)
)-C(223)-C(224)	107.9(4)	Ni(22)-C(224)-C(223)	72.1(2)
)-C(224)-C(225)	71.0(2)	C(223)-C(224)-C(225)	107.9(4)
)-C(225)-C(221)	71.7(3)	Ni(22)-C(225)-C(224)	69.5(2)
)-C(225)-C(224)	108.1(4)	Ni(21)-S(21)-Ni(22)	68.5(1)
)-S(21)-N(21)	110.9(1)	Ni(22)-S(21)-N(21)	113.4(1)
)-S(22)-Ni(22)	68.4(1)	Ni(21)-S(22)-N(22)	112.1(1)
)-S(22)-N(22)	113.0(1)	S(21)-N(21)-C(231)	125.2(2)
)-N(22)-C(231)	125.0(2)	N(21)-C(231)-N(22)	127.7(3)
)-C(231)-C(232)	115.7(2)	N(22)-C(231)-C(232)	116.6(2)
1)-C(232)-C(233)	121.1(3)	C(231)-C(232)-C(237)	120.5(3)
3)-C(232)-C(237)	118.4(3)	C(232)-C(233)-C(234)	120.8(3)
3)-C(234)-C(235)	119.5(3)	C(234)-C(235)-C(236)	119.9(4)
5)-C(236)-C(237)	121.4(3)	C(232)-C(237)-C(236)	119.9(4)

able 3.2

nisotropic thermal parameters (Å²x10³)

he anisotropic temperature factor exponent takes the form
$2\pi^2(\underline{h^2a^{*2}U_{11}} + ... + 2\underline{hka^*b^*U_{12}})$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
i(11)	40(1)	44(1)	40(1)	2(1)	9(1)	0(1)
(111)	67(2)	90(3)	66(2)	3(2)	-1(2)	-32(3)
(112)	63(3)	39(2)	214(6)	38(3)	59(3)	9(2)
(113)	77(3)	274(8)	110(4)	148(5)	-54(3)	-102(4)
(114)	127(4)	182(6)	101(3)	-83(4)	84(3)	-103(4)
(115)	47(2)	58(3)	177(5)	25(3)	42(3)	11(2)
i(12)	51(1)	41(1)	37(1)	-4(1)	7(1)	0(1)
(121)	84(3)	41(2)	58(2)	-7(2)	-6(2)	4(2)
(122)	67(2)	85(3)	67(2)	-35(2)	6(2)	8(2)
(123)	97(3)	79(3)	36(2)	-16(2)	12(2)	-22(2)
(124)	83(3)	48(2)	51(2)	-9(2)	-13(2)	3(2)
(125)	63(2)	52(2)	60(2)	-12(2)	2(2)	-9(2)
(11)	42(1)	42(1)	38(1)	1(1)	5(1)	4(1)
(12)	44(1)	45(1)	41(1)	3(1)	10(1)	9(1)
(11)	44(1)	40(1)	40(1)	-1(1)	8(1)	3(1)
(12)	44(1)	41(1)	40(1)	3(1)	7(1)	2(1)
(131)	35(1)	38(2)	39(1)	-6(1)	1(1)	-4(1)
(132)	50(2)	40(2)	37(2)	-7(1)	8(1)	-1(1)
(133)	60(2)	123(4)	48(2)	-4(2)	16(2)	21(2)
(134)	85(3)	194(6)	61(3)	4(3)	39(2)	38(4)
(135)	115(4)	140(4)	43(2)	1(3)	31(2)	19(3)
(136)	107(3)	100(3)	38(2)	-6(2)	8(2)	17(3)
(137)	61(2)	65(2)	41(2)	-1(2)	3(1)	1(2)
i(21)	45(1)	41(1)	61(1)	1(1)	9(1)	5(1)
(211)	93(3)	59(3)	138(4)	40(3)	54(3)	31(2)
(212)	95(3)	77(3)	109(4)	7(3)	-11(3)	42(3)
(213)	56(2)	60(3)	152(5)	15(3)	31(3)	18(2)
(214)	130(4)	69(3)	91(3)	-2(3)	43(3)	43(3)
(215)	80(3)	43(2)	173(5)	-19(3)	16(3)	7(2)
i(22)	45(1)	45(1)	46(1)	2(1)	8(1)	1(1)
(221)	66(2)	77(3)	75(3)	23(2)	17(2)	7(2)
(222)	112(3)	93(3)	46(2)	6(2)	18(2)	-32(3)
(223)	79(3)	62(2)	88(3)	14(2)	44(2)	9(2)
(224)	56(2)	77(3)	85(3)	26(3)	11(2)	-12(2)
(225)	100(3)	49(2)	77(3)	0(2)	39(3)	-10(2)
(21)	37(1)	53(1)	44(1)	-4(1)	0(1)	0(1)
(22)	48(1)	54(1)	46(1)	-10(1)	2(1)	-5(1)
(21)	42(1)	53(2)	41(1)	-5(1)	2(1)	1(1)
(22)	40(1)	50(2)	49(1)	-2(1)	1(1)	-3(1)
(231)	38(2)	34(2)	40(2)	7(1)	-3(1)	1(1)
(232)	41(2)	39(2)	44(2)	7(1)	5(1)	6(1)
(233)	47(2)	62(2)	53(2)	-5(2)	2(1)	5(2)
(234)	67(2)	69(2)	59(2)	-3(2)	12(2)	15(2)
(235)	61(2)	63(2)	82(2)	7(2)	30(2)	9(2)
(236)	38(2)	97(3)	114(3)	-17(3)	16(2)	-10(2)
(237)	52(2)	87(3)	71(2)	-20(2)	9(2)	-7(2)

able 3.3

omic coordinates (x10^4)

om	x	y	z
(11)	6743(1)	2884(1)	3180(1)
(111)	5721(3)	1887(4)	2849(2)
(112)	6239(3)	1303(3)	3281(4)
(113)	6345(3)	1828(6)	4011(3)
(114)	5824(3)	2735(5)	3929(3)
(115)	5476(2)	2726(4)	3239(3)
(12)	7751(1)	4309(1)	3568(1)
(121)	8074(2)	5928(3)	3965(2)
(122)	7429(2)	5486(3)	4387(2)
(123)	7732(3)	4526(3)	4778(2)
(124)	8537(2)	4380(3)	4580(2)
(125)	8747(2)	5248(3)	4095(2)
11)	8058(1)	2740(1)	3043(1)
(12)	6853(1)	4449(1)	2583(1)
11)	8274(1)	2888(2)	2140(1)
12)	7255(1)	4254(2)	1756(1)
131)	7862(2)	3558(2)	1638(2)
(132)	8137(2)	3547(2)	840(2)
133)	8952(2)	3356(4)	700(2)
134)	9186(3)	3376(5)	-36(3)
135)	8623(3)	3544(5)	-645(2)
(136)	7829(3)	3745(4)	-518(2)
137)	7576(2)	3748(3)	215(2)
(21)	6176(1)	3442(1)	6857(1)
211)	5974(3)	4983(3)	6288(3)
(212)	5269(3)	4317(4)	6175(3)
213)	4986(3)	4114(4)	6891(4)
(214)	5490(4)	4615(4)	7429(3)
215)	6114(3)	5166(3)	7080(3)
(22)	6314(1)	1659(1)	7517(1)
221)	6469(3)	363(3)	8340(2)
222)	6178(3)	1328(4)	8694(2)
223)	5407(2)	1572(3)	8340(3)
224)	5240(2)	807(3)	7766(3)
225)	5908(3)	44(3)	7782(2)
21)	6253(1)	1858(1)	6273(1)
22)	7295(1)	2873(1)	7488(1)
21)	7143(1)	1715(2)	5902(1)
22)	8002(1)	2524(2)	6915(1)
231)	7862(2)	2028(2)	6237(2)
232)	8592(2)	1821(2)	5785(2)
233)	8510(2)	1329(3)	5069(2)
234)	9200(2)	1153(3)	4639(2)
235)	9965(2)	1448(3)	4946(2)
236)	10048(2)	1941(4)	5643(3)
237)	9370(2)	2127(4)	6076(2)

Table 3.4 Crystallographic Data for $Cp_2NiPhCN_2S_2$

Crystal System	Monoclinic
Space Group	$P2_1/m$
Unit Cell Measurements	
a (Å)	16.270(1)
b (Å)	12.069(1)
c (Å)	17.365(1)
ß (°)	93.863(7)
U ($Å^3$)	3402.1
D_c(gcm^{-3})	-
Z	8
F(000)	1752 electrons
T (°C)	22
No. Unique Reflections	6002
No. Observed Reflections	4746
R	0.0351
R_w	0.0284
$\mu(Mo\text{-}K_2)(mm^{-1})$	2.46

20-electron compound. It seems that the bond order of the metal-metal bond in $Cp_2Ni_2PhCN_2S_2$ lies between 0 and 1, but somewhat closer to 1 (which corresponds to a 19 electron count around nickel).

One possible explanation for this loss of bond order may lie in the existence of low energy antibonding orbitals in $Cp_2Ni_2PhCN_2S_2$ which can accept electrons without any great destabilisation. In nickelocene[57] (see Figure 3.2) the occupation of orbitals ($2e_{1g}$) which are antibonding with respect to the Ni-Cp interaction causes the average Ni-C bond length to lengthen relative to this distance in normal 18-electron CpNi species (d(Ni-C)=2.196Å in Cp_2Ni; 2.107Å in $Cp_2Ni_2(C_{10}Cl_4S_4)$[45]).

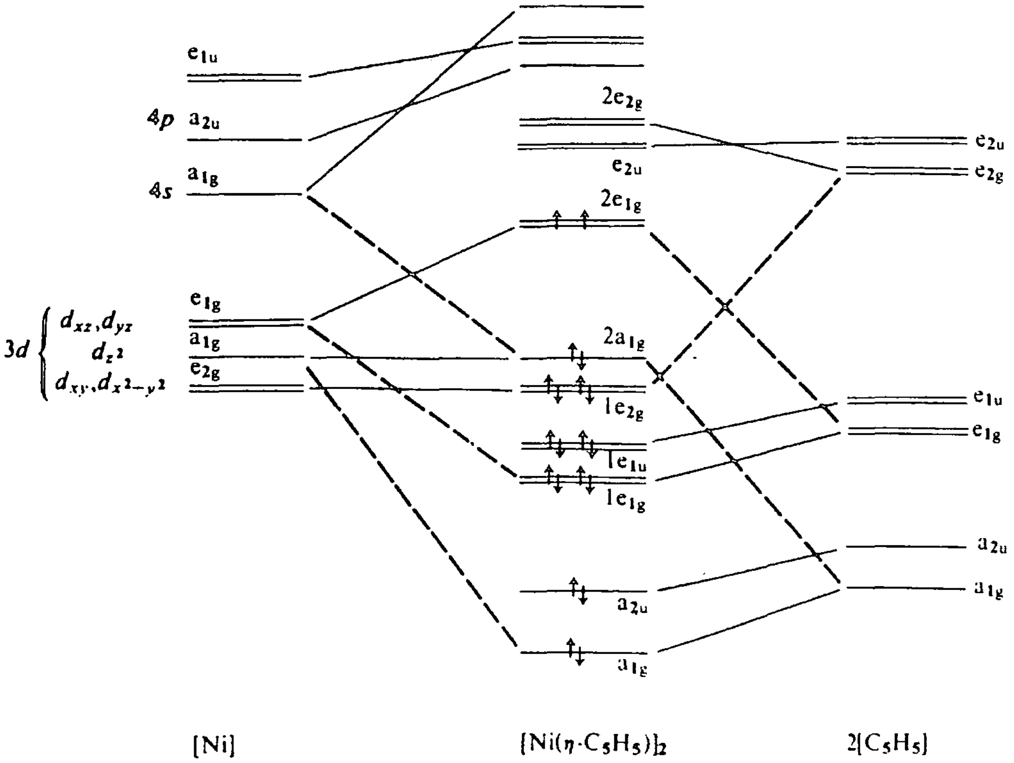


Figure 3.2

In $Cp_2Ni_2PhCN_2S_2$ it is proposed that low lying antibonding orbitals, arising from interaction between the two CpNi fragments[58], are occupied causing slight lengthening of the Ni-Ni bond. This is illustrated in Figure 3.3:

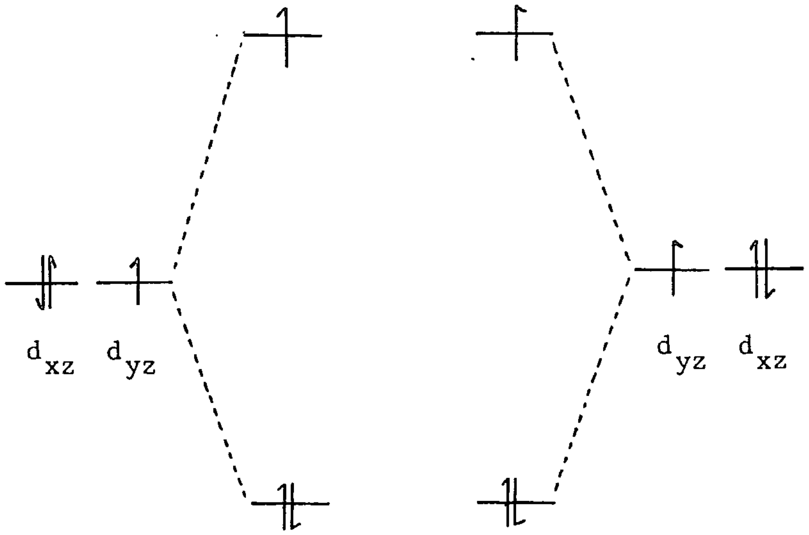


Figure 3.3 Simplified Orbital Interaction Diagram for 2CpNi Fragments.

Similar arguments have been used to explain the difference in Ni-Ni distances between $Cp_3Ni_3S_2$ (d(Ni-Ni)=2.801Å with 5 antibonding electrons) and $Cp_3Ni_3(CO)_2$ (d((Ni-Ni)=2.389Å with 1 antibonding electron). The Ni-Cp distances in $Cp_2Ni_2PhCN_2S_2$ are quite normal; the average values for the four rings in the asymmetric unit is 2.105Å. It is hoped that an Extended Hückel molecular orbital analysis to be carried out by Dr K A Jorgensen of Arhus University, Denmark, will enable a more definitive description of the bonding in this compound to be made.

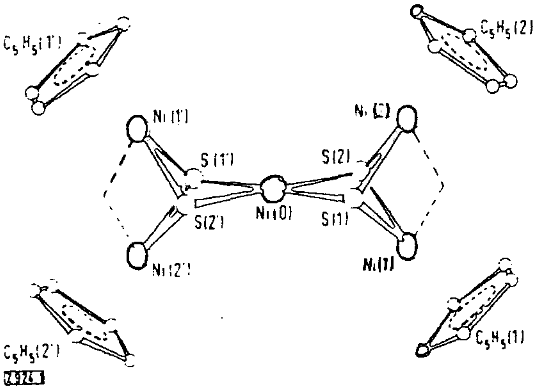
The magnetic susceptibility of the complex was found to be 0.022 JT^2Kg^{-1}. This result is discussed in Appendix 3.

There are two molecules of $Cp_2Ni_2(PhCN_2S_2)$ in the asymmetric unit. The major difference between them is the dihedral angle between the phenyl groups and the dithiadiazole rings. These have values of 33.1° and 1.9°, the difference presumably being due to packing forces. Some pertinent structural parameters for several CpNi-sulphur complexes are given in Table 3.6 (values for $Cp_2Ni_2(PhCN_2S_2)$ and $Cp_2Ni_2(C_{10}Cl_4S_4)$ are average values for the two molecules in the asymmetric unit).

Table 3.6 Structural Data (in Å and °) for some CpNi-Sulphur Complexes

COMPOUND	Ni-S	Ni-Ni	S-S	Ni-S-Ni	S-Ni-S
$Cp_2Ni_2(PhCN_2S_2)$	2.172(1)	2.441(1)	2.905(3)	68.4(1)	83.9(1)
$Cp_2Ni_2(C_{10}Cl_4S_4)$[45]	2.167(4)	2.880(4)	2.955(8)	83.44(16)	
$[Cp_2Ni_2S_2]_2$ Ni[59]	2.18(1)	2.495(3)		70.0(1)	

These show that the data (apart from Ni-Ni) for $Cp_2Ni_2(PhCN_2S_2)$ are typical. It is interesting that the Ni-Ni distance in $Cp_2Ni_2(PhCN_2S_2)$ is shorter than that in $[Cp_2Ni_2S_2]_2Ni$, XXXVIII, which is described as possessing a full metal-metal single bond. The longer distance in the latter can be rationalised as follows. In $[Cp_2Ni_2S_2]_2Ni$, the sulphur atoms are bridging three nickel centres (each half of the molecule can be considered to be formally analogous to $Cp_3Ni_3S_2$[52] but with Ni(0) receiving only four electrons from S(1) and S(2), rather than five from a third Cp). Using the simple bonding scheme, previously applied to such species[59,60], each $Cp_2Ni_2S_2Ni$ fragment in XXXVIII contains only two metal-based bonding electrons which leads to a general increase in the Ni-Ni distance (average d(Ni-Ni) in $[Cp_2Ni_2S_2]_2Ni$=2.818Å; in $Cp_3Ni_3S_2$=2.801Å). The still shorter value for d(Ni(1)-Ni(2)) in $[Cp_2Ni_2S_2]_2Ni$ is presumably due to a further stabilisation (lowering of a Ni-Ni based MO) on the replacement of Cp by S_2.



[XXXVIII]

The Ni_2S_2 core in $Cp_2Ni_2(PhCN_2S_2)$ is based on the well-known butterfly array. The average angle between the Ni-Ni vector and the S-S vector is 90.1°, indicating C_{2v} symmetry.

The dithiadiazole ring structural data for some relevant species is given in Table 3.7:

Table 3.7 Structural Parameters (in Å and °) for some Dithiadiazole Systems

COMPOUND	S-S	S-N	C-N	N-C-N	C-N-S
$(PhCN_2S_2)_2$	2.09	1.63	1.33	121	115
$Fe_2(CO)_6PhCN_2S_2$	2.930(2)	1.705(5)	1.322(8)	127.8(5)	125.4(4)
$Cp_2Ni_2(PhCN_2S_2)$	2.905(2)	1.634(3)	1.334(4)	128.4(3)	124.8(2)

These show that although the angles in the nickel and iron complexes are very similar, the S-N and C-N distances of the nickel compound are shorter than those in the iron complex and, in fact, are identical (within experimental error) to those in the free ligand. The S--S distance in $Cp_2Ni_2(PhCN_2S_2)$ is indicative of non-bonding (or very weak bonding) between the sulphurs (Section 2.5.2). The lengthening of the S-N bond length in $Fe_2(CO)_6PhCN_2S_2$ was thought to arise from occupancy of a π^* SOMO (Singly Occupied Molecular Orbital) located primarily on nitrogen (leading to short N--N inter-ring distances). The shorter

S-N distance in the nickel complex suggests that an analogous scheme cannot be applied and this is borne out by the absence of any intermolecular contacts less than 4.1Å involving the dithiadiazole ring (or the nickel atoms). The odd electron in the nickel compound may well occupy an orbital which is antibonding with respect to S--S only. Again the Extended Hückel calculations should shed more light on this matter.

Finally, the carbon-carbon bond lengths in the fcur rings in the asymmetric unit are given in Table 3.8:

Table 3.8 Bond Lengths (in Å) in the Cp Rings

BOND	1	2	3	4
C_1-C_2	1.295(7)	1.401(5)	1.387(8)	1.391(6)
C_2-C_3	1.298(7)	1.375(5)	1.395(8)	1.372(6)
C_3-C_4	1.417(8)	1.423(6)	1.403(6)	1.424(6)
C_4-C_5	1.387(9)	1.414(6)	1.376)8	1.341(6)
C_5-C_1	1.290(8)	1.388(6)	1.345(7)	1.414(6)

These figures show that there is no evidence for distortion[61], due to extensive ring-metal π-bonding, to give an "allyl-ene" or diene type Cp ring. For example, in ring 1 the difference between the shortest and longest distances is 0.127(12)Å (the e.s.d. of the difference is the root-mean-square value for the individual e.s.d.s). Since the e.s.d. is ca. 10% of the actual values, such differences are not statistically significant.

3.8 CONCLUSION AND SUGGESTIONS FOR FURTHER WORK

The results discussed in this chapter indicate that $[CpV(PhCN_2S_2)]_2$, $[CpCo(PhCN_2S)]_2$ and $Cp_2Ni_2PhCN_2S_2$ can be isolated in fair yield (ca.40%). The reactions involving $[CpMo(CO)_3]_2$ and $[CpFe(CO)_2]_2$ gave complicated mixtures but chromatography may lead to the isolation of molecular species. The magnetic properties of the vanadium complex merit further investigation. The growth of single crystals may be aided by the use of substituted Cp groups (e.g. C_5Me_5 or C_5H_4Me). The preparation of the niobium and tantalum analogues should also prove interesting. Finally, the electrochemistry of the nickel complex, especially oxidation[66], should yield positive results, e.g. the preparation of $[Cp_2Ni_2PhCN_2S_2]^{2+}$.

3.9 EXPERIMENTAL

3.9.1 Reaction between $CpV(CO)_4$ and $(PhCN_2S_2)_2$

3.9.1(a) ^1H NMR Experiments

A solution of $CpV(CO)_4$ (22.4mg, 0.1mmol) and $(PhCN_2S_2)_2$ (17.7mg, 0.05mmol) was made up in d_8-toluene. The spectrum showed a singlet at 4.23ppm., assigned to $CpV(CO)_4$. All lines were broadened (f.w.h.h. 120Hz). The solution was then heated to 60°C for 3h but no change was observed in the spectrum. After heating to 100°C for 18h, a very weak signal was observed at 6.12ppm.

A similar solution exhibited this weak resonance after 5h photolysis at 350nm and after 20h a singlet at 6.10ppm. was almost as intense as that due to $CpV(CO)_4$ (1:1.2). The lines were also noticeably sharper (f.w.h.h. 40Hz).

A solution of $CpV(CO)_4$ (29.7mg, 0.13mmol), $(PhCN_2S_2)_2$ (23.5mg, 0.07mmol) and Me_3NO (38.9mg, 0.52mmol) (Section 7.6.14) was made up in d_6-benzene. No new signals were observed after the solution had been heated to 60°C for 6h.

3.9.1(b) Preparative Scale Experiment

A solution of CpV(CO)$_4$ (0.23g, 1mmol) and (PhCN$_2$S$_2$)$_2$ (0.18g, 0.5mmol) in toluene (30cm^3) was photolysed at 350nm for 18h. A black solid (0.03g) was filtered off, washed with toluene (2 x 2cm^3) and pumped dry. Analysis: V,19.2%; S,16.4%. The solvent was pumped off the filtrate and the black solid obtained (0.14g) recrystallised from a 1:1 toluene:petroleum ether mixture (30cm^3) to give [CpV(PhCN$_2$S$_2$)]$_2$, 0.12g, 39%. Found: C,47.6; H,3.5; N,8.5; S,20.7; V,16.5%. C$_{24}$H$_{20}$N$_4$S$_2$V$_2$ requires C,48.5; H,3.4; N,9.4; S,21.6, V,17.1% ν_{max} 3078w, 1314m*, 1295sh, 1280s, 1265sh, 1178w*, 1136m*, 1129sh, 1070w*, 1027m*, 1015m, 928w*, 885w*, 840w*, 825sh*, 818s, 809s*, 790m*, 784m*, 750w, 730w, 710s, 695sh, 680sh*, 667w, 527w, 460w cm^{-1}. Underlined bands are assigned to the η^5-Cp rings[62a] while those marked with an asterisk are due to the PhCN$_2$S$_2$ units.[63] The weak bands at 460, 695 and 730cm^{-1} are assigned to toluene.[64] m/z (E.I.) (M$^+$,3%), 529(M-Cp,I), 477(M-PhCN$_2$,2), 464(M-2Cp,1), 413(M-PhCN$_2$S$_2$,2), 392(Cp$_2$V$_2$S$_5$$^+$,44), 360(Cp$_2V_2S_4$$^+$,76), 342(Cp$_2V_2$S3N+,10), 328(Cp$_2V_2S_3$$^+$,60), 296(Cp$_2V_2S_2$$^+$,25), 264(Cp$_2V_2S^+$,10), 232(Cp$_2V_2$$^+$,11), 116(CpV$^+$,10), 103(PhCN$^+$,100), 77(Ph$^+$,9). The D.S.C. trace showed decomposition to begin at ~170°C (peak temperature 183°C). The reaction was initially monitored by solution phase i.r. spectrosocopy in the carbonyl region, which established 18h as the optimum reaction time. ν(CO)[62b] for CpV(CO)$_4$: 1920,2030cm^{-1}.

3.9.2 Reaction between [CpMo(CO)$_3$]$_2$ and (PhCN$_2$S$_2$)$_2$

3.9.2(a) ^{1}H NMR Experiments

A solution of [CpMo(CO)$_3$]$_2$ (35.4mg,0.07mmol) and (PhCN$_2$S$_2$)$_2$ (13.0mg, 0.036mmol) was prepared in d_8-toluene. The spectrum showed a singlet at 4.68ppm. assigned[65] to [CpMo(CO)$_3$]$_2$. The solution was heated to

60°C for 3h, but no change was observed. However, after 18h at 100°C new lines were observed at 4.33, 4.35, 4.37, $\underline{4.40}$, 4.74, 4.79, $\underline{4.94}$, $\underline{5.00}$, 5.02, 5.14, $\underline{5.53}$, 6.68 (2H,t,J(HH)=7.5Hz), 6.84 (1H,t, J(HH)=7.5Hz), $\underline{7.09}$, 7.13, 7.21ppm. These lines were very sharp and well resolved unlike the original spectrum (f.w.h.h. 90Hz). All were very weak; the more intense lines are underlined. The signal at 4.74ppm. is assigned[65] to $[CpMo(CO)_2]_2$. A similar solution was photolysed at 350nm for 26h but no change was observed, although a little black solid was precipitated.

A solution of $[CpMo(CO)_3]_2$ (20.4mg, 0.04mmol) and $(PhCN_2S_2)_2$ (15.0mg, 0.04mmol) was also made up in d_8-toluene. However, after 8h at 100°C much solid was precipitated and good spectra could not be obtained.

3.9.2(b) Preparative Scale Experiments

Thermolysis: A mixture of $[CpMo(CO)_3]_2$ (0.245g,0.5mmol) and $(PhCN_2S_2)_2$ (0.18g,0.5mmol) dissolved in toluene ($30cm^3$) was heated to 85°C for 14h. A black solid was then filtered off, washed with toluene (2 x $2cm^3$) and pumped dry. Yield, 0.16g. Analysis: C,38.4; H,2.8; N,5.9; Mo,27.9; S,18.8%. νmax 3060w, 2205vs, 1425sh, 1170vw, 1118vw, 1064w, 1020w, 970vw, 920vw, 838sh, 823s, 770w, 734m, 697m, 468w cm^{-1}. The last three bands are assigned to absorbed toluene[64]. m\z (C.I.(+),i-C_4H_{10}) 418($Cp_2Mo_2S_3^+$,1%), 206(2), 178(7), 160(MoS_2^+,3), 150(15), 143(28), 122(18), 121(73), 108(6), 104(64), 103($PhCN^+$,100), 65(Cp^+,30), 64(S_2^+,17). $\delta_H(C_7D_8)$ 4.32, 4.36, 4.73, 4.79, $\underline{4.85}$, 4.94, 4.96, $\underline{5.00}$, 5.02, $\underline{5.23}$, 5.42, 5.43, $\underline{5.50}$, 5.53, $\underline{6.66}$ (2H,t,J(HH)=7.5Hz), 6.82(1H,t,J(HH)=7.5Hz), 7.20, 7.33, 7.97 (2,H,t,br), 8.51 (2H,d,J(HH)=7.5Hz),8.66(m)ppm. The D.S.C. showed decomposition to begin at ~190°C (peak temperature 214°C). The filtrate was pumped dry to give a black solid, 0.05g, νmax 2220m, 1960m, 1898m (CO), 1178m, 1139vw, 1120vw, 1072vw, 1027m, 920vw, 896vw, 877vw, 835sh, 829s, 820sh, 806s, 780s, 770s, 728m, 703sh, 692s, 655s, 510m cm^{-1}. All bands below $1180cm^{-1}$ are assigned[63] to $(PhCN_2S_2)_2$, apart from that at $819cm^{-1}$. The reaction was monitored by solution phase i.r. spectroscopy. After 4h bands were present at 1912, 1959, $2020cm^{-1}$; after 12h only the high frequency band remained. The bands at 1912 and $1959cm^{-1}$ are due to $[CpMo(CO)_3]_2$.[62c]

Photolysis: A solution of $[CpMo(CO)_3]_2$ (0.12g,0.25mmol) and $(PhCN_2S_2)_2$ (0.09g,0.25mmol) in toluene ($10cm^3$) was photolysed at 350nm for 28h. This reaction was also monitored by solution phase i.r. spectroscopy which established 28h as the optimum reaction time (bands due to $[CpMo(CO)_3]_2$ had completely disappeared; no new bands appeared). The mixture was then filtered to give a black solid which was washed with toluene (2 x $2cm^3$) and pumped dry. Yield 0.04g. ν max 3060w, 2215m, 2070m, 2025s, 1960s, 1920sh, 1825sh, 1685w, 1620sh, 1600w, 1585sh, 1510sh, 1490m, 1427m, 1350m, 1290w, 1208w, 1172w, 1110m, 1070m, 1028m, 1014m, 960w, 923m, 838sh, 825vs, 805sh, 782w, 733m, 712s, 698s, 670m, 608w, 535w, 480w, 470w cm^{-1}. This material was too involatile for a mass spectrum to be recorded. The filtrate was pumped dry to give a black solid, 0.07g, ν max 3060w, 2210m, 2030m, 1950vs, 1920s, 1890vs, 1675w,bd, 1490m, 1420sh, 1355m, 1288w, 1238w, 1208w, 1177m, 1160w, 1140m, 1120w, 1070m, 1026m, 1018sh, 923m, 898w, 838s, 825s, 806s, 780s, 770s, 729m, 710m, 690s, 654m, 589m, 550s, 510s, 465m cm^{-1}. See above for assignments.

A solution of $[CpMo(CO)_3]_2$ (0.245g,0.5mmol) and $(PhCN_2S_2)_2$ (0.09g,0.25mmol) in toluene ($20cm^3$) was photolysed at 350nm for 28h. Solution phase i.r. spectroscopy of the reaction mixture showed no carbonyl containing species to be present in solution. Filtration of the resulting mixture gave a black solid, 0.05g. Analysis: C,37.2;

H,2.6; N,5.4; Mo,30.2; S,12.5%. ν max 3060w, 2205w, 2020sh, 1958s, 1912s, 1818m, 1675w, 1640sh, 1600sh, 1565m, 1365sh, 1350m, 1170w, 1110w, 1063vw, 1012m, 923w, 835sh, 825m, 788sh, 770sh, 630m, 610m, 594m cm^{-1}. m\z (C.I.(+)i-C_4H_{10}) 336(1%), 226(1), 236(1), 221(1), 213(1), 195(3), 178(9), 170(10), 163(1), 162(1), 152(1), 150(1), 146(2), 139(2), 138(25), 137(3), 130(2), 122(33), 121(100), 89(1), 77(9), 76(3), 65(1). The filtrate was pumped dry to give a black solid, 0.3g. ν max 3060w, 2210w, 2010m, 1948vs, 1920s, 1875vs, 1830sh, 1650m,bd, 1540m, 1420sh, 1170w, 1060w, 1012s, 910s, 900s, 836s, 820sh, 810vs, 780sh, 723m, 690m, 582m, 548m, 500w, 462m cm^{-1}. This was extracted with dichloromethane (5 x $10cm^3$) to give a dark solution from which a shiny black solid was recovered after the solvent had been pumped off. This was washed with petroleum ether (5 x $2cm^3$) and dried in vacuo. Yield 0.05g, ν max 3060w, 2210m, 2025m, 1960m, 1910m, 1825bd, 1680m, 1635sh, 1604sh, 1575m, 1430sh, 1355m, 1170w, 1110m, 1068w, 1018m, 923w, 835sh, 819s, 789m, 730m, 710m, 690s, 460m cm^{-1}. $\delta_H(CD_2Cl_2)$ 5.32, 5.33, 5.34, 5.56, 6.05, 6.08, 6.10, 7.37(m), 7.53(m), 7.86(d,J(HH)=8.9Hz), 8.00(m)ppm. The material was too involatile for a mass spectrum to be recorded. The residue from the dichloromethane extraction showed very few i.r. bands - 1170vw, 1022vw, 1000vw, 837vw, 818vw, 791m, 699w, 616vw cm^{-1} and was discarded.

3.9 .3 Attempted Reaction between $CpMn(CO)_3$ and $(PhCN_2S_2)_2$

A solution of $CpMn(CO)_3$ (20.5mg,0.10mmol) and $(PhCN_2S_2)_2$ (18.1mg, 0.10mmol) was made up in d_8-toluene. The proton n.m.r. spectrum exhibited a singlet in the Cp region at 3.92ppm. assigned to $CpMn(CO)_3$. No change was observed after the tube had been heated to 100°C for 18h.

A similar solution was photolysed at 350nm for 20h, but again, no change was observed.

A solution of $CpMn(CO)_3$ (15.3mg,0.08mmol), $(PhCN_2S_2)_2$ (13.5mg, 0.04mmol) and Me_3NO (22.3mg,0.30mmol) was prepared in d_6-benzene. However, after 6h at 60°C no change was observed in the spectrum.

3.9.4 Reaction between $[CpFe(CO)_2]_2$ and $(PhCN_2S_2)_2$

3.9.4(a) ^1H N.M.R. Experiments

A solution of $[CpFe(CO)_2]_2$ (22.0mg,0.06mmol) and $(PhCN_2S_2)_2$ (18.7mg, 0.05mmol) was prepared in d_8-toluene. The spectrum showed one resonance in the Cp region at 4.22ppm. and this was assigned to $[CpFe(CO)_2]_2$. After 3h at 60°C, two new signals were observed at 4.43 and 4.48ppm. (1:1) and after 6h a third new signal was observed at 4.33ppm. (4:4:1). After 12h these signals were still present with those at 4.43 and 4.48ppm. being as intense as that due to $[CpFe(CO)_2]_2$. After 24h, the peak at 4.22ppm. had almost disappeared and the resonances remaining were at 4.48, 4.43 and 4.33ppm. (4:4:1).

A solution of $[CpFe(CO)_2]_2$ (30.5mg,0.09mmol) and $(PhCN_2S_2)_2$ (15.5mg, 0.043mmol) was also made up in d_6-benzene solution. Unfortunately, after heating to 60°C for 4h, much solid was precipitated and n.m.r. spectra could not be obtained.

A solution of $[CpFe(CO)_2]_2$ (32.5mg,0.09mmol) and $(PhCN_2S_2)_2$ (16.5mg, 0.046mmol) was prepared in d_6-benzene, and photolysed for 3h at 350nm. One new signal was observed at 4.43ppm. After 26h, another new signal had appeared at 4.37ppm. The ratio of peak integrations was 5(4.43):1(4.36):2(4.22).

3. 9 .4(b) Preparative Scale Experiments

A mixture of $[CpFe(CO)_2]_2$ (0.36g,1.0mmol) and $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) dissolved in toluene ($30cm^3$) was stirred at 80°C for 4h. A black solid was then filtered off, washed with toluene (2 x $3cm^3$) and pumped dry. Yield 0.05g. Analysis: C,36.7; H,2.9; N,5.1; Fe,20.0; S,13.2%. ν max 2030m, 1974s, 1940sh, 1510w, 1348m, 1117w, 1025w, 924w, 830w,bd, 782w, 730m, 710m, 696s cm^{-1}. The solvent was pumped off the filtrate to give a black solid. Yield 0.1g. νmax 2038s, 1975s, 1945sh, 1772w, 1358w, 930vw, 820m,bd, 732w, 716w, 700w, 650w, 620w, 572m, 555w cm^{-1}. This solid was dissolved in dichloromethane ($10cm^3$) and sent down an alumina chromatography column. A black stationary band was obtained and an orange eluate: νmax 2038s, $\underline{1990sh}$, 1982s, $\underline{1955m}$, $\underline{1772m}$ cm^{-1}. Underlined bands are due[62d] to $[CpFe(CO)_2]_2$.

A mixture of $[CpFe(CO)_2]_2$ (0.18g,0.05mmol) and $(PhCN_2S_2)_2$ (0.18g, 0.05mmol) in toluene ($25cm^3$) was heated to 80°C for 4h, when a black solid was filtered off, washed with toluene (2 x $3cm^3$) and pumped dry. Yield 0.1g. Analysis: C,50.0; H,3.6; N,7.1; Fe,16.3%. ν max 2030m, 1970sh, 1950s, 1350m, 1112w, 925w, 820w, 780w, 729m, 710sh, 696s cm^{-1}. The filtrate was pumped to dryness to give a brown solid. Yield 0.08g, νmax 2030s, 1970s, 1942sh, $\underline{928w}$, 820sh, $\underline{780s}$, $\underline{770sh}$, 728w, 708sh, $\underline{692s}$, $\underline{657m}$, 610m, 570m, 546m, $\underline{509m}$ cm^{-1}. Underlined bands are assigned[63] to $(PhCN_2S_2)_2$. This solid was dissolved in toluene and poured onto an alumina column. Elution with dichloromethane gave two bands; firstly a green component:νmax 2040s, 1988s cm^{-1} and then an orange component:νmax 2040s, 1988s, 1965sh cm^{-1}.

A solution of $[CpFe(CO)_2]_2$ (0.35g,1mmol) and $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) in toluene ($25cm^3$) was photolysed at 350nm. After 28h, carbonyl bands were observed in the i.r. at 2030s, $\underline{1996s}$, 1982s, 1950s, $\underline{1784s}$. Underlined bands are due to $[CpFe(CO)_2]_2$. After 44h photolysis the bands due to starting material had disappeared and the remaining bands had decreased in intensity with respect to the solvent bands. A black solid was filtered off, washed with toluene (4 x 2cm^3) and pumped dry. Yield 0.21g. Analysis: Fe,15.6; S,9.5%. ν max 2030s, 1980s,bd, 1955sh, 1800w,bd, 1640w, 1525w, 1352m, 1118m, 1070w, 1028w, 924w, 838m, 820sh, 780w, 730m, 709m, 692s, 668w, 610w, 570w, 550w, 469w cm^{-1}. This product was washed with toluene in a dog (Figure 7.2) until the washings were colourless but, although the shoulder at 1955cm^{-1} was reduced in intensity, no overall change was observed in the i.r.

3.9.5 Reaction of $CpCo(CO)_2$ with $(PhCN_2S_2)_2$

An attempt was made to make up a solution of $CpCo(CO)_2$ (94.6mg, 0.53mmol) and $(PhCN_2S_2)_2$ (95.0mg,0.26mmol) in d_8-toluene. However, as soon as the $(PhCN_2S_2)_2$ was added to the carbonyl solution, a black solid was precipitated. Consequently, n.m.r. spectra could not be obtained.

A solution of $(PhCN_2S_2)_2$ (0.13g,0.36mmol) was added dropwise to a stirred solution of $CpCo(CO)_2$ (0.13g,0.72mmol), both in toluene (10cm^3) at 21°C. After 2h a solid was observed to have precipitated but starting material remained in solution[62e], νmax 2035s, 1962s. No change, apart from reduction in band intensity, was observed after 5h, but after 21h, both carbonyl bands had disappeared.

A solution of $(PhCN_2S_2)_2$ (0.3g,0.83mmol) was added dropwise to a stirred solution of $CpCo(CO)_2$ (0.61g,3.4mmol), both in toluene (10cm^3) at 21°C. The mixture was stirred for 24h, νmax 2035s, 1963s, before being filtered to give a black solid, which was washed with toluene (4 x 2cm^3) and pumped dry. Yield 0.27g. νmax 2210w, 1600w, 1498w, 1462m, 1412w, 1362w, 1329m, 1292w, 1263w, 1171m, 1150m, 1114w, 1083vw, 1071w, 1058vw, 1020m, 1014w, 1003sh, 920w, 855sh, 839m, 820s, 778w, 738s, 700s, 682s, 658w, 587m, 470w, 444s cm^{-1}. This was recrystallised from a 2:1 mixture of dichloromethane-petroleum ether ($30cm^3$) to give black CpCo($PhCN_2S$), 0.14g, 31%. Found: C,48.9; H,3.1; N,6.2; Co,21.8; S,10.2%. $C_{12}H_{10}N_2CoS$ requires C,52.8; H,3.7; N,10.2; Co,21.6, S,11.7%. ν max 3060w, 2200vw, 1412w, 1362m, 1333m, 1322m, 1290w, 1171m, 1150m, 1070m, 1053vw, 1028m, 1012m, 997sh, 887w, 850w, 838m, 817sh, 806s, 774w, 732vs, 692vs, 677m, 583m, 442m cm^{-1}. m/z (E.I.) 548(M^+,11%), 436(6,$Cp_3S_2^+$), 399(5,M-$PhCN_2S^+$), 274(100,$CpCoPhCN_2S^+$), 189(7,Cp_2Co^+), 171(4,$CpCoNS^+$), 124(3,$CpCo^+$), 103(12,$PhCN^+$), 77(5,Ph^+). The D.S.C. trace showed decomposition to begin at 190°C (peak temperature 212°C). The original filtrate was pumped to dryness to give a black solid which was recrystallised from a 1:1 toluene-petroleum ether mixture ($25cm^3$). Yield 0.11g, ν max 3060w, 2200vw, 1610m, 1490w, 1412w, 1360m, 1325s, 1170m, 1148m, 1112w, 1069vw, 1024w, 920w, 832m, 810s, 772w, 732s, 692s, 677m, 584w, 422m cm^{-1}.

3.9.6 Reaction of $[CpNi(CO)]_2$ with $(PhCN_2S_2)_2$

An attempt was made to prepare a d_8-toluene solution of $[CpNi(CO)]_2$ (27.0mg,0.09mmol) and $(PhCN_2S_2)_2$ (16.0mg,0.044mmol). However, as soon as the solvent was added, a black solid was precipitated and no n.m.r. signals could be observed.

A solution of $[CpNi(CO)]_2$ (0.3g,1mmol) and $(PhCN_2S_2)_2$ (0.18g,0.5mmol) in toluene ($25cm^3$) was stirred for 14h at 21°C. Solution phase i.r. spectroscopy showed that no carbonyl species remained in solution after this time: ν(CO) for $[CpNi(CO)]_2$[62f] at 1845 and 1885cm^{-1}. The mixture was then filtered to give a black solid which was washed with toluene (3 x $2cm^3$) and pumped dry. Yield 0.15g. Analysis: Ni,17.3; S,9.1%. νmax 1630m, 1340w, 1322w, 1271w, 1028w, 790m.bd, 730m, 695m, 668w cm^{-1}. The dark red filtrate was pumped dry to give a black solid. Yield 0.27g. νmax 1730w, 1625w, 1598w, 1410w, 1343w, 1326s, 1172s, 1158m, 1109vw, $\underline{\text{1070vw}}$, 1048w, $\underline{\text{1030m}}$, 1112m, 998w, $\underline{\text{927w}}$, $\underline{\text{894w}}$, $\underline{\text{830w}}$, 810s, 794s, 775m, 732s, 702s, 695sh, 672s, $\underline{\text{654m}}$, 610w, $\underline{\text{510w}}$, 467w, 439m cm^{-1}. Underlined bands are due to $(PhCN_2S_2)_2$. This solid was recrystallised from 1:1 toluene-petroleum ether ($25cm^3$) to give very dark red-black crystals of $(CpNi)_2PhCN_2S_2$, 0.18g, 42%. Found: C,48.3; H,3.5; N,6.8; Ni,27.4; S,8.3 (Repeat 10.5%). $C_{17}H_{15}N_2Ni_2S_2$ requires C,47.6; H,3.5; N,6.5; Ni,27.4; S,15.0%. νmax 1410w, 1342m, 1338s, 1180sh, 1172m, 1138w, 1070w, 1050w, 1030m, 1010m, 1000vw, 840w, 816s, 803sh, 795s, 775w, 762w, 731s, 705sh, 698s, 672s, 432m cm^{-1}. m/z (C.I.+) 427(M^+,11%), 195(2), 189(Cp_2Ni^+,3), 121(100). (E.I.) 427(M^+,2%), 278($M-PhCN_2S$,3), 194(4), 189(Cp_2Ni^+,15), 186(6), 149($PhCN_2S^+$,9), 130(Cp_2^+,100), 121(14), 103($PhCN^+$,66), 89(PhC^+,7), 77(Ph^+,12), 76(S_2N^+,20), 65(Cp^+,35), 64(S_2^+,23). The D.S.C. trace showed decomposition to begin at ~140°C (peak temperature 196°C with a shoulder at 184°C).

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CHAPTER 4

REACTIONS OF PHENYL DITHIADIAZOLE WITH SOME TRANSITION METAL HALOGENO- AND PHOSPHINE COMPOUNDS

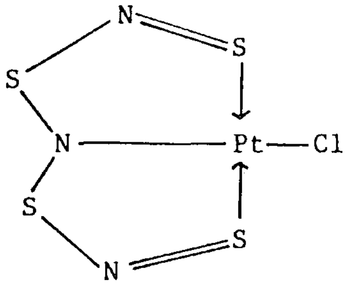
4.1 GENERAL INTRODUCTION

This chapter is divided into three sections. Section 4.2 describes the reactivity of a series of transition-metal dihalides toward $(PhCN_2S_2)_2$. In Section 4.3 an account of the reactivity of $(PhCN_2S_2)_2$ toward $TiCl_4$, Cp_2TiCl_2 and $NiCl_2$ in the presence of magnesium metal is given together with a discussion of the reactions with $MoCl_4(CH_3CN)_2$ and CuCl. Finally, in Section 4.4, the reactions of $(PhCN_2S_2)_2$ with the phosphine complexes $(Ph_3P)_4M$ (M=Pt,Pd) and $(Ph_3P)_3RhCl$ (with and without magnesium) are presented.

4.2 REACTIVITY OF $(PhCN_2S_2)_2$ TOWARDS SOME TRANSITION METAL DIHALIDES

4.2.1 Introduction

The reactions of S_4N_4 with transition metal dihalides are many and varied. The halides, MCl_2 (M=Co,Ni,Pd,Pt), form complexes containing $S_2N_2H^-$ and S_3N^- as ligands[1a] whereas $CuCl_2.2H_2O$ gives a mixture of products (originally formulated[1b] as $Cu(SN)_2Cl_2$) but now known to include $CuCl.S_4N_4$ (IX)[2], $CuCl_2.S_4N_4$[3a] and, in acetonitrile, $[Cu(CH_3CN)Cl_2]_2S_2N_2$.[3b] The copper complexes are polymeric and feature metal to nitrogen coordination, whereas the other metal complexes are mononuclear, square planar species. Also, $PtCl_2(PhCN)_2$ has been found[4] to react with S_4N_4 to give I:



[I]

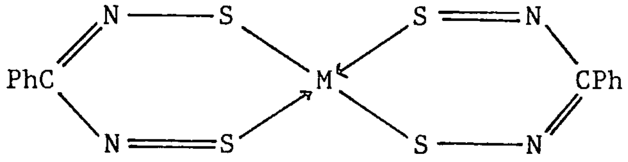
In the present work it was thought that $(PhCN_2S_2)_2$ may form sulphur or nitrogen-coordinated complexes but that oxidation of the dithiadiazole ring may be an alternative pathway for reaction.

The dehalogenating action of $(PhCN_2S_2)_2$ is now well established[5] (see also Sections 6.2.4 and 6.2.5) and it was of interest to see if such a strategy could be applied to transition metal systems. Two possible reaction schemes are given below:

$$2(PhCN_2S_2)_2 + MCl_2 \longrightarrow (PhCN_2S_2)_2M + 2[PhCN_2S_2]Cl \qquad (1)$$

$$(PhCN_2S_2)_2 + 2MCl_2 \longrightarrow [PhCN_2S_2]_2MCl_4 + M \qquad (2)$$

In reaction (1) M(II) oxidises one equivalent of $(PhCN_2S_2)_2$; the second equivalent may then stabilise M(0) in the form of a π-complex or a redox reaction may occur with the formation of II:



[II]

Such a species could be thought of as analogous to 1,1-dithiolato-complexes.[6] The formation of II is probably more likely than the formation of a π-complex since none of the metals under discussion require 14 electrons (see ref.7. for a theoretical study of S_2N_2 sandwich compounds).

Reaction (2) is less likely to occur than reaction (1) since it implies $(PhCN_2S_2)_2$ to be a better reducing agent than a metal, which, in general, will not be the case, although it may occur for copper (the steady increase in effective atomic number across the transition series tends to lower the stability of higher oxidation states and hence the reducing power of the metal).

$(PhCN_2S_2)_2$ was reacted with the following compounds in thf: MCl_2 (M=Cr,Mn,Co,Ni,Pd) and $FeBr_2$; and with $CuCl_2$ in acetonitrile.

4.2.2. Results and Discussion

$(PhCN_2S_2)_2$ failed to react with MCl_2 (M=Cr,Mn,Co,Ni) and $FeBr_2$ in refluxing thf (Section 4.6.1). This behaviour is probably connected with the inability of the halides to oxidise $(PhCN_2S_2)_2$. Certainly, M(II) (M=Cr,Fe,Co) are usually regarded as reducing agents, being readily oxidised to the M(III) oxidation state, although this effect is heavily dependent upon the ligand for cobalt (II).[8] Also, the above halides are not very soluble in thf[9], although all, apart from $NiCl_2$, form adducts. ($MnCl_2(thf)_2$ has been reported[10] to be soluble in thf but only very limited solubility was observed in this work). A further factor regarding the formation of adducts may be that $(PhCN_2S_2)_2$ is unable to compete for any vacant coordination positions that arise on the metal in the presence of a vast excess of thf.

N.B. The isolation of a purple material from the reaction with $CrCl_2$ indicates a substantial amount of chromium (III) to have been present ($CrCl_2(thf)_2$ is pale green; $CrCl_3(thf)_3$ is violet).[9] The chromium (III) adduct is insoluble in thf and, anyway, is kinetically inert toward substitution (as are all Cr(III) complexes).[8]

The reactions with $CuCl_2$ and $PdCl_2$ both proceeded differently.

Addition of an acetonitrile solution of $(PhCN_2S_2)_2$ to a solution of $CuCl_2$ in acetonitrile caused the immediate precipitation of an orange-yellow solid, assumed to be $[PhCN_2S_2]Cl$, in an orange solution. Further addition of $(PhCN_2S_2)_2$ caused the solution to darken and after 24h a dark red solid was filtered off from a yellow-brown solution, which was pumped dry to give a black solid. The i.r. spectra for these solids were very similar and show some resemblance to that of a dithiadiazolium salt, although additional bands were also present, some of which were dithiadiazole-like bands (Section 4.6.1(f)). This evidence, together with the analytical data suggest a redox reaction of the type shown as (3) to have occurred:

$$(PhCN_2S_2)_2 + CuCl_2 \longrightarrow [PhCN_2S_2]_2CuCl_2 \qquad (3)$$

The cation $[PhCN_2S_2]_2^+$ has previously been prepared as the chloride salt (Section 4.6.1(f) and is probably formed in this work due to the low reactivity of CuCl, obtained in situ according to:

$$(PhCN_2S_2)_2 + 2CuCl_2 \longrightarrow 2[PhCN_2S_2]Cl + 2CuCl \qquad (4)$$

A mixture of $(PhCN_2S_2)_2$ and $PdCl_2$ was stirred in thf for 14h to give an orange solid which was filtered off from an orange-red solution. The i.r. spectrum of this solid was very similar to that obtained[43] for $[PhCN_2S_2]Cl$. This evidence together with the analytical data (Found: Pd,19.5; Cl,22.2%; $[PhCN_2S_2]_2PdCl_4$ requires Pd,17.4; Cl,23.2%) suggest the following to have occurred:

$$(PhCN_2S_2)_2 + 2PdCl_2 \longrightarrow [PhCN_2S_2]_2PdCl_4 + Pd$$

The palladium metal was not observed but was presumably responsible for the high Pd and low Cl analyses obtained for the product.

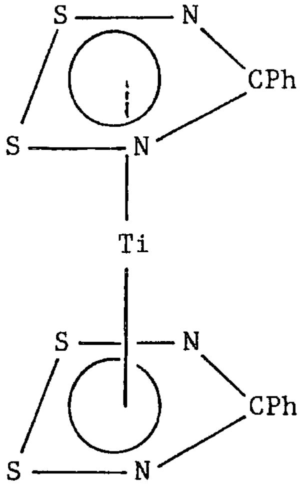
4.2.3 Conclusion

Reactions of MCl_2 (M=Cr,Mn,Co,Ni) and $FeBr_2$ with $(PhCN_2S_2)_2$ did not occur most probably due to the inability of $(PhCN_2S_2)_2$ to reduce these systems (a thermodynamic effect), the low solubility of MCl_2 in thf or, for adduct formation, the presence of an oxygen donor ligand in vast excess (thf) (kinetic effects). It may be worthwhile preparing soluble species such as $MCl_3(thf)_3$ (M=Cr,Fe)[9,11] and trying to react these with $(PhCN_2S_2)_2$ in a non-donor solvent in the presence[4] of magnesium. The reaction with $CuCl_2$ is interesting and it is probably worth trying to grow a single crystal of the product. The palladium reaction product may be interesting structurally as both the cation and anion are planar and may form stacks. Partial oxidation or reduction (e.g. by doping) may lead to a conducting solid[12], although a ligand capable of back-bonding is usually necessary.

4.3 REACTIVITY OF $(PhCN_2S_2)_2$ TOWARD SOME TRANSITION METAL HALOGENO-SPECIES

4.3.1 Reaction of $(PhCN_2S_2)_2$ with $TiCl_4$ in the Presence of Magnesium

The reaction between S_4N_4 and $TiCl_4$ to give a 1:1 adduct was first reported[13] ca. 80 years ago. I.r. spectra were later obtained[14] on a product obtained in refluxing carbon tetrachloride but more recent work led to the isolation[15] of a yellow compound, from dichloromethane at r.t., with an entirely different i.r. spectrum. The situation was resolved when two isomers (yellow and brown) were separated[16] and their structures determined. In the yellow isomer two $TiCl_4$ groups are bridged by two S_4N_4 rings which coordinate to each titanium through nitrogen. The brown isomer contains two μ-Cl bridges and monodentate S_4N_4 rings on each titanium. The yellow isomer has been decomposed[17] to give $S_2N_2.TiCl_4$ and S_4N_4. The experiment reported here was carried out to try and prepare the 18 electron sandwich compound shown below:

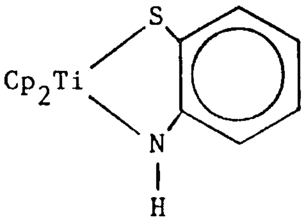


[III]

However, the available evidence indicates that III was not formed and, in fact, it seems unlikely that any significant amount of dithiadiazole complex was formed. The i.r. spectra of the solid materials recovered from this reaction showed $(PhCN_2S_2)_2$ still to be present in high concentration in the soluble components. The isolation of an insoluble red-brown solid, showing only coordinated thf in the i.r., suggested that reduction to $TiCl_2(thf)_2$ had occurred[18], and that this had reacted to some extent with $(PhCN_2S_2)_2$ to give an insoluble polymeric product. The mass spectrum of the isolated solid showed only $PhCN_2S_2$ and thf peaks and the analyses indicated a mixture (S:N 1:1,Ti:Cl 2:5).

4.3.2 Reaction of $(PhCN_2S_2)_2$ with Cp_2TiCl_2 in the Presence of Magnesium

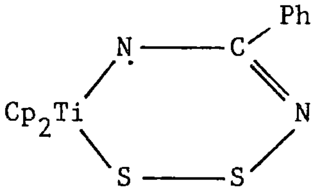
Metallocene dichlorides of titanium (IV), $Cp^1_2TiCl_2$ (Cp^1=C_5H_5,C_5H_4Me) have been found to react[19] with the dilithium salt of 2-$NH_2C_6H_4SH$ to give IV:



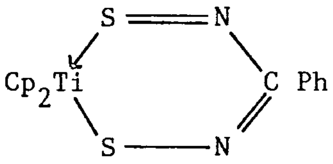
[IV]

Reaction of Cp_2TiCl_2 with KNSO in acetonitrile gave $Cp_2Ti(NSO)_2$ in 80% yield[20] and this reacted with $LiN(SiMe_3)_2$ to give $Cp_2Ti(NSNSiMe_3)_2$ in 65% yield. With $K[NSN^tBu]$, Cp_2TiCl_2 yielded[21] $Cp_2TiCl(NSN^tBu)$ or $Cp_2Ti(NSN^tBu)_2$ depending on the stoichiometry of the starting materials. Hydrolysis of the latter complex on silica gave $Cp_2Ti(NSO)_2$. The compounds $Cp_2{}^1TiCl(NSN^tBu)$, $Cp_2{}^*Ti(NSN^tBu)_2$ and $Cp_2{}^1Ti(NSO)_2$ ($Cp^1=C_5H_4Me$; $Cp^*=C_5Me_5$) were also characterised.

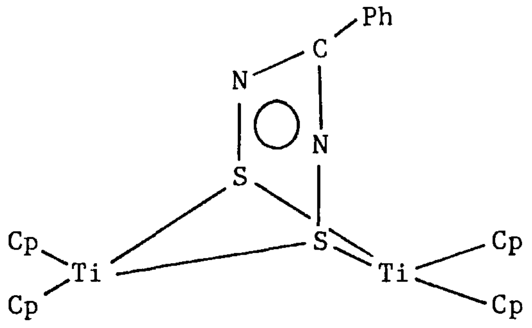
In the present work it was hoped to prepare radical complexes, such as V, VI or VII.



[V]



[VI]



[VII]

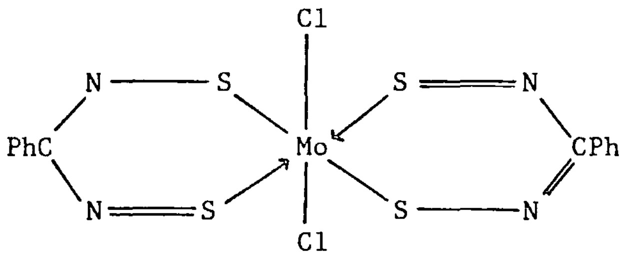
Magnesium has been used[22] previously to dechlorinate Cp_2TiCl_2 in the presence of neutral ligands, which form titanium (II) and (IV) complexes. However, the results obtained from the reaction described in this work (Section 4.6.3) indicate that a mixture of products is obtained. The mass and i.r. spectra both show coordinated thf and acetonitrile to be present and the mass spectrum of the material soluble in acetonitrile also showed a peak due to the $PhCN_2S_2$ fragment. The analytical data are too low in carbon and hydrogen for any of the compounds V - VII (C:H:N 9:10:2) and, anyway, significant amounts of chlorine and magnesium are present (Ti:Cl:Mg ≈1:5:4). In summary, a complicated mixture is obtained and further work seems unwarranted. (N.B. $(PhCN_2S_2)_2$ did not react with Cp_2TiCl_2 in the absence of magnesium).

4.3.3. Attempted Reaction of $(PhCN_2S_2)_2$ with $NiCl_2$ in the Presence of Magnesium

The lack of reactivity of $NiCl_2$ toward $(PhCN_2S_2)_2$ has been discussed in Section 4.2.2. The aim of the present work was to prepare the nickel derivative of II by reduction with magnesium in thf. However, no reaction occurred, possibly due to the low solubility of $NiCl_2$ in thf.

4.3.4 Reaction of $(PhCN_2S_2)_2$ with $MoCl_4(CH_3CN)_2$

The lability of the MeCN groups in the above complex has been employed[23] to prepare a wide variety of molybdenum (IV) complexes of general formula $MoCl_2L_2$ (L is a uninegative bidentate ligand). Therefore, one possibility for the reaction under discussion here would be the formation of VIII and $[PhCN_2S_2]Cl$.



[VIII]

Alternatively, a simple redox reaction could occur:

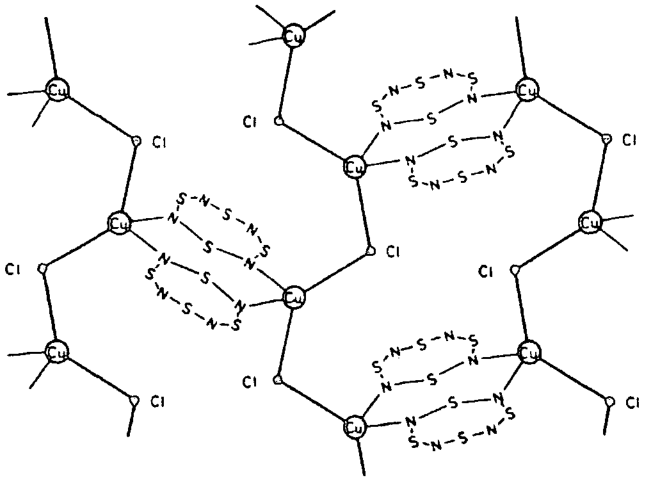
$$(PhCN_2S_2)_2 + 2MoCl_4(MeCN)_2 \longrightarrow [PhCN_2S_2]_2MoCl_6 + MoCl_2$$

However, in this work, the green colour of the solution obtained and the strong i.r. band at 970cm^{-1} suggest that a molybdenum (V) oxo-species has been prepared, most probably $[PhCN_2S_2]_2MoOCl_5$. The source of the oxygen was most probably gas dissolved in the solvent. The isolated solid is obviously a mixture. (Found: Cl,23.7; Mo,11.5%; $[PhCN_2S_2]_2MoOCl_5$ requires Cl,27.2; Mo,14.7%). The yellow precipitate at the start of the reaction may have been $[PhCN_2S_2]Cl$ but was more likely[24] $MoCl_4(thf)_2$.

4.3.5 Reaction of $(PhCN_2S_2)_2$ with CuCl

Halogeno- complexes of copper (I), containing neutral ligands, adopt a wide range of structural types[25,26], in which copper usually assumes either trigonal planar or tetrahedral coordination. Although copper (I) has been classified as a 'soft' acid[26a], and sulphur ligands occur more frequently than oxygen ligands[26b], in sulphur-nitrogen chemistry only nitrogen-bonded complexes have been isolated.

The structure of $CuCl.S_4N_4$, prepared from $CuCl_2.H_2O$ and S_4N_4 in benzene-ethanol (the latter acting as a reducing agent), has been determined[2a] and is shown as IX:

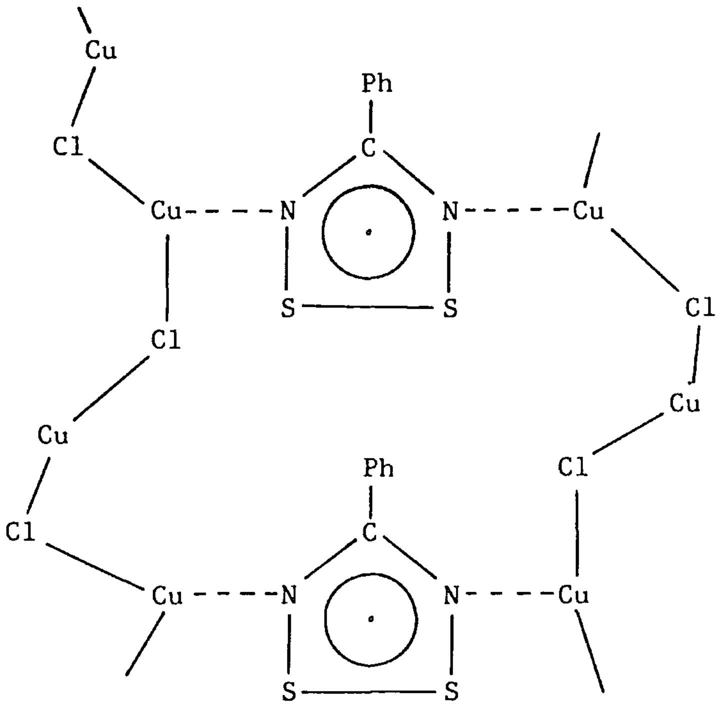


[IX]

The analogous bromine compound has also been prepared[2b] from $Cu(NO_3)_2$ $3H_2O$, NH_4Br and S_4N_4 in methanol. It is isostructural with IX.

The acetonitrile complex of copper (I) chloride was found to react with $(PhCN_2S_2)_2$ in dichloromethane to give a black, insoluble, presumably polymeric material with the empirical formula $PhCN_2S_2(CuCl)_2$. It is important to note that this reaction does not occur in acetonitrile (in which $(PhCN_2S_2)_2$ is only sparingly soluble) or dichloromethane (in which CuCl is insoluble) to any measurable extent. The initial treatment with acetonitrile is necessary which renders polymeric CuCl soluble in dichloromethane by forming a complex, $[Cu(MeCN)_4]Cl$[26a].

The infrared and mass spectra indicated the dithiadiazole ring to be intact and relatively unperturbed and it is suggested that the structure of $PhCN_2S_2(CuCl)_2$ is based upon that of $CuCl.S_4N_4$, in which S_4N_4 adopts a conformation very similar to that in the free state. This structure is shown below:



[X]

4.4. REACTION OF $(PhCN_2S_2)_2$ WITH SOME PHOSPHINE COMPLEXES

4.4.1 Reaction of $(PhCN_2S_2)_2$ with $(Ph_3P)_4Pt$

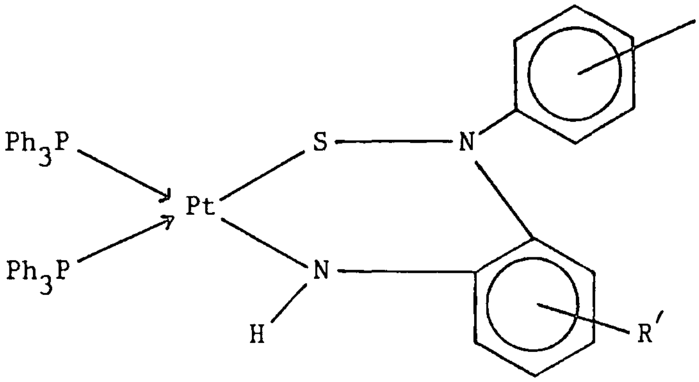
4.4.1.1 Introduction

The chemistry[27] of $(Ph_3P)_4Pt$ is dominated by loss of triphenylphosphine and facile oxidation to platinum (II) species. The following equilibria are thought[27] to occur in solution.

$$(Ph_3P)_4Pt \longrightarrow (Ph_3P)_3Pt + Ph_3P$$
$$(Ph_3P)_3Pt \longrightarrow \text{"}(Ph_3P)_2Pt\text{"} + Ph_3P$$

Although $(Ph_3P)_3Pt$ has been isolated, attempts to prepare $(Ph_3P)_2Pt$ only resulted in the formation of a dimer, $[(Ph_3P)_2Pt]_2$ of unknown structure. However, $(Ph_3P)_4Pt$ and $(Ph_3P)_3Pt$ act as sources of the $(Ph_3P)_2Pt$ fragment.[27]

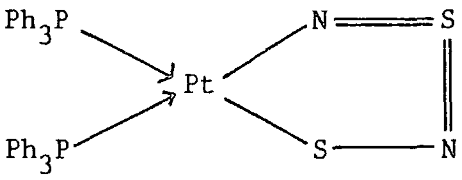
In sulphur-nitrogen chemistry $(Ph_3P)_4Pt$ has been reacted[28] with compounds of general formula RSNSR to give S-N bond insertion and rearrangement products shown as XI ($R=CH_3C_6H_4$, ClC_6H_4, $3,5-(CH_3)_2C_6H_3$)



[XI]

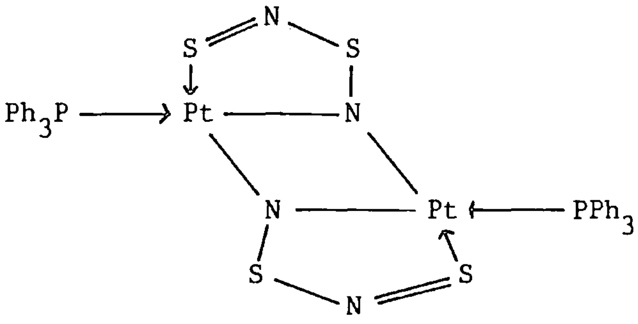
The reaction between $(Ph_3P)_4Pt$ and S_4N_4 has been reported[29] to give species formulated as $(Ph_3P)_2PtS_4N_4$ and $(Ph_3P)_2Pt(S_2N_2)$ whereas $S_4N_4H_4$ gave $(Ph_3P)_2Pt(SNH)_2$. The formulations were made on the basis of elemental analyses and ultraviolet spectra. However, a later X-ray analysis[30] showed the latter to be $(Ph_3P)_2Pt(OSNH)_2 \cdot 0.5H_2O$.

Subsequently, a five-membered, mononuclear cyclometallathiazene, $(Ph_3P)_2PtS_2N_2$, with the structure shown as XII, was isolated[31] from this reaction



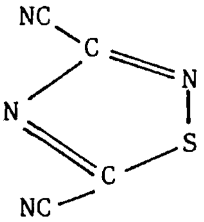
[XII]

and was also obtained from the reaction between $(Ph_3P)_4Pt$ and S_4N_4. Reaction[32] of $S_4N_4H_4$ with $(Ph_3P)_3Pt$ also gave XII, but with S_4N_4 the latter gave a dinuclear compound[33] $[Pt(S_2N_2)(Ph_3P)]_2$, shown as XIII.

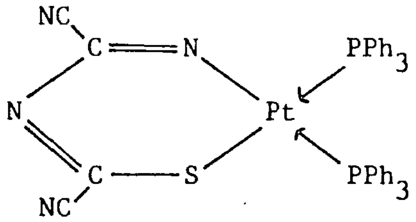


[XIII]

Incidentally, this complex can also be prepared[34] from S_4N_4 and an alternative source of "$(Ph_3P)_2Pt$", viz. $(Ph_3P)_2Pt(C_2H_4)$. This species also reacts[35] with 1,2,4-thiadiazole-3,5,-dicarbonitrile, shown as XIV, to give XV.

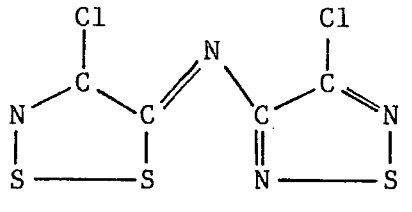


[XIV]

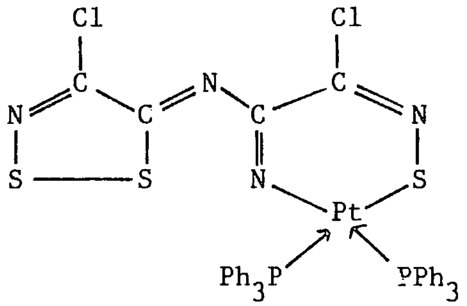


[XV]

Interestingly, when given a choice of an S-N or S-S bond in which to insert, $(Ph_3P)_2Pt(C_2H_4)$ reacts with the S-N bond of XVI to give the species[36] shown in XVII.



[XVI]

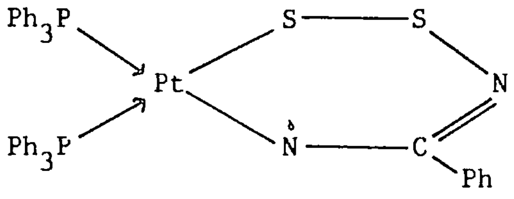


[XVII]

Bis (trimethylsilyl) sulphurdiimide yields[37] cis-$[Pt(NSNSiMe_3)_2(PPh_3)_2]$ after reaction with $(Ph_3P)_2Pt(C_2H_4)$ and the latter also reacts with $Hg(NSO)_2$ to give trans-$[Pt(NSO)_2(PPh_3)_2]$. Finally, $(Ph_3P)_3Pt$ reacts with S_4N_4 in air to give $[Ph_3PNH_2][Pt(S_2N_2H)(S_2O_3)(Ph_3P)]$.[38]

4.4.1.2 Results and Discussion

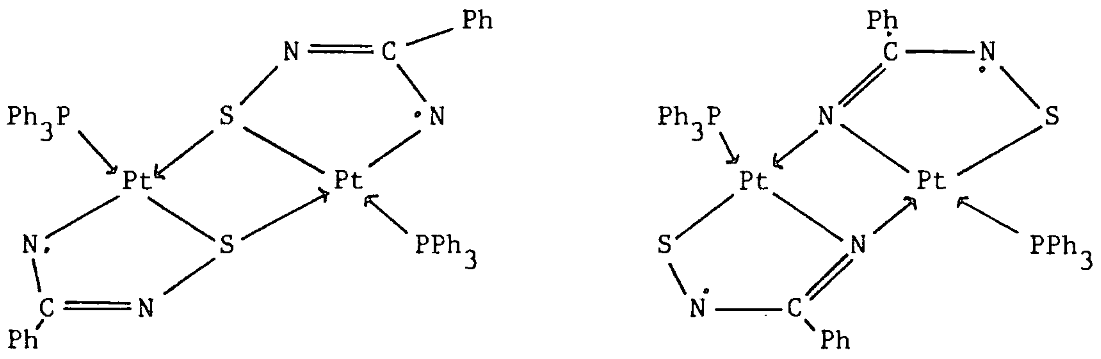
(a) $(PhCN_2S_2)_2$ was found to react with $(Ph_3P)_4Pt$ in toluene at r.t. to give an insoluble green compound which was identified on the basis of ^{31}P n.m.r. and analytical data as XVIII.



[XVIII]

The ^{31}P n.m.r. of the filtrate obtained in this reaction showed Ph_3P (rather than Ph_3PS) to be the only phosphorus-containing species present in solution. The n.m.r. spectra of the green compound, dissolved in dichloromethane-d_2, exhibited two resonances as expected for XVIII. The larger of the two observed ^{195}Pt-^{31}P coupling constants (3680Hz) can be associated[32] with the chemical shift (13.3ppm.) of the phosphine trans to nitrogen, with the other shift (14.1ppm., J=3503Hz) due to the phosphine trans to sulphur. After 1h, additional signals at -6.4ppm. and 17.1ppm. had appeared, and after 4h a new signal at 42.4ppm. was apparent. The peaks at -6.4 and 42.4ppm. are due to Ph_3P and Ph_3PS respectively; the signal at 17.1ppm. is discussed in part (b) of this Section. The solution was now orange and much orange solid had precipitated (see part (b)). The mass spectra do not show the molecular ion but do show a large assortment of breakdown peaks, most of which have been tentatively assigned.

(b) At 85°C, $(PhCN_2S_2)_2$ reacted with $(Ph_3P)_4Pt$ in toluene to give an insoluble orange solid. Unfortunately, this compound was found to be only sparingly soluble in dichloromethane and insoluble in all other common organic solvents. However, after 2000 scans, a weak signal was observed in the ^{31}P n.m.r. at 15.1ppm. (J=3665Hz). Significantly, the n.m.r. spectrum of the filtrate indicated a high concentration of Ph_3PS to be present. This result, together with the analytical data suggest the following structure, the $PhCN_2S$ analogue of XIII.



[XIX]

Although the above structure could be drawn with platinum (III), previous work[39] suggests that the odd electrons will be delocalised on the ligand, although the magnetic data (Appendix 3) indicate the compound to be essentially diamagnetic. This may be due to spin pairing resulting in the formation of a polymeric product. The F.A.B. mass spectrum is of low quality due to the insolubility of the material in the glycerol matrix.

A small quantity of pale yellow compound was recovered from the filtrate, and although only preliminary data have been obtained, it is possible that it is an isomer of XVIII, in which the platinum has inserted into the S-S bond of $PhCN_2S_2$. A single peak, at 18.8ppm. (J=3284Hz), was observed in the ^{31}P n.m.r. spectrum, indicative of a single phosphorus environment and the analytical data show values for Pt and P quite close to those expected for an isomer of XVIII. The similarity in shift and coupling constant between the above values and those at 17.3ppm. (J=3264.5Hz) observed in the spectrum of XVIII after 1h suggest that XVIII may isomerise to some extent in solution. The signal due to XIX was not observed in these spectra due to its insolubility.

4.4.1.3 Conclusion

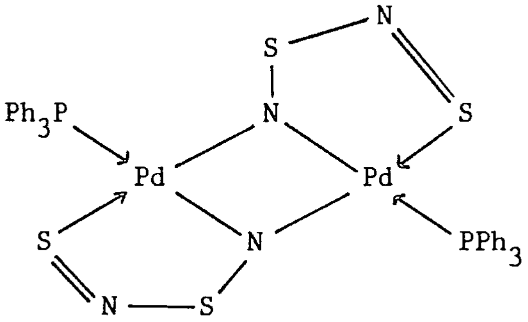
$(PhCN_2S_2)_2$ reacts with $(Ph_3P)_4Pt$ at r.t. to give the green complex, XVIII, which, on standing, converts to the dimer, XIX, with loss of Ph_3PS. There is some evidence that XVIII also isomerises, to give a species in which Pt has inserted into the S-S, rather than the S-N bond of $PhCN_2S_2$; this may be an intermediate in the formation of XIX. Reaction of $(PhCN_2S_2)_2$ with $(Ph_3P)_4Pt$ at elevated temperatures gives XIX, as the major product, together with a little of the isomer of XVIII and Ph_3PS.

4.4.2 Reaction of $(PhCN_2S_2)_2$ with $(Ph_3P)_4Pd$

4.4.2.1 Introduction

The chemistry of $(Ph_3P)_4Pd$ is very similar to that of the platinum analogue in that much of its reactivity[40] can be rationalised in terms of oxidative addition to the "$(Ph_3P)_2Pd$" fragment. However, the palladium (II) complexes which result are, kinetically and thermodynamically, much more labile than their platinum counterparts.

The palladium species $(Ph_3P)_4Pd$, has been utilised much less frequently than the platinum complex in sulphur-nitrogen chemistry. Only the palladium analogue of XIII has been prepared by reaction of either $(Ph_3P)_4Pd$[33] or $(Ph_3P)_2Pd(C_2H_4)$ with S_4N_4.

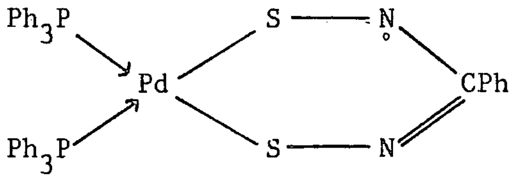


[XX]

It is noteworthy that whereas $(Ph_3P)_4Pt$ reacts with S_4N_4 to give $(Ph_3P)_2PtS_2N_2$, $(Ph_3P)_3Pt$ and $(Ph_3P)_2Pt(C_2H_4)$ both give the dinuclear platinum analogue of XX. However, both $(Ph_3P)_4Pd$ and $(Ph_3P)_2Pd(C_2H_4)$ give XX.

4.4.2.2. Results and Discussion

In this work, reaction of $(PhCN_2S_2)_2$ with $(Ph_3P)_4Pd$ in dichloromethane at r.t. or toluene at 60°C gave an orange-red compound, which on the basis of analytical data, is formulated as XXI.



[XXI]

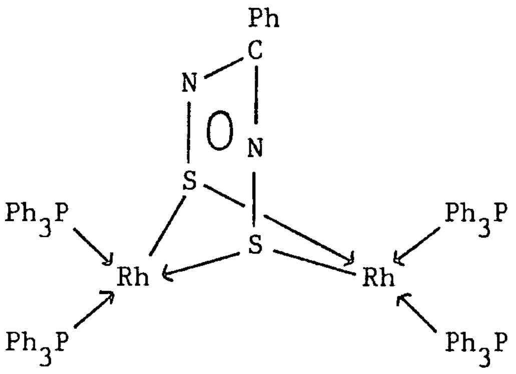
The F.A.B. mass spectra are of low quality due to the insolubility of the compound. The ^{31}P n.m.r. spectra show a single resonance at 24.8ppm. This value is close to the chemical shift of Ph_3PO but there was no evidence for this species in the i.r. spectra of XXI. The filtrate gave a signal at 42.6ppm., due to Ph_3PS, and a much weaker line at 14.5ppm. The presence of Ph_3PS in the filtrate is surprising since sulphur has not been lost (apparently) from the dithiadiazole ring (cf. platinum reaction, Section 4.4.1.2). However, since the reaction of $(Ph_3P)_xPd$ (x = 2 or 3) with $(PhCN_2S_2)_2$ is much slower the analogous reaction involving the platinum species, free Ph_3P may desulphurise $(PhCN_2S_2)_2$. The ^{31}P n.m.r. signal at 14.5ppm. may be due to another Ph_3P-$(PhCN_2S_2)_2$ reaction product (Section 5.2.2). The observation of only one line in the spectrum of the product indicates that the Pd atom has inserted into the S-S rather than the S-N bond of $(PhCN_2S_2)_2$.

4.4.3 Reaction between $(Ph_3P)_3RhCl$ and $(PhCN_2S_2)_2$

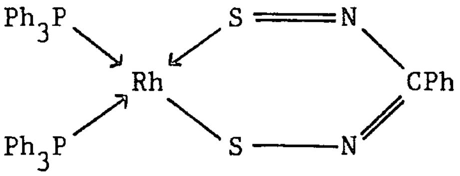
4.4.3.1 Introduction

Chlorotris (triphenylphosphine) rhodium (I) (Wilkinson's catalyst) has a rich and varied chemistry.[41,42] Apart from its well-known use in catalysis (especially hydrogenation) the compound can also take part in (for instance) reactions involving (1) chlorine substitution (with or without loss of Ph_3P), (2) triphenylphosphine displacement, (3) oxidative addition, and (4) decarbonylation reactions.

Since $(PhCN_2S_2)_2$ is known to dehalogenate certain species, e.g. bromotrimethylsilane, acetyl bromide (Sections 6.5 and 6.6) and sulphuryl chloride[5], it is possible that $(Ph_3P)_3RhCl$ might be dechlorinated to give species such as:



[XXII]



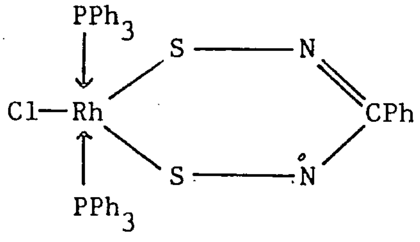
[XXIII]

An example of oxidative addition of a disulphide linkage[41] is given below:

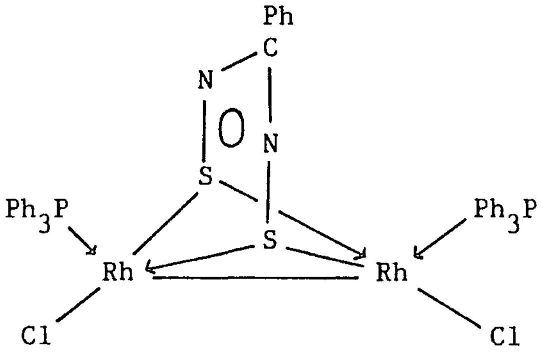
$$(Ph_3P)_3RhCl + R^1SSR^2 \;\rule[0.5ex]{5em}{0.4pt}\; (Ph_3P)_nRhCl(SR^1)(SR^2)$$

where R^1=Me, R^2=$CNME_2$, n=2; R^1=Me_2NC, R^2=$CSNMe_2$, n=1.

This suggests that the following complexes may be products of the reaction between $(Ph_3P)_3RhCl$ and $(PhCN_2S_2)_2$.

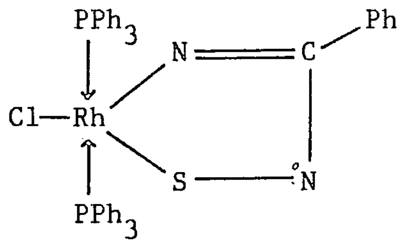


[XXIV]



[XXV]

Also, sulphur may be lost as Ph_3PS to give XXVI.



[XXVI]

4.4.3.2 Results and Discussion

The i.r. and n.m.r. spectra obtained on the solid materials isolated from this reaction show complicated mixtures to be present. Even after 48h extraction with petroleum ether, Ph_3PS is still observed in both spectra, although the ^{31}P n.m.r. also show signals at 18.1ppm. (J(RhP)=136Hz) and 28.5-36.8ppm. The analytical data suggest that a rhodium monochloro (bis) phosphine species has been formed but the figures do not correspond to those expected for XXIV or XXVI. The F.A.B. mass spectra are uninformative. The ^{31}P n.m.r. signals observed in the filtrate at 17.2 and 18.5ppm. may be due to $(PhCN_2S_2)_2$-Ph_3P reaction products (Section 5.2.2).

Very similar results were obtained when magnesium was added to the reaction mixture; the magnesium was recovered unchanged (Section 4.6.9). In summary, the reaction gave rise to a complex mixture, containing a rhodium-phosphine (chloro) complex and Ph_3PS.

4.5 CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

$(PhCN_2S_2)_2$ was found to react with $(Ph_3P)_4M$ (M=Pt,Pd) to give insoluble complexes whose structures have been inferred from spectroscopic data. The reaction with $(Ph_3P)_3RhCl$ was more difficult to rationalise, probably due to the solubility of the product rendering it susceptible to attack, at the $PhCN_2S_2$ ring, by Ph_3P.

The reactions with halides did not, in general, proceed although interesting copper species were isolated. It may be worthwhile carrying out electrochemical reduction of $(PhCN_2S_2)_2$ in the presence of transition metal halide compounds (see Appendix 2).

Although the reactions involving titanium compounds did not proceed simply, it may be worthwhile using $Cp_2Ti(CO)_2$ as a source of the Cp_2Ti fragment (Section 3.1). A convenient synthesis of this carbonyl, from Cp_2TiCl_2 and Li_3N, has been published recently[43a]; magnesium can also be used as the reducing agent.[43b]

4.6 EXPERIMENTAL

4.6.1 Reaction of $(PhCN_2S_2)_2$ with MCl_2 (M=Cr,Mn,Co,Ni,Cu,Pd) and $FeBr_2$

(a) $CrCl_2$: $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) and $CrCl_2$ (0.065g, 0.53mmol) were stirred in thf (25cm^3) for 2h at 60°C. The solvent was removed from a purple-pink solution to give a purple solid, νmax 1320w, 1178w, 1160w, 1140m, 1075m, 1040sh, 1025m, 920w, 858s, 840sh, 808s, 780s, 770sh, 690s, 657s, 514s cm^{-1}. The bands at 1040 and 858cm^{-1} are assigned[9] to coordinated thf, the remainder[5] to $(PhCN_2S_2)_2$.

(b) $MnCl_2$: $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) and $MnCl_2$ (0.125g, 1.0mmol) were stirred in thf (25cm^3) at 60°C for 24h. The solid present was allowed to settle and the supernatant liquor syringed off and pumped dry, νmax 1322w, 1240w, 1228w, 1188w, 1180w, 1162w, 1149m, 1141s, 1079m, 1070sh, 1030m, 1025sh, 924m, 902m, 845sh, 839s, 830m, 808s, 782vs, 770s, 692vs, 658vs, 512vs cm^{-1}. The bands at 1025 and 845cm^{-1} are assigned[9] to coordinated thf, the remainder[5] to $(PhCN_2S_2)_2$.

(c) $FeBr_2$: $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) and $FeBr_2$ (0.215g, 1.0mmol) were stirred in dry thf (25cm^3) at 65°C for 6h. The solid present was allowed to settle out and the supernatant liquor syringed off and pumped to dryness, ν max 1342m, 1238m, 1180m, 1140m, 1078w, 1036vs, 932m, 918m, 870vs, 806s, 780vs, 770s, 690s, 656s, 512s cm^{-1}. The bands at 1036 and 870cm^{-1} are assigned[9] to coordinated thf, the rest[5] to $(PhCN_2S_2)_2$.

(d) $CoCl_2$: $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) and $CoCl_2$ (0.13g, 1.0mmol) were stirred in thf (25cm^3) at 60°C for 6h. A deep red solution was obtained which was pumped to dryness to give a purple solid, ν max 1138m, 1079w, 1030vs, 924m, 880s, 840m, 808s, 780vs, 771s, 730m, 692s, 658s, 512s cm^{-1}. The bands at 1030 and 880cm^{-1} are due[9] to coordinated thf while the remaining bands are due[5] to $(PhCN_2S_2)_2$.

(e) $NiCl_2$: $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) and $NiCl_2$ (0.13g, 1.0mmol) were stirred together in thf (25cm^3) at 65°C for 18h. The mixture was filtered to give a colourless solid and a red solution which was pumped dry to give a red solid, νmax 1230m, 1140m, 1078w, 1030w, 924w, 902w, 830m, 820sh, 808m, 780m, 770m, 692s, 650m, 512 cm^{-1}. All of these bands can be assigned[5] to $(PhCN_2S_2)_2$.

(f) $CuCl_2$: a solution of $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) in acetonitrile (20cm^3) was added dropwise to a well-stirred solution of $CuCl_2$ (0.067g, 0.05mmol) in acetonitrile (15cm^3) at r.t. An orange-yellow solid was immediately precipitated but on addition of more $(PhCN_2S_2)_2$ solution the mixture darkened and after 24h a dark red solid (0.06g) was filtered off from a yellow-brown solution. Found: Cu,10.0; Cl,16.8%. ν max 1660m.bd, 1602m, 1580w, 1510w, 1406s, 1300m, 1212w, 1160sh, 1154s, 1072w, 1034m, 930m, 918m, 908s, 889s, 849s, 827s, 793s, 787s, 702vs, 695vs, 683s, 556s, 535s, 507m, 302m, 285m cm^{-1}. The solution was pumped dry to give a brown-black solid (0.20g), ν max 3240m.bd, 3100m.bd (NH), 1675s, 1600w, 1480sh, 1465sh, 1405sh, 1356sh, 1304w, 1263w, 1182w, 1173m, 1161m, 1153m, 1108w, 1090w, 1072w, 1032m, 1002w, 927m, 918w, 909w, 892s, 880w, 858w, 849w, 826vs, 790s, 720m, 702vs, 690sh, 682s, 668m, 620w, 592w, 557w, 540m, 520w cm^{-1}. The spectrum[44] of $[PhCN_2S_2]_2Cl$ is given for comparative purposes: ν max 1175m, 1169w, 1160w, 1142s, 1140sh, 1022s, 1018w, 1000w, 935w, 924w, 909s, 901s, 893w, 877m, 854w, 832m, 802vs, 781s, 772s, 720w, 695s, 689s, 675w, 666m, 536m, 522w, 469s cm^{-1}. The spectra[5] for $(PhCN_2S_2)_2$ and $[PhCN_2S_2]Cl$ are also of interest in this work.

(g) $PdCl_2$: $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) and $PdCl_2$ (0.18g, 1.0mmol) were stirred in thf ($25cm^3$) at r.t. for 14h. An orange solid was filtered off from an orange solution. Yield 0.19g. Found: Cl,22.2; Pd,19.5%. ν max 1592w, 1395sh, 1295w, 1259w, 1180m, 1158m, 1029m, 932m, 909s, 849s, 840sh, 803w, 789s, 702vs, 692sh, 663w, 560m cm^{-1}. The solvent was pumped off the filtrate to give a gum which was discarded.

4.6.2 Reaction of $(PhCN_2S_2)_2$ with $TiCl_4$ in the Presence of Magnesium

$TiCl_4$ ($0.11cm^3$, 0.19g, 1.0mmol) was added via micropipette to a vigorously stirred mixture of $(PhCN_2S_2)_2$ (0.36g, 1.0mmol) and magnesium turnings (0.1g, 4.2mmol) in thf ($30cm^3$) at r.t. Stirring was continued for 36h when a deep red solution was syringed off from a small quantity of magnesium. The solvent was removed *in vacuo* to give a dark red solid. ν max 1597w, 1345m, 1297w, 1226w, 1178w, 1160vw, 1140w, 1074m, 1034vs, 920m, 885s, 838w, 805s, 780s, 770m, 707sh, 691s, 658s, 545w, 512m cm^{-1}. The bands at 1034 and $885cm^{-1}$ are assigned[9] to coordinated thf, the remainder[5] to $(PhCN_2S_2)_2$. The solid was extracted with toluene (2 x $15cm^3$) to give a red solution which, on pumping to dryness gave a red solid (0.33g), νmax 1598w, 1325w, 1262m, 1240w, 1238w, 1180w, 1142m, 1078m, 1024vs, 923w, 902w, 838m, 830sh, 808s, 780s, 770m, 690s, 666s, 512s cm^{-1}. All bands can be assigned[5] to $(PhCN_2S_2)_2$.

The residue was a brown material (0.16g) ν max 1672w, 1600w, 1348w, 1298w, 1175w, 1030s, 960w, 924m, 890s, 735m, 700m, 680sh cm^{-1}. The red solid was extracted with pentane in an enclosed extractor (Figure 7.1) to give an insoluble red solid (0.16g). Found: C,35.6; H,3.7; N,8.1; Cl,17.0; S,17.4; Ti,9.3%. m/z (E.I.) 181 (100%), 135(6), 117(1), 103(8), 77(13), 72(23). ν max 1675w, 1600w, 1345w, 1300w, 1020s, 920w, 880w, 804w, 775w, 694m, 660w, 550w cm^{-1}. The soluble compound was shown to be $(PhCN_2S_2)_2$ by i.r. spectroscopy.

4.6.3 Reaction of $(PhCN_2S_2)_2$ with Cp_2TiCl_2 in the Presence of Magnesium

A mixture of $(PhCN_2S_2)_2$ (0.18g, 0.5mmol), Cp_2TiCl_2 (0.25g, 1.0mmol) and magnesium turnings (0.05g, 2.1mmol) were vigorously stirred in thf (20cm^3) at r.t. for 24h. Filtration gave a black solid (0.1g) ν max 3080w, 1585w, 1545sh, 1535m, 1448sh, 1408w, 1370sh, 1285w, 1068w, 1028s, 1020sh, 918w, 868w, 843w, 818vs, 700m cm^{-1}; and a deep red solution which was pumped dry to give a black solid (0.33g) ν max 1585w, 1502sh, 1343w, 1280m, 1220w, 1178w, 1065w, 1030s, 918m, 880s, 800s, 762m, 710m, 550vw cm^{-1}. This was extracted with acetonitrile in an enclosed extractor (Figure 7.1) for 24h to give a black insoluble solid (0.1g). ν max 2310w, 2280w, 2250w (CN), 1590m, 1542m, 1510sh, 1368w, 1270m, 1228w, 1104w, 1070w, 1020s (thf)[9], 918w, 882w, 840sh (thf)[9], 804vs, 703vs, 658sh, 610vw, 392sh cm^{-1}. m/z (E.I.) 103(100%), 76(37), 66(11), 65(6), 64(2), 52(5), 50(20), 44(4), 41(9), 39(13), 37(5), 32(1), and a soluble black solid (0.2g). Found: C,40.6; H,4.0; N,10.8; Cl,23.8; Mg,13.7; Ti,6.5%. ν max 2315m, 2290s, 2160m (CN), 1675w, 1645vw, 1600s, 1522s, 1430sh, 1290m, 1227m, 1200w, 1098w, 1072w, 1025s (thf)[9], 1002vw, 940w, 920vw, 840sh (thf)[9], 800vs, 758w, 718vs, 684m, 612vw, 556w, 400sh cm^{-1}. m/z (E.I.) 221(3%), 181(36), 152(5), 149(3), 135(9), 120(100), 104(100), 103(100), 93(4), 77(57), 76(57), 65(4), 64(12), 51(43), 50(41), 43(24), 39(19), 32(5). C.I.(+) 320(4%), 303(6), 286(5), 256(2), 253(5), 246(21), 234(2), 229(2), 222(30), 217(18), 200(30), 181(77), 150(57), 122(100), 121(100), 103(12), 35(100).

The D.S.C. trace showed two endotherms at 114.8 and 219.3°C as well as a broad exotherm starting at 228°C (peak maximum at ca. 255°C).

4.6.4 Attempted Reaction between $(PhCN_2S_2)_2$ and $NiCl_2$ in the Presence Magnesium

A mixture of $(PhCN_2S_2)_2$ (0.18g, 0.5mmol), $NiCl_2$ (0.13g, 1.0mmol) and magnesium turnings (0.1g, 4.2mmol) were stirred in thf ($25cm^3$) at r.t. for 24h. No change was observed and a red solution was syringed off and pumped to dryness to give a red solid. ν max 1320m, 1232m, 1220m, 1172w, 1152w, 1133m, 1070m, 1020m, 918m, 896m, 835m, 828sh, 802s, 775s, 768sh, 672s, 652s, 508s cm^{-1}. All of these bands can be assigned[5] to $(PhCN_2S_2)_2$.

4.6.5 Reaction of $(PhCN_2S_2)_2$ with $MoCl_4(CH_3CN)_2$

A mixture of $(PhCN_2S_2)_2$ (0.13g, 0.36mmol) and $MoCl_4(CH_3CN)_2$ (0.11g, 0.34mmol) were stirred in thf at r.t. for 24h. After ca. 10min a yellow solid was observed but this soon disappeared and after 24h a deep green solution was present. This was pumped dry to give a black solid which was washed with toluene and pumped dry. Yield, 0.07g. Found: Cl,23.7; Mo,11.5%. ν max 1675m, 1640w, 1600w, 1540vw, 1501vw, 1475sh, 1400sh, 1300vw, 1180w, 1160m, 1098vw, 1075vw, 1029m, 1003vw, 970s, 932m, 910s, 848s, 805w, 793sh, 789s, 740w, 704vs, 668w, 560s, 412vw, 387w, 335vs, 282w cm^{-1}.

4.6.6 Reaction between $(PhCN_2S_2)_2$ and CuCl

A mixture of $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) and CuCl (0.2g, 2mmol) was stirred in acetonitrile ($10cm^3$) at 60°C for 12h. The solvent was then pumped off and dichloromethane ($10cm^3$) added. This mixture was stirred at 45°C for 12h to give an insoluble black solid which was filtered off, washed with dichloromethane (2 x $5cm^3$) and pumped dry to give $PhCN_2S_2.2CuCl$, 0.28g, 74%. m.pt. 198.2°C (decomp.). Found: C,21.2; H,1.1; N,6.5; Cl,17.9; Cu,34.5; S,10.1%. $C_7H_5N_2Cl_2Cu_2S_2$ requires C,22.2; H,1.3; N,7.4; Cl,18.7; Cu,33.5; S,16.9%. ν max 1452sh, 1368sh, 1320w, 1245m, 1190w, 1163w, 1142m, 1080w, 1026m, 962w, 920m, 822m, 798s, 759s, 722w, 686s, 660m, 544m, 388m cm^{-1}. m/z (E.I.) 181($PhCN_2S_2^+$,100%), 149($PhCN_2S^+$,2), 135($PhCNS^+$,15), 117($PhCN_2^+$,1), 103($PhCN^+$,17), 89(PhC^+,1), 78(S_2N^+,31), 77(Ph^+,9), 64(S_2^+,4), 46(SN^+,15).

4.6.7 Reaction of $(PhCN_2S_2)_2$ with $(Ph_3P)_4Pt$

(a) At r.t.: A solution of $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) in toluene ($20cm^3$) was added dropwise to a well-stirred suspension of $(Ph_3P)_4Pt$ (Section 7.6.4, 1.25g, 1.0mmol) in toluene ($40cm^3$) at 21°C. Almost immediately a green colouration was observed in the solution at the point of entry of the $(PhCN_2S_2)_2$. Stirring was continued for 2h when a green solid was filtered off from a green solution, washed with toluene (2 x $5cm^3$) and pentane ($5cm^3$) and pumped dry. Yield 0.52g, 47%. m.p. 144.45°C (decomp.). Found: C,56.6; H,3.8; N,3.0; P,7.1; Pt,22.3; S,0.0%. $C_{43}H_{35}N_2P_2PtS_2$ requires C,57.3, H,3.9; N,3.1; P,6.9; Pt,21.7; S,7.1%. νmax 3040w,sh, 1568w, 1476sh, 1430s, 1318m, 1305sh, 1254w, 1230vw, 1172w, 1150w, 1095sh, 1088s, 1065sh, 1022m, 992w, 914w, 842w, 819m, 793w, 758s, 749s, 735s, 729sh, 712s, 700sh, 688vs, 648vw, 610w, 546sh, 538s, 520s, 512vs, 496s, 460w, cm^{-1}. δ_P

(CD_2Cl_2) T=0:13.3ppm., J(PtP)=3680Hz; 14.0, J=3503; T=1h: -6.4(4), 13.1(24), J=3680; 13.8(24), J=3503; 17.1(17), J=3264.5. T=4h:-6.2(1) 13.3(3), J=3673; 14.05(3); 17.3(10), J=3264.5; 42.4(2). m/z (F.A.B.) 868(M-S,10%), 823(M-Ph,8), 791(M-S-Ph,2), 781(6), 750(5), 746(M-2Ph,3), 719(($Ph_3P)_2Pt$,29), 714(M-S-2Ph,3), 673(6), 669(M-3Ph,2), 642(($Ph_3P)(Ph_2P)Pt$,6), 638(M-Ph_3P,2), 637(M-S-2Ph,2), 606(M-S-Ph_2P,7), 565((Ph_3P)(PhP)Pt,4), 561(M-Ph_3P-Ph,3), 560(M-S-4Ph,3), 529(M-S-Ph_3P-Ph,2), 488((Ph_3P)PtP,5), 484(M-Ph_3P-2Ph,5), 483(M-S-5Ph,5), 457(16), 452(M-S-Ph_3P-2Ph,7), 411(Ph_3P)PtP,3), 407(M-Ph_3P-3Ph,2), 406(M-S-6Ph,2), 380(Ph_2PPt,18), 376(M-2Ph_3P,19), 375(M-S-Ph_3P-2Ph,3), 334(PhPPtP,6), 303(PhPPt,11), 294(Ph_3PS,80), 262(Ph_3P,27), 217(24), 195(9), 185(17), 181(($PhCN_2S_2$,47), 149($PhCN_2S$,9), 135(PhCNS,2), 103(PhCN,6)), 89(PhC,100), 77(Ph,26), 32(S,11), 31(P,65).

(b) At 85°C: A suspension of $(Ph_3P)_4Pt$ (2.5g, 2.0mmol) in toluene (40cm^3) was added dropwise to a stirred solution of $(PhCN_2S_2)_2$ (0.36g, 1mmol) at 80°C. After 10 min. a green colouration appeared where the $(PhCN_2S_2)_2$ entered the mixture. When the addition was complete, after 30 min, the reaction mixture consisted of a green solution containing an orange-yellow solid. Stirring was continued for 2h, during which time the solution became orange-yellow and the solid became orange. The solid was filtered off at 80°C, washed with hot toluene (10cm^3) and diethyl ether (2 x 5cm^3) and pumped dry. Yield 1.03g, 85%. Found: C,51.9; H,3.5; N,2.2; P,5.0; Pt,35.5; S,5.7%. $C_{50}H_{40}N_4P_2Pt_2S_2$ requires C,49.5; H,3.3; N,4.6; P,5.1; Pt,32.2; S,5.3%. δ_P(CD_2Cl_2) 15.1ppm. J(PtP) 3665Hz. νmax 3055m, 1479m, 1434s, 1405w, 1312s, 1182w, 1170m, 1160sh, 1148w, 1104sh, 1095s, 1069w, 1029m, 1002m, 920vw, 904vw, 850w, 765m, 757m, 746s, 717s, 700vs, 683sh, 550m, 539vs, 527vs, 510vs, 503sh, 468w, 450w, 430w cm^{-1}. m/z 868(5%), 719(2), 606(4), 488(2), 456(4), 452(2), 380(6), 339(2), 303(6), 294(48), 279(15), 271(2), 262(11), 256(2), 241(2), 217(18), 201(4), 195(9), 185(12), 181(32), 170(2), 165(8), 152(6), 149(5), 138(8), 133(6), 128(2), 121(100), 117(4), 109(14), 103(12), 91(65), 77(10), 73(28), 64(4), 61(16). The D.S.C. trace showed a very weak, broad exotherm at 220-250°C.

The solvent was pumped off the filtrate to give a red gum. This was dissolved in dichloromethane ($5cm^3$) and diethyl ether ($30cm^3$) was added which precipitated a yellow solid. This was filtered off, washed with diethyl ether ($2cm^3$) and pumped dry. Yield 0.06g. Found: P,6.6; Pt,22.5%. ν max 3055w, 1468sh, 1432s, 1309m, 1182w, 1169w, 1160w, 1142w, 1097s, 1070w, 1028w, 1000w, 849w, 746s, 694vs, 670sh, 618vw, 533s, 522s, 510s, 498m, 458w, 428w cm^{-1}. $\delta_P(CD_2Cl_2)$ 18.8ppm. J(PtP) 3284Hz. This filtrate was pumped to low volume and more solid precipitated with ether, 0.39g, ν max 3040w, 1432s, 1304w, 1180w, 1104s, 1070w, 1027w, 1000w, 752sh, 748m, 714vs, 692s, 638s, 612w, 540w, 517sh, 512s, 479w, 458w, 429w cm^{-1}. This spectrum is assigned[46] to Ph_3PS.

4.6.8 Reaction of $(PhCN_2S_2)_2$ with $(Ph_3P)_4Pd$

A solution of $(PhCN_2S_2)_2$ (0.12g, 0.33mmol) and $(Ph_3P)_4Pd$ (0.48g, 0.42mmol) was stirred in toluene ($20cm^3$) at 60°C for 16h. Filtration gave an orange-red solid which was washed with petroleum ether in an extractor (Figure 7.1) for 11h to give a final yield of $(Ph_3P)_2Pd((PhCN_2S_2)$ 0.12g, 22%. ν max 3055w, 1598w, 1480m, 1437s, 1320s, 1312sh, 1182vw, 1171m, 1160w, 1152w, 1100sh, 1093m, 1068w, 1029m, 1020sh, 1000w, 848w, 820w, 752w, 743s, 730w, 718s, 703sh, 695s, 672s, 529s, 522s, 508s, 469w, 449w cm^{-1}. $\delta_P(CD_2Cl_2)$ 24.8ppm. m/z

(F.A.B.) 549(2%), 462(2), 448(5), 416(2), 411(3), 371(2), 367(8), 362(48), 347(11), 339(6), 329(3), 301(2), 293(2), 262(2) 257(3), 245(3), 228(4), 197(2), 189(2), 185(3), 181(13), 176(3), 160(3), 150(8), 141(3), 137(2), 129(2), 89(16). Found: C,61.1; H,4.1; N,2.7; P,7.3; Pd,14.3; S,8.4%. $C_{43}H_{35}N_2P_2PdS_2$ requires C,63.6; H,4.3; N,3.5; P,7.6; Pd,13.1; S,7.9%. The D.S.C. trace showed decomposition to begin at ca. 270°C (peak temperature ca. 290°C).

4.6.9 Reaction between $(Ph_3P)_3RhCl$ and $(PhCN_2S_2)_2$

A solution of $(PhCN_2S_2)_2$ (0.09g, 0.25mmol) and $(Ph_3P)_3RhCl$ (0.46g, 0.5mmol) in toluene ($30cm^3$) was stirred at 60°C for 6h. The solvent was pumped off leaving a shiny, dark red solid which was washed (in apparatus shown in Figure 7.1) with petroleum ether for 48h. Yield 0.18g. Analysis: Cl,3.6; P,5.5; Rh,8.3; S,8.3%. ν max 3050w, 1642m, <u>1589w</u>, <u>1482sh</u>, <u>1438s</u>, 1318m, <u>1183m</u>, 1174sh, <u>1160sh</u>, 1158m, <u>1110sh</u>, 1092s, <u>1070w</u>, 1036w, 1028m, <u>1000m</u>, 980w, 924vw, 909vw, 852w, 846sh, 810m, 795m, 772m, <u>745s</u>, 721s, 700sh, <u>692vs</u>, 658sh, <u>640w</u>, <u>614w</u>, 527vs, 520sh, <u>515sh</u>, 500m, <u>460w</u> cm^{-1}. Underlined bands are assigned[46] to Ph_3PS. $\delta_P(CD_2Cl_2)$ 18.1 (J(RhP)=136Hz), 27.0 (Ph_3PO)[45c], 28.5-36.8 (12 lines) 43.5ppm. (Ph_3PS).[45b] m/z (F.A.B.) 381(7%), 262(2), 121(5), 75(30), 56(24), 45(21), 31(9).

The petroleum ether washings were pumped dry to give a white solid, $\delta_P(CD_2Cl_2)$-5.3(Ph_3P)[45a], 17.2, 18.5, 43.2(Ph_3PS).[45b]

A solution of $(PhCN_2S_2)_2$ (0.09g, 0.25mmol) and $(Ph_3P)_3RhCl$ (0.46g, 0.5mmol) in thf ($30cm^3$) was stirred with magnesium turnings (0.1g, 4.2mmol) at r.t. for 30h and then at 60°C for 6h. Filtration gave magnesium turnings (0.1g) and a deep red filtrate. The solvent was pumped off leaving a red-black solid. ν max 1640w, 1588w, 1480sh, 1438s, 1315w, 1183w, 1172w, 1160w, 1148w, 1005m, 1070w, 1030m, 1002w, 972w, 850w, 800m, 782w, 748m, 718s, 695s, 642m, 617w, 544sh, 523s, 515sh, 455w cm^{-1}. See above for assignment.

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CHAPTER 5

REACTIONS OF PHENYL DITHIADIAZOLE WITH SOME NUCLEOPHILES

5.1 GENERAL INTRODUCTION

The electron-rich nature of sulphur-nitrogen compounds might be thought to make them less susceptible to nucleophilic attack, than, for example, the phosphazenes.[1] However, cyclic SN compounds possess empty, low-energy, antibonding orbitals and occupation of these by the electron pairs of nucleophilic species can result in the formation of both ring-contracted and chain products.[2]

Previous studies[3] on the reactivity of dithiadiazoles, in particular, $(PhCN_2S_2)_2$, towards nucleophiles have been limited to hydrolysis and reaction with triphenylphosphine. Hydrolysis was thought to give $[PhC(NH)N(H)SO]_2$ formed by loss of sulphur from $PhC(NH)NS_2OH$. Reaction with Ph_3P did not proceed in carbon tetrachloride solution.

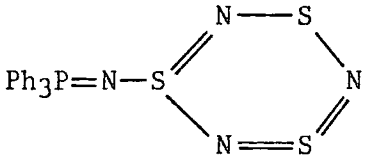
In this work the reactivity of $(PhCN_2S_2)_2$ toward R_3P, (R=Me,Ph), Ph_3As, S_8, Me_3NO, N_3^-, H^- and Me_nNH_{3-n} (n=0-3) was investigated. Results are discussed with reference to the chemistry of S_4N_4, where appropriate.

5.2 REACTION BETWEEN $(PhCN_2S_2)_2$ AND R_3P(R=Ph,Me)

5.2.1 Introduction

The first product to be isolated from the reaction of Ph_3P with S_4N_4 was formulated[5] as $Ph_3PS_3N_4$ (N.B. although the summary in ref. 4 states that $Ph_3PS_3N_4$ was prepared from Ph_3P and S_4N_4, the text only describes the formation of a mixture containing Ph_3PS, and, since the solution was heated it is likely that the decomposition product Ph_3PNSNS_2 was obtained;[10] $Ph_3PS_3N_4$ was actually prepared from Ph_3P=CH_2

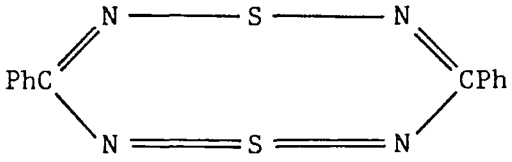
and S_4N_4 in this work) and this was subsequently confirmed[6] by X-ray analysis which showed the structure to be I:



[I]

The reaction was reinvestigated, within the wider context of studies on the general nucleophilic degradation of S_4N_4. As a result of this work[7] two further products were isolated, viz. $[(Ph_3P{=}N)_3S]S_4N_5$, obtained in both acetonitrile and benzene as solvents, and $(Ph_3P{=}N)_2S_4N_4$, only obtained in acetonitrile. (I is not obtained in acetonitrile.) These reactions must be carried out at ambient temperature since both $S_4N_5^-$ and I can be thermally decomposed; the former[8] to give S_4N^- and the latter to give[9,10] $Ph_3PNSNSS$. Both of these products are chain compounds. It should be noted that in all the above reactions Ph_3PS is always obtained as a by-product.

The object of the present work was to employ the thiophilic nature of Ph_3P to prepare the dithiatetrazocine derivative shown as II, via abstraction of one sulphur from each of two $PhCN_2S_2\cdot$ units, which could then couple.



[II]

This compound was first prepared by Woodward[11], in 7% yield, from benzamidine and SCl_2 (in the presence of the base, diazabicycloundecane).

5.2.2 Results and Discussion

Reaction of $(PhCN_2S_2)_2$ with Ph_3P in the molten state generally led to the recovery of Ph_3PS and unreacted $(PhCN_2S_2)_2$, although two very weak signals appeared near 17ppm. in the ^{31}P n.m.r. spectra of a $(PhCN_2S_2)_2$ - Ph_3P melt sublimation residue (Section 5.11.1c). These signals cannot be assigned to Ph_3P or Ph_3PS which occur at ca. -3.0[12a] and 43.0[12c]ppm., respectively.

The infrared spectra of solids recovered from reactions of $(PhCN_2S_2)_2$ and Ph_3P in dichloromethane or acetonitrile at room temperature, again showed Ph_3PS to be, by far, the major product and attempts at recrystallisation or sublimation on the product mixtures only yielded more Ph_3PS (in red, orange and yellow forms!).

It is apparent that II is not obtained in these reactions to any great extent but in order to observe any phosphorus-containing species which might be present and whose i.r. bands may be masked by those of Ph_3PS, reactions were performed in n.m.r. tubes (Sections 5.11.1f and g) and monitored by both ^{31}P and ^{1}H n.m.r.

The ^{31}P n.m.r. results are presented in Table 5.1.

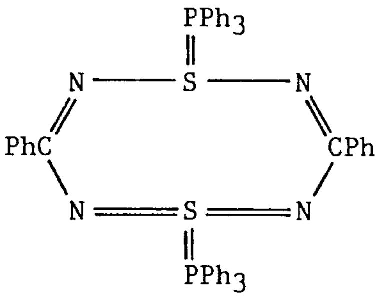
Table 5.1 ^{31}P N.M.R. signals (in ppm.) from $(PhCN_2S_2)_2$ - Ph_3P Reaction

TIME(h)	SIGNAL (RELATIVE INTENSITY)							
0	-4.7(103)			8.0(1)			26.0(2)	43.6(10)
3.5	-5.0(48)	0.4(15)	1.8(28)	7.9(5)	15.6(57)	17.1(21)	26.0(6)	43.4(225)
7.0		0.4(11)	1.6(15)	8.0(1)	15.6(49)	17.1(20)	26.0(2)	43.3(178)
24		0.5(9)	1.7(11)		15.7(36)	17.2(15)	26.2(3)	43.4(112)

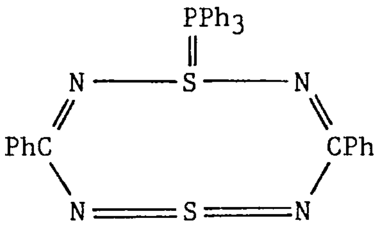
Very minor peaks are also present at 42.2ppm., after 0 and 3.5h, and at 15.3ppm. throughout the reaction. The signal at 26.0ppm. which remains relatively constant in intensity during the reaction is due[12b] to Ph_3PO; that at $\sim$-5.0ppm. is due[12a] to Ph_3P and the signal at

-43.4ppm. is due[12c] to Ph_3PS.

The first obvious conclusion that can be drawn is that Ph_3PS is formed almost immediately in this reaction (it took ca. 5min. to allow the tube to warm to r.t. after sealing under vacuum and take it to the spectrometer) and that after 3.5h it is the major phosphorus-containing species in solution. The other relatively strong signals at 15.6 and 17.1ppm. probably correspond to those observed in the sample of the melt-sublimation residue (vide infra) and may be due to phosphorus-sulphur species such as III and IV:



[III]



[IV]

The resonance at ca. 1.7ppm. is quite broad (f.w.h.h. 70Hz) and is probably given by a phosphorus atom bonded to quadrupolar nitrogen (^{14}N:I=1). The signals at 0.4 and 8.0ppm. remain unassigned. Since the above species cannot be isolated, it may be that they are unstable with respect to Ph_3PS, PhCN and nitrogen. Proton spectra were recorded to try and identify phenyl containing species but the spectra were very complicated. They are reported in Table 5.2.

Table 5.2 ^1H N.M.R. Signals from $(PhCN_2S_2)_2$ - Ph_3P Reaction

TIME	SIGNALS (ppm.)						
0	7.31	7.37					
3.5	7.28	7.35	7.48		7.68	7.85	8.01
7.0	7.29	7.36	7.48	7.57	7.68	7.84	8.05
24			7.49	7.57	7.69	7.85	8.02

The signals at ~7.3 and ~7.35ppm. which diminish in relative intensity and are absent after 24h can be assigned[13a] to Ph_3P, whereas those at 7.48 and 7.68ppm., which increase in relative intensity, and are the major species after 3.5h, are due[13b] to Ph_3PS. The resonance at 7.57ppm. may be due[13c] to PhCN. The signals at 7.85 and 8.02ppm. were always very weak in intensity and remain unassigned although they may well be due to species such as III and IV or even II (the signals were broad and overlapped, consequently accurate intensity data could not be obtained).

In order to obtain more information on the species formed in this reaction, which contain phenyl groups (apart from Ph_3PS; i.e. derived from $(PhCN_2S_2)_2$), a sample of a $(PhCN_2S_2)_2$ - Me_3P mixture in $CDCl_3$ was studied by ^1H n.m.r. The results are presented in Table 5.3.

Table 5.3 ^1H N.M.R. Signals (in ppm.) from $(PhCN_2S_2)_2$ - Me_3P Reaction

TIME(h)	SIGNAL (RELATIVE INTENSITY)								
0	7.60	7.22	7.13	2.23(3)	1.70(3)	1.63(6)	1.62(18)	1.39(4)	0.85(124)
3	7.60(2)	7.21(7)	7.12(7)		1.68(48)		1.59(68)		0.82(360)
24		7.19(7)	7.10(7)		1.65(38)	1.64(14)	1.56(48)		0.79(230)

The signal at ca. 0.82ppm. (J_{PH}=2.1Hz) can be immediately assigned[13d] to Me_3P and that at ca. 1.70ppm. (J_{PH}=13.5Hz) which increases in relative intensity as the reaction proceeds is due[13d] to Me_3PS. The low intensity signal at 1.63ppm. (J_{PH}=13.25) which remains constant throughout the reaction is probably due[13d] to Me_3PO. The resonance at ca. 1.59ppm. (J_{PH}=13.0Hz) is present at t=0 in high concentration and remains so throughout the reaction (ca. 3:2 with Me_3PS after 24h.). The compound giving this signal may also be giving rise in part, to the phenyl resonances at 7.13 and 7.22ppm. and so could be due to the Me_3P derivatives of III or IV. The signal at 7.60ppm., which increases and then decreases in intensity, as the reaction proceeds, could possibly be due to II, which could also contribute to the signal intensity at 7.13 and 7.22 ppm. The signals at 1.39 and 2.23ppm. are of very low intensity and remain unassigned.

5.2.3 Conclusion

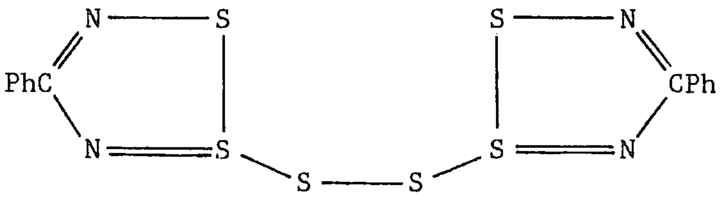
The reaction of $(PhCN_2S_2)_2$ with Ph_3P gave Ph_3PS as the only characterisable product. Other phosphorus containing species were detected in solution but appear to decompose to Ph_3PS. Further work on the reaction is probably not worthwhile but preliminary results with Me_3P are encouraging in that phosphorus species, other than Me_3PS, are present in reasonable concentration and might be isolable.

5.3 ATTEMPTED REACTION BETWEEN $(PhCN_2S_2)_2$ AND Ph_3As

Since Ph_3As is less thiophilic than Ph_3P ($\nu(As{=}S)^{14}{=}495cm^{-1}$, cf. $\nu(P{=}S)^{51}{=}637cm^{-1}$) it was hoped that any arsenic analogues of III or IV that might form, would be less susceptible to loss of Ph_3AsS. The arsenic analogue of I has been prepared[15] previously. (Ref. 10 of ref. 10 of this chapter reports the use of boiling benzene as the reaction solvent in this paper.[15] This does not seem to be correct; Ph_3As and S_4N_4 are simply allowed to react.) However, $(PhCN_2S_2)_2$ and Ph_3As did not react in the molten state up to 200°C, most probably due to the low strength of the As$=$S bond.

5.4 ATTEMPTED REACTION BETWEEN $(PhCN_2S_2)_2$ AND S_8

Reaction between $(PhCN_2S_2)_2$ and sulphur, generated by hydrolysis of $(PhCN_2S_2)_2$ in wet chlorobenzene, has been reported[3] to give species V;



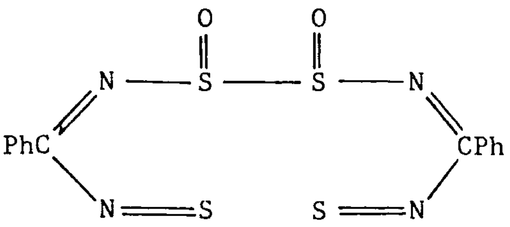
[V]

However, D.S.C. showed that no reaction occurred between $(PhCN_2S_2)_2$ and S_8 in the molten state up to 200°C. In fact, the observation of two separate endotherms indicates that the two components did not mix (Section 5.11.3).

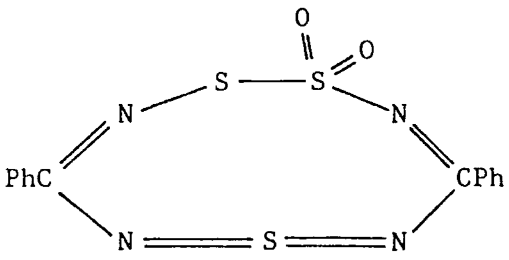
This is not conclusive proof that the above compound was not obtained earlier[3] due to (a) the lack of mixing and (b) the polymerisation of S_8 upon melting[16] (which may have caused (a)).

5.5 ATTEMPTED REACTION BETWEEN $(PhCN_2S_2)_2$ AND Me_3NO

This reaction was attempted as a control experiment, since Me_3NO was used as a decarbonylating agent in reactions of $(PhCN_2S_2)_2$ with $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ (Section 2.4.2). Various sulphur species have been oxidised by Me_3NO including $P_4(NMe)_6S_n$ (n=0-3) to give[17a] $P_4(NMe)_6S_nO_{4-n}$ and certain sulphoxides[17b] to give sulphones. In the present work it was thought that compound VII might be formed via (i) coupling of two thioimino groups with elimination of sulphur[18a], and (ii) conversion of two adjacent sulphoxide units to a sulphide adjacent to a sulphone[18b] in an intermediate such as VI.



[VI]



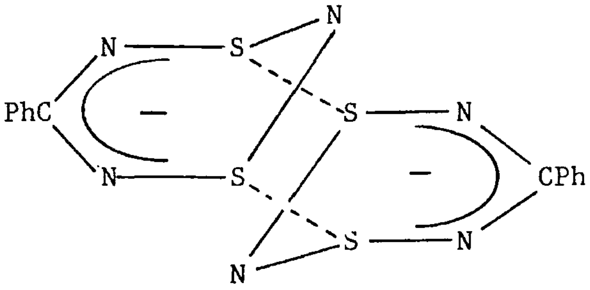
[VII]

However, $(PhCN_2S_2)_2$ and Me_3NO did not react in toluene at 80°c.

5.6 ATTEMPTED REACTION BETWEEN $(PhCN_2S_2)_2$ AND Me_4NN_3

The nature of the products of the reaction between azides and S_4N_4 has been found to be dependent upon the cation involved. Smaller cations such as Li^+, Na^+ and K^+ gave[19,21] $S_4N_5^-$ salts, whereas Cs^+ or R_4N^+ (R=Me,Et,^{n}Pr,^{n}Bu) gave[20,21] $S_3N_3^-$ salts; with RbN_3 a mixture of the two was obtained.

The object of the present work was to try and prepare the potentially 8π anionic species VIII:

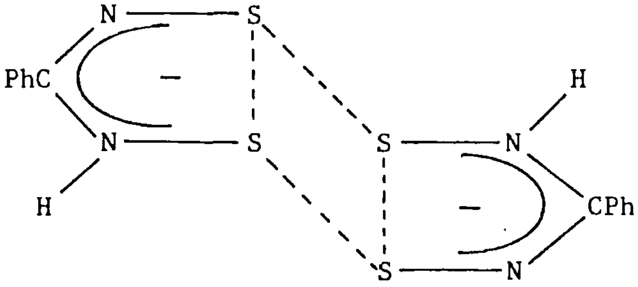


[VIII]

However, no reaction occurred. In fact, a cyclic voltammetry study of the neutral species $(PhCN_3S_2)_2$ showed the reduction to be highly irreversible[22], indicating the preparation of VIII to be unlikely.

5.7 ATTEMPTED REACTION BETWEEN $(PhCN_2S_2)_2$ AND NaH

This reaction was attempted to see if NaH would reduce $(PhCN_2S_2)_2$ to the formally 8π anion $[PhCN_2S_2]^-$ (see Appendix 2). Another possibility would be the 8π dimer shown below:



[IX]

The only previous study[23] of a reaction between S_4N_4 and a hydridic species involved $LiAlH_4$ and gave S_7NH in very low yield. However, NaH did not react with $(PhCN_2S_2)_2$ in the presence of 18-crown-6 ether. The latter was added to provide a large sodium-crown coordinated cation[24] as a suitable counter ion, in order to achieve better packing in the crystal (Section A2.1).

5.8 REACTION BETWEEN $(PhCN_2S_2)_2$ AND AMMONIA

5.8.1 Introduction

The earliest report[25] of a reaction between S_4N_4 and ammonia described the product as $S_4N_4.2NH_3$ which reacted as a 2:1 mixture of H_2NSN and HNS(S)NH. Later work[26] yielded HNS and $(HN)_2S$ (also formulated as $HNSNSNH_2$) from the same reaction. None of the above mentioned species were isolated by the authors. Spectrophotometric studies[27] assigned a band at 360nm, observed in solutions of S_4N_4 in liquid ammonia, to $S_4N_4.2NH_3$ (i.e. $2H_2NSN$ + HNS(S)NH) or its ionization products. The conductometric behaviour[28] of S_4N_4 in liquid ammonia, i.e. as a 1:1 electrolyte was ascribed to $HNSNSNH_2$, possessing only one acidic hydrogen.

More recent work[29] has resulted in the isolation of $NH_4[S_4N_5]$ from these solutions, in 26% yield, and Chivers[30] has confirmed this and drawn attention to the central role of the $[S_4N_5]^-$ ion in reactions of S_4N_4 with nucleophiles. Low yields of $[S_3N_3]^-$ were also obtained and the u.v. band at 360nm[27] has been assigned to this species. This assignment was later substantiated[31] but $[S_4N_5]^-$ was not mentioned (even though the paper reporting the preparation[30] of $NH_4[S_4N_5]$ from S_4N_4-NH_3 solutions was referenced) and the reaction was thought to proceed according to:

$$S_4N_4 + NH_3 \longrightarrow S_3N_3^- + SN_2^{2-} + H^+ \rightleftharpoons S_4N_4.NH_3\text{(solid)}$$

However, the SN_2^{2-} ion would probably be insoluble in liquid ammonia[32], and the evidence for $NH_4[S_4N_5]$ is quite conclusive. Therefore, it is highly likely that $NH_4[S_4N_5]$ and $NH_4[S_3N_3]$ were obtained, rather than $S_4N_4.NH_3$, which was originally proposed[25] in 1904 (reactions thought likely to give $S(NH)_2$, in fact, gave S_4N_4 or $[S_4N_5]^-$).[33] Finally, the presence of $[S_3N_3]^-$ and $[S_4N_5]^-$ in solutions of S_4N_4 in liquid ammonia has been verified[34] by ^{14}N n.m.r. spectroscopy.

5.8.2 Results and Discussion

$(PhCN_2S_2)_2$ was found to dissolve in liquid ammonia to give a deep blue solution. Originally, it was thought that this colour was due to the presence of solvated electrons[32], however, no e.s.r. signal was obtained.[35] U.V.-visible spectra of a very dilute solution of $(PhCN_2S_2)_2$ in ammonia showed absorptions at 228, 295, 398, 468 and 580nm (see Figure 5.1). The latter band can be immediately assigned to the blue S_4N^- anion whereas those at 295 and 468nm are due[36] to S_3N^-. Both of these anions have been previously observed[31,36] in solutions of sulphur in liquid ammonia. The band at 228nm is assigned to a phenyl chromophore.[37] After 10 weeks the spectrum was dominated by an intense band at 609nm, due to the radical anion S_3^-, also observed[31,36] in solutions of sulphur in ammonia. Removal of the ammonia from the $(PhCN_2S_2)_2$ solution gave a sticky red gum which was extracted by dichloromethane to give a red compound and a minute quantity of a colourless compound. Single crystals of both were grown and their structure determination attempted by Dr R G Hazell of Århus University, Denmark. Although neither structure could be adequately

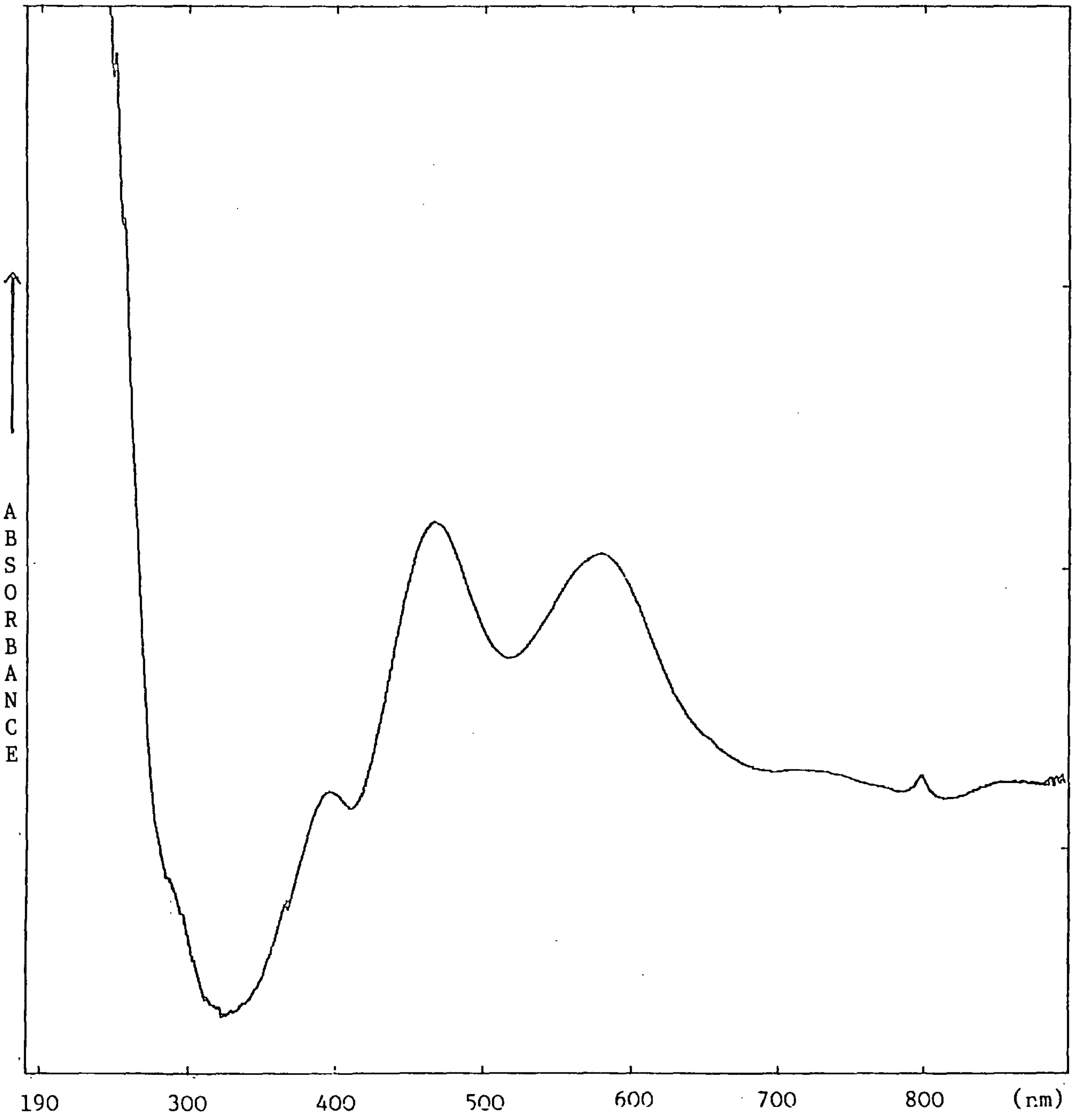
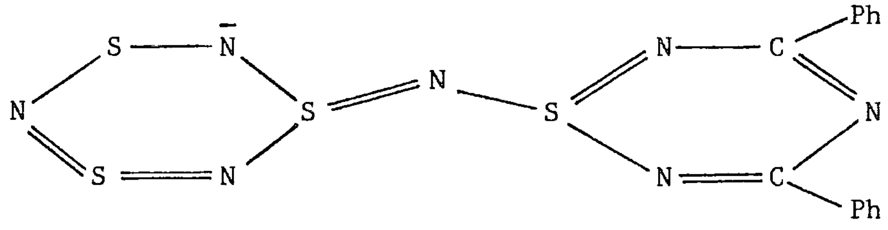


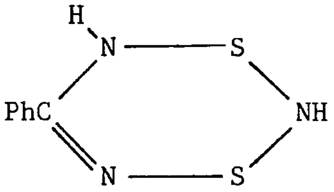
Figure 5.1 U.V.-Visible Absorption Spectrum of a $(PhCN_2S_2)_2$-NH_3 Solution

refined (R≈20%)[38] the red compound was found to be the benzamidinium salt of the anion shown as X:



[X]

The visible absorption band at 398nm lies relatively close to that expected for $[S_3N_3]^-$ (at 360nm) and so is now assigned to X.
The structure of the colourless compound was less certain but the relative atomic positions appeared to be as shown in XI.



[XI]

The hydrogen atoms were not located.
Structure X can be thought of as consisting of two known species, i.e. $[S_3N_3]^-$[20,21] and $Ph_2C_2N_3S\cdot$[39], linked by a nitrogen-atom bridge. A mechanism of the formation of X is difficult to deduce but several relevant points may be noted. The proposed mechanism for the formation of $[S_3N_3]^-$ from S_4N_4 and azide ion[21] calls for the production of a poly-SN chain which can cyclise to give the anion. Such a chain might be formed via attack of ammonia at the dithiadiazole carbon (the major component of the LUMO of $PhCN_2S_2\cdot$ is based on the CN_2 unit)[40] followed by hydrogen transfer and rupture of the S-S bond to give SN units which could cyclise to give an S_3N_3 unit. This procedure would also generate the benzamidinium cation which could itself react with available SN units to give the $Ph_2C_2N_3S$ fragment. The radical species $Ph_2C_2N_3S\cdot$ is prepared[39] by reduction of

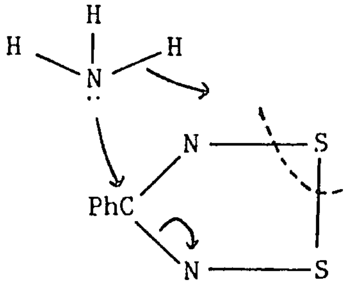
the chloride, which is itself obtained from benzamidine and $(NSCl)_3$ (a source of SN units). An alternative scheme would involve cyclization of benzonitrile (2 equiv.) with an SN unit but this is less likely since benzonitrile reacts with $(NSCl)_3$ to give[41] only $[PhCN_2S_2]Cl$.

The formation of XI obviously involves insertion of NH_3 into the S-S bond followed by hydrogen transfer but this only occurred to a very limited extent.

Neither S_3N^- nor S_4N^- were detected in the i.r. spectra of the reaction products and so must be present in very low concentration in solution. The origin of these species is a matter for speculation. The could arise via decomposition[8] of $[S_3N_3]^-$ or via reaction of elemental sulphur with ammonia.[31,36]

5.8.3 Conclusion

$(PhCN_2S_2)_2$ reacts with liquid ammonia by what must be a very complicated mechanism to give the benzamidinium salt of X as the major product. The fate of the labile hydrogen atoms is not clear. It may be that nucleophilic attack at the dithiadiazole carbon is followed by one C-N bond breaking and hydrogen transfer to the remaining dithiadiazole nitrogen. This could be followed by loss of one SN unit as well as sulphur. This is shown schematically below:



However, in the absence of N-labelling experiments this is highly speculative.

The addition of a large cation amide, e.g. $CsNH_2$, may enable better quality crystals containing anion X to be grown.

5.9 REACTION BETWEEN $(PhCN_2S_2)_2$ AND AMINES, Me_nNH_{3-n} (n=1-3)

5.9.1 Introduction

Reactions of S_4N_4 with a variety of primary amines have been reported.[42] The products were usually found to be S_8, NH_3 and a thiadiazole, although benzylamines gave benzylidenimine sulphides, $(RCH{=}N)_2S_n$ (n=1-4) and N-benzylidene benzylamines, $RCH{=}NCH_2R$, (R=Ph, 4-ClC_6H_4, 4-$CH_3OC_6H_4$).[43] Although early workers described the formation of thiobis (amines), $S(NR_2)_2$ (R=CH_3[44] C_5H_{10}[44,45]) from S_4N_4 and secondary amines, Chivers[30] obtained the piperidinium and dimethylammonium salts of a sulphur-nitrogen anion ($[S_4N_5]^-$) from S_4N_4 and the corresponding amine. However, reaction of S_4N_4 with very dilute solutions of dimethylamine in hexamethylphosphoramide gave $[S_3N_3]^-$, S_4N^- and S_3^-. Those results were interpreted[30] in terms of (in dilute solution) the formation of $[S_3N_3]^-$ from S_4N_4 and secondary amines followed (in more concentrated solution) by reaction of $[S_3N_3]^-$ with S_4N_4 to give $[S_4N_5]^-$. The dimethylammonium salt decomposed to S_4N_4 during attempted purification but the piperidinium salt was isolated along with $S(NC_5H_{10})_2$.

Reactions of S_4N_4 with tertiary amines do not seem to have been reported.

5.9.2 Results and Discussion

(a) Reaction with Methylamine

Methylamine dissolved $(PhCN_2S_2)_2$ to give a pale yellow mixture which darkened on warming to room temperature, and subsequently, to give a green-brown solution. The solution reverted to the paler colour on cooling and the change was found to be reversible (Section 5.11.8a). The increase in intensity of the green-brown colouration was accompanied by an increase in the intensity of the visible band at 610nm. This can be immediately assigned to the blue $S_3^{\cdot -}$ radical anion, previously observed in solutions of sulphur[46] and S_4N_4[30] in hexamethylphosphoramide containing dimethylamine, and also in solutions of sulphur in ammonia.[31,36] All of the u.v.-visible spectra were dominated by a very intense band or a set of bands, (band tops not observed even in dilute solution) centred in the region, 400-450nm and assigned to yellow S_6^{2-} (420-450nm).[36] The colour changes can now be associated with the position of the equilibrium between $S_3^{\cdot -}$ and S_6^{2-}. The presence of $S_3^{\cdot -}$ is favoured at higher temperatures and lower concentrations.[36] When $(PhCN_2S_2)_2$ dissolves in methylamine at ca. -6°C (m.p. $MeNH_2$), S_6^{2-} is formed and some of this dissociates to give $S_3^{\cdot -}$ on approaching room temperature.

Removal of the volatile phase, which was shown to be a mixture of methylamine and a low concentration of ammonia, gave an orange gum. This was extracted with acetonitrile to give an insoluble orange crystalline solid contaminated with a small quantity of yellow product (ca. 5%). The orange compound was characterised by Dr W Clegg of Newcastle University as bis-NN^1-methylbenzamidinium hexasulphide, using X-ray analysis. The structure of the S_6^{2-} anion has been reported[47] as the caesium salt and the present study shows no major differences.

It is difficult to be exact about the mechanism of such a complex reaction. The yield obtained shows that almost all of the sulphur from $(PhCN_2S_2)_2$ is incorporated in the S_6^{2-} ion, indicating the yield to be essentially quantitative. Since three $PhCN_2S_2$ units are required for S_6^{2-} formation, one of the $PhCN_2$ fragments must be present in the gum, probably as a benzamidine. Nucleophilic attack may occur at the ring carbon (as postulated for the ammonia reaction) and if this is followed by proton transfer to ring nitrogen which is then lost as ammonia (observed in the i.r. spectra), then free sulphur would be generated. Amines are known to react with sulphur to give sulphides[48] which may explain the formation of S_6^{2-}. Finally, a very small quantity of the eight membered ring compound, $(PhCN_2S)_2$[11], was obtained which may suggest nucleophilic attack at sulphur, followed by desulphurisation, although only to a very limited extent.

(b) Reaction with Dimethylamine

Dimethylamine dissolved $(PhCN_2S_2)_2$ to give a deep red solution. The red colour slowly faded and after 48h, excess amine was removed from a colourless solution to give a red liquid with a negligible vapour pressure. Interestingly, the first volatile material to be pumped away was a mixture of ammonia and dimethylamine. A colourless liquid was then condensed from the red liquid at 77K, and was identified from spectroscopic data, as bis (dimethylamino) sulphide, $(Me_2N)_2S$ (see Table 5.1; the i.r. data[49a] for $(Me_2N)_2S$ are given on the upper of each pair of lines, those for the colourless liquid isolated in this work are below).

Table 5.1 Infrared Data for $(Me_2N)_2S$ and Compound

2980s	2920s	2870vs	2820s	2779s	1472m	1460m
2980s	2910s	2850s	2815s	2775s	1474sh	1460sh
1449m	1430m	1240m	1197s	1138m	1046m	971s
1443s	1420sh	1237m	1193s	1134m	1037m	967s
947vs	645vs	450m				
940s	640s	454m				

The mass spectrosocopic and n.m.r. data also agree well with the literature values[49b], as does the melting point[49c] ($(Me_2N)_2S$:δ_H=2.98ppm., m.p.=20°C; colourless liquid:δ_H=2.99ppm., m.p.=21°C).

The residual red gum was not fully characterised. However, the u.v.-vis. spectra of a dilute $(PhCN_2S_2)_2$-Me_2NH solution showed only a weak band at 458nm and this disappeared as the solution lost its yellow colouration. This band is assigned to S_3N^-. No evidence was obtained for the presence of S_3^- or S_6^{2-}. All attempts to isolate a solid phase from the gum were unsuccessful (Section 5.11.8b).

The yield of $S(NMe_2)_2$ indicates that for every 64mg of sulphur present in the starting material, only 35mg is present in the product as $S(NMe_2)_2$. The nature of the other sulphur-containing species is a matter for speculation.

A strong peak in the mass spectrum at 149 could be assigned to (i) the $PhCN_2S$ fragment (perhaps derived from a polymer), (ii) the $PhC(NHMe)_2^+$ cation or (iii) an isomer of dimethylbenzamidine (the latter would occur at 149 using C.I. mass spectrometry). However, if the $PhCN_2S$ fragment were present, higher oligomers should also be observed in the mass spectrum and $PhC(NHMe)_2^+$ is unlikely to be present since this was precipitated in acetonitrile for the methylamine product (Section 5.9.2(a)). This leaves a dimethylbenzamidine as the most likely candidate for the major species present in the gum. Such a species would also explain the NH bands observed in the i.r. spectrum and the methyl signals in the ^1H n.m.r spectrum. Therefore, it may be that some, if not all, of the sulphur unaccounted for, was originally present as $(Me_2N)_2S$ but was pumped away with the excess dimethylamine.

The mechanism of this reaction is obscure, but as discussed for the methylamine reaction (Section 5.9.2(a)), nucleophilic attack is likely to occur at the ring carbon, followed by proton transfer to nitrogen (which is lost as ammonia) and liberation of free sulphur which then reacts with the amine to give $(Me_2N)_2S$.[48]

(c) Reaction with Trimethylamine

$(PhCN_2S_2)_2$ dissolved in trimethylamine to give a deep red solution. This was stirred for 5d at 21°C but no change was observed and when the amine was pumped off, only $(PhCN_2S_2)_2$ was recovered.

5.9.3 Conclusions

The reactions of $(PhCN_2S_2)_2$ with primary and secondary amines proceed by complicated mechanisms to give highly unexpected products. The one unifying theme is the preparation of products which have been formed via ring rupture and rearrangement, in accord with the presence of relatively low-lying antibonding orbitals able to accept electron density from a nucleophile. The site of nucleophilic attack could be either ring carbon or sulphur but since the LUMO is largely carbon based, the former is perhaps more likely. Another pointer to preliminary coordination of the nucleophile to carbon is the isolation of the $PhC(NHMe)_2^+$ cation from the reaction with methylamine. The formation of this cation via attack at sulphur would require transfer of a methyl group from the amine nitrogen to the ring nitrogen, and such processes are much slower than proton transfers. Since equilibrium seems to be rapidly achieved in these reactions it is not thought that such a mechanism is feasible. The use of an amine containing labelled nitrogen would clarify the situation, but this is probably not worthwhile. The next stage, after coordination may be transfer of protons to the ring nitrogens. This seems to be the rate-determining step, since trimethylamine does not react, although it may form an adduct from which the amine can be easily pumped away. Ammonia is released and free sulphur generated. The sulphur reacts with the amine to give a sulphide (for methylamine) or a thiobis (amine) (for dimethylamine).

5.10 CONCLUSIONS

$(PhCN_2S_2)_2$ was treated with the following nucleophiles: Ph_3P, Me_3P, Ph_3As, NH_3, $MeNH_2$, Me_2NH, Me_3N, Me_3NO, S_8, H^- and N_3^-. However, only the phosphines, ammonia, methylamine and dimethylamine reacted. The reaction with triphenylphosphine gave Ph_3PS as the only isolable product but the reaction with trimethylphosphine seems to be more promising since species, as yet unknown, other than Me_3PS are formed in good yield. The products obtained from the reaction with ammonia included one of special structural interest, X. Since the crystal data could not be adequately refined, it may be worthwhile attempting to grow better crystals. The reactions with amines did not give interesting species and further work in this area seems unwarranted.

In general, $(PhCN_2S_2)_2$ appears to be less reactive towards nucleophiles than S_4N_4, perhaps because of the existence of a lower energy LUMO in the latter.[50]

5.11 EXPERIMENTAL

5.11.1 Reaction between $(PhCN_2S_2)_2$ and R_3P (R=Ph,Me)

(a) $(PhCN_2S_2)_2$ (0.02g, 0.055mmol) and Ph_3P (0.029g, 0.11mmol) were intimately mixed together and the i.r. spectrum of the mixture recorded. ν max 1138w, 1089w, 1069w, 1023w, 840m, 802m, 777s, 768s, 742s, 720m, 690s, 653m, 505s cm^{-1}. The D.S.C. was then recorded and this showed melting to occur at 69°C followed by decomposition at 72°C. Another melting followed at 104°C with a further decomposition profile at 238°C. The infrared spectra of the residues obtained after stopping the D.S.C. at 120°C and 300°C were both identical. ν max 1430s, 1300vw, 1175vw, 1158w, 1098s, 1055w, 1022w, 995w, 753m, 748m, 712vs, 689s, 638m, 612w, 515m, 509m cm^{-1}. These bands can all be assigned[51] to Ph_3PS.

(b) $(PhCN_2S_2)_2$ (0.24g, 0.66mmol) and Ph_3P (0.32g, 1.22mmol) were heated to 125°C for 8h in a sealed Pyrex tube. After cooling to 20°C the tube was opened in the glove box and the orange-red solid removed. ν max 1437s, 1310w, 1275vw, 1183w, 1162w, 1108vs, 1072w, 1031m, 1002m, 980sh, 938vw, 840vw, 810vw, 772sh, 760s, 752m, 718vs, 694s, 642s, 620m, 521s, 515s, 482vw cm^{-1}. Underlined bands are assigned[52] to $(PhCN_2S_2)_2$ while the remainder are due[51] to Ph_3PS. m/z (E.I.) 326($Ph_3PS_2^+$,4%), 294(Ph_3PS^+,23), 262(Ph_3P^+,3), 256(S_8^+,3), 224(S_7^+,2), 192(S_6^+,3), 185(Ph_2P^+,13), 181($PhCN_2S_2^+$,96), 160(S_5^+,5), 149($PhCN_2S^+$,6), 135($PhCNS^+$,99), 128(S_4^+,2), 117($PhCN_2^+$,12), 108(PhP^+,22), 103($PhCN^+$,93), 96(S_3^+,2), 89(PhC^+,6), 77(Ph^+,77), 64(S_2^+,44), 46(SN^+,33), 32(S^+,15).

Sublimation of this solid under high vacuum (4 x 10^{-6} torr) at 80°C gave a minute quantity of a mixed sublimate of $(PhCN_2S_2)_2$ and Ph_3PS (identified by i.r. spectroscopy) and a dark orange-red residue, νmax 1430s, 1302vw, 1270sh, 1175w, 1157w, 1098vs, 1065m, 1022m, 995m, 970sh, 930vw, 747s, 710vs, 688vs, 632m, 612w, 509vs, 435sh cm^{-1}. All bands are due to Ph_3PS. m/z (C.I.(+),NH_3) 294(Ph_3PS^+,100%), 181($PhCN_2S_2^+$,33), 103($PhCN^+$,1), 77(Ph^+,5), 64(S_2^+,2).

(c) An intimate mixture of $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) and Ph_3P (0.52g, 2.0mmol) was sealed on a Pyrex tube _in vacuo_ and heated to 110°C for 12h. The resulting melt was cooled to 22°C and transferred to a sublimer where, at 100°C with water cooling, a white sublimate and a yellow residue were obtained. ν max (sublimate) 1480sh, 1438s, 1309m, 1185w, 1162w, 1108s, 1101s, 1071w, 1029m, 1102m, 756m, 751s, 718vs, 697vs, 642vs, 618s, 548w, 522s, 515s, 482w, 460w, 432w cm^{-1}. ν max (residue) _1580w_, 1510m, _1477sh_, _1435m_, 1400sh, 1350sh, _1310m_, 1290m, 1200sh, _1185m_, _1162m_, _1110vs_, _1072m_, _1029s_, _1002s_, _977w_, 948vw, _933vw_, 865sh, 848m, 788w, _761s_, _752s_, _720vs_, _697vs_, 690sh, _642vs_, _618s_, 595w, 575w, 550sh, 530sh, _522vs_, _512vs_, _483w_, _470w_, _433w_ cm^{-1}. The bands observed in the spectrum of sublimate are all due[51] to Ph_3PS which also gives rise to those underlined in the spectrum of the residue. The residue was dissolved in dichloromethane ($10cm^3$) and toluene ($10cm^3$) added which precipitated a yellow solid. The supernatant liquid was syringed off and the solid washed with pentane and pumped dry. δ_P(CH_2Cl_2)-2.5(Ph_3P)[12a], 0.0, 15.7, 16.9, 43.0 (Ph_3PS)[12c]ppm., supernatant liquid -3.9(Ph_3P), 15.1, 17.9, 24.0(Ph_3PO)[12b], 42.3(Ph_3PS)[12c]; the relative intensities Ph_3P:Ph_3PS were 23:9 and 1:17 respectively; the other peaks were very weak in both spectra.

(d) A solution of $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) and Ph_3P (0.26g, 1mmol) in dichloromethane ($30cm^3$) was stirred at 21°C for 94h. The solvent was then pumped off leaving an orange-yellow solid. ν max _1480sh_, _1437s_, _1310w_, 1290vw, _1264w_, 1200sh, _1186m_, _1162w_, 1142m*, 1115sh, _1109vs_, _1073m*_, _1030s_, _1004m*_, _975w_, 930w*, 904vw*, 842w*, 835sh*, 810s*, 784s*, 772s*, _760m_, _752m_, _722vs_, _698vs*_, 660s*, _643s_, _619m_, 548m, 537m, 524s, _517s_, _483w_, _462w_, _436w_ cm^{-1}. Underlined bands are due[51] to Ph_3PS, those marked with an asterisk[52] to $(PhCN_2S_2)_2$.

(e) A solution of $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) and Ph_3P (0.26g, 1mmol) in acetonitrile ($2cm^3$) was stirred at 21°C for 26h during which time a white solid was precipitated. This was filtered off, washed with acetonitrile ($2cm^3$) and pumped dry, 0.04g, ν max 1433s, 1306w, $\underline{\text{1249w}}$, $\underline{\text{1224w}}$, 1180w, 1160w, $\underline{\text{1139m}}$, 1106s, $\underline{\text{1100sh}}$, 1070w, 1026m, 1000m, 930w, 921w, 900w, $\underline{\text{836m}}$, $\underline{\text{805m}}$, $\underline{\text{780s}}$, $\underline{\text{770s}}$, 758m, 748m, $\underline{\text{740w}}$, 719vs, 692vs, $\underline{\text{656s}}$, 640s, 614m, 532w, 520s, 512s, 478w, 459w, 430w cm^{-1}. The filtrate was pumped to dryness. ν max 1435s, 1310w, 1182w, 1160vw, $\underline{\text{1140vw}}$, 1120sh, 1118s, $\underline{\text{1100sh}}$, 1070w, 1029m, 1000m, $\underline{\text{840w}}$, $\underline{\text{808w}}$, $\underline{\text{780m}}$, $\underline{\text{770w}}$, 758m, 749m, 720s, 695s, $\underline{\text{658w}}$, 640s, 615w, 545sh, 532sh, 520s, 512s cm^{-1}. In both spectra underlined bands are assigned[52] to $(PhCN_2S_2)_2$ and the remainder[51] to Ph_3PS.

(f) $(PhCN_2S_2)_2$ (0.09g, 0.25mmol) and Ph_3P (0.13g, 0.5mmol) were sealed in a 10mm O.D. n.m.r. tube together with acetonitrile ($4cm^3$) and dichloromethane -d_2 ($1cm^3$). The tube was taped to a rotating wooden disc to ensure mixing.

(g) $(PhCN_2S_2)_2$ (21mg, 0.056mmol) and Ph_3P (30mg, 0.116mmol) were sealed up in a 5mm O.D. n.m.r. tube with acetonitrile -d_3 ($4cm^3$). Again the tube was taped to a rotating wooden disc for mixing. A similar experiment was carried out with an excess of Me_3P in $CDCl_3$.

5.11.2 Attempted Reaction between $(PhCN_2S_2)_2$ and Ph_3As

The D.S.C. of an intimate mixture of $(PhCN_2S_2)_2$ (15.0mg, 0.043mmol) and Ph_3As (25.3mg, 0.083mmol) was recorded. The process was repeated for a mixture of $(PhCN_2S_2)_2$ (9.0mg, 0.025mmol) and Ph_3As (30.6mg, 0.1mmol). In both cases melting occurred at 55.7°C (cf. m.pt.

$(PhCN_2S_2)_2$[53]:126°C, Ph_3As[54]:61°C). No exotherm was observed below 200°C.

5.11.3 Attempted Reaction between $(PhCN_2S_2)_2$ and S_8

An intimate mixture of $(PhCN_2S_2)_2$ (0.09g, 0.25mmol) and S_8 (0.016g, 0.063mmol) was made up and a sample (1.6mg) taken for D.S.C. The trace showed two endotherms at 97.0°C and 105.3°C. A re-run of the same sample gave an identical result, no exotherm being observed up to 200°C (cf. m.pt. $(PhCN_2S_2)_2$[53]:126.6°C, S_8[53]:119°C).

5.11.4 Attempted Reaction between $(PhCN_2S_2)_2$ and Me_3NO

A solution of $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) and Me_3NO (0.15g, 2mmol) in toluene (20cm^3) was stirred at 80°C for 6h. After cooling, the solvent was pumped off leaving a dark red solid. ν max $\underline{1475sh}$, $\underline{1440sh}$, $\underline{1410w}$, $\underline{1370sh}$, 1320w, $\underline{1260m}$, 1240m, 1225m, 1185w, 1178w, 1160w, 1145sh, 1139s, 1078m, 1026s, 924m, 903m, 845sh, 840s, 832m, 808vs, 782vs, 771vs, $\underline{750w}$, 715w, 690vs, 656vs, 610w, 575w, 510vs, 460w, 430w, 400w cm^{-1}. Underlined bands are due[53] to Me_3NO, the remainder[52] to $(PhCN_2S_2)_2$.

5.11.5 Attempted Reaction between $(PhCN_2S_2)_2$ and Me_4NN_3

A solution of $(PhCN_2S_2)_2$ (0.36g, 1mmol) and Me_4NN_3 (0.24g, 2mmol) in methanol (20cm^3) was stirred at 60°C for 2h. After cooling to 21°C the red supernatant liquid was syringed off from green crystals of $(PhCN_2S_2)_2$. The red solution was pumped to dryness to give a pale red solid. ν max 1970vs,bd, $\underline{1308m}$, 1283m, $\underline{1187w}$, $\underline{1170w}$, 1102s, $\underline{1068w}$, 1042w, $\underline{1021w}$, $\underline{930w}$, $\underline{894w}$, 820m, $\underline{800w}$, 740s, 705sh, $\underline{690s}$, $\underline{650m}$, 600m, $\underline{510m}$ cm^{-1}. Underlined bands are due[52] to $(PhCN_2S_2)_2$, the remainder[53] to Me_4NN_3.

5.11.6 Attempted Reaction between $(PhCN_2S_2)_2$ and NaH

A solution of $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) and 18-crown-6 ether (0.26g, 1mmol) in thf ($20cm^3$) was stirred with NaH (0.023g, 1mmol) at 21°C for 18h. The hydride was allowed to settle out and the red supernatant liquid transferred to another Schlenk via syringe and pumped dry giving a red solid. ν max 1352s, $\underline{\text{1320m}}$, 1298m, 1289m, 1250m, 1110vs,bd, $\underline{\text{1026m}}$, 962m, 950m, $\underline{\text{900w}}$, $\underline{\text{833m}}$, $\underline{\text{803m}}$, $\underline{\text{770m}}$, 754w, $\underline{\text{698s}}$, $\underline{\text{655m}}$, 595w, 548m, $\underline{\text{507w}}$ cm^{-1}. The experiment was repeated at 60°C for 17h but an identical spectrum was obtained. Underlined bands are due[52] to $(PhCN_2S_2)_2$, the reminder[53] to 18-crown-6 ether.

5.11.7 Reaction between $(PhCN_2S_2)_2$ and Ammonia

Ammonia (1.50g, 0.09mol) was condensed onto $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) in a dog (Figure 7.2) at 77K. On warming to 21°C a purple solution was obtained which gradually darkened and after 20 to 30 min. became an intense blue colour. After ~24h the ammonia was pumped off to give a red gum. This was extracted with dichloromethane to give a red solution which, on removal of solvent gave a red crystalline solid. Yield 0.08g. νmax 3300bd,s 1675s, 1610w, 1525w, 1480m, 1350m, 1298w, 1262w, 1180m, 1150w, 1110w, 1070w, 1030sh, 1020s, 930s, 888m, 853w, 815m, 793sh, 780s, 740m, 697s, 678w, 650w, 639w, 620w, 600m, 532m, 488m, 462m cm^{-1}. $\delta_H(CD_2Cl_2)$ 7.55(br m), m/z(E.I.)252(7%), 197(4), 195(3), 182(96), 181(69), 175(12), 163(51), 161(35), 138(2), 121(92), 103(95), 92(7), 77(10), 64(30), 58(100), 46(47), 42(98), 41(94), 40(18).

A very small quantity of a colourless compound was also obtained (ca. 5mg). The temperature ripple method (Section 7.3) was used to grow crystals of both compounds together in a concentrated dichloromethane solution.

A solution suitably dilute for a u.v.-visible study was made up in a silica ampoule (8mm O.D.) by dissolving a few crystals (<1mg) of $(PhCN_2S_2)_2$ in ca. 2.5cm^3 ammonia.

5.11.8 Reaction between $(PhCN_2S_2)_2$ and Me_nNH_{3-n} (n=1-3)

(a) Reaction with Methylamine

Methylamine (ca. 2.0g, 0.06mol) was condensed onto $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) in a 'dog' (Figure 7.2) at -196°C. When the methylamine melted at ca. -6°C, the $(PhCN_2S_2)_2$ immediately dissolved to give a purple solution which almost at once changed to a pale yellow-brown colour which darkened over ca. 12h. The amine was pumped off and was monitored by gas phase i.r. spectroscopy. ν max (initial, P=30cmHg) 3360m*, 3330w, ~2900v.br,vs, 2320w,br, 2100w, 2080w, 1830br,m, 1623vs, 1460vs, 1411s, 1198vw, 1179vw, 1162w, 1154w, 1134w, 1125w, 1120w, 1108w, 1090m, 1090sh, 1082s, 1060s, 1049s, 1039s, 1018s, 997m, 972s*, 952w, 935s*, 910w, 896w, 891w, ~780v.br,vs cm^{-1}. Other samples were very similar. Finally, when the vapour pressure had fallen to 5cmHg the spectrum showed only methylamine to be present. ν max 2900vs, 1622m, 1450m, 1065m, 1042s, 1025m, 800s, 780s, 760s cm^{-1}. The above bands marked with an asterisk are due to the fundamental vibrational modes of ammonia[55a], while those underlined are due to methylamine.[56] The remainder are the rotational fine structure bands of ammonia.[55b] An attempt was made to vacuum transfer any more volatile component that remained into a Rotoflo vessel held at -196°C, but no material was collected. The residue, an orange gum, was washed with acetonitrile to give the sparingly soluble orange crystalline solid $[PhC(NHMe)_2]_2S_6$. Yield, 0.16g, m.p. 155.1°C (decomp.), Found, C,43.1; H,5.1; N,10.6%. $C_{18}H_{26}N_4S_6$ requires C,44.1; H,5.3; N,11.4%. ν max

3130m, 2720sh, 1642s, 1606m, 1570m, 1490w, 1448m, 1435sh, 1390m, 1370m, 1198s, 1165w, 1150w, 1075w, 1040s, 1030sh, 1002vw, 978vw, 946vw, 928vw, 867vw, 780s, 772s, 746sh, 730w, 712s, 704s, 644w, 561w, 515sh, 509sh, 500s, 450w cm^{-1}. $\delta_H(CD_3CN)$ 3.58(6H,s,$2CH_3$), 8.21(5H,m,C_6H_5), m/z(E.I.) 149($PhC(NHMe)_2^+$,89%), 134($PhC(NHMe)NH^+$,6), 128(S_4^+,2), 119($PhC(NH)_2^+$,100), 104($PhCNH^+$,37), 96(S_3^+,10), 89(PhC^+,14), 77(Ph^+,50), 70($(MeN)_2C^+$,42), 64(S_2^+,4), 55($MeNCN^+$,29), 41($MeNC^+$,30). A minute quantity (<u>ca</u>. 10mg) of a yellow compound was also observed using a microscope. This was separated by hand. m/z 298(12%), 266(100), 252(5), 149(100), 117(22). cf. m/z $(PhCN_2S)_2$[11]: 298, 253, 252, 195, 181, 167, 149, 135, 103, 77, 64, 46. The acetonitrile washings were pumped dry to give an orange gum. ν max 3420sh, 3200v.bd,s, 2900bd,s, 2780sh, 1650sh, 1630vs, 1600s, 1385w, 1375bd,w, 1272w, 1260m, 1232m, 1198m, 1180sh, 1155m, 1114m, 1072w, 1030m, 1000bd,m, 916m, 855bd,w, 774s, 701s, 563w, 496m, 451m cm^{-1}.

The u.v. spectra were recorded on samples prepared in the same manner as those discussed for ammonia in Section 5.11.7. Two samples were made up: one containing 0.1g $(PhCN_2S_2)_2$ in <u>ca</u>. 2.5cm^3 $MeNH_2$, the other containing 0.02g $(PhCN_2S_2)_2$ in <u>ca</u>. 2.5cm^3 $MeNH_2$.

(b) <u>Reaction with Dimethylamine</u>

Dimethylamine (ca. 2.0g, 0.04mol) was condensed onto $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) contained in a Rotoflo ampoule at 77K. On warming to 21°C a red solution was obtained which slowly faded over 48h to give a very pale yellow (almost colourless) solution. The excess amine was then pumped away and was monitored by gas-phase i.r. spectroscopy.

ν max (initial, P=33cm Hg) 3415vw*, 3340m*, <u>3180</u>br,m, ~<u>2900</u>v.br,vs, <u>2390w</u>, <u>2075m</u>, <u>1890</u>br,m, 1761w, 1739w, 1722w, 1712w, 1709w, 1693m, 1678w, 1669w, 1662w, 1641w, 1629s, 1615w, 1596w, 1580w, 1561w, 1544m,

~1470v.br,vs, 1214w, 1198m, 1170v.br,vs, 1105w, 1088m, 1078m, 1070m, ~1030v.br,vs, 998s, 970vs*, 952s, 935vs*, 912s, 895s, 890s, 875m, 872s, 859s, 852m, 838m, 832s, 820s, 810s, ~720v.br,vs cm^{-1}. The bands marked with an asterisk are the fundamental modes of ammonia[55a], those underlined are due to dimethylamine[56] while the remainder are the rotational fine structure bands of ammonia.[55b] Later samples taken from the volatile phase were very similar. When the vapour pressure had fallen to 10cm Hg, only dimethylamine was observed in the gas phase, ν max ~2900v.br,vs, 2390vw, 2075w, 1880w, ~1470br,vs, 1170vs, 1028s, 940m, 920m, ~730v.br,vs cm^{-1}. When a negligible pressure was recorded, a colourless liquid was condensed into another Rotoflo vessel cooled to 77K. Yield 0.13g; m.p. 21°C, ν max (contact film) 2980s, 2910s, 2850s, 2815s, 2775s, 1474sh, 1460sh, 1443s, 1420sh, 1400w, 1285w, 1237m, 1193s, 1134m, 1091w, 1037m, 967s, 940s, 802w, 640s, 454m, 380w, 350w cm^{-1}. $\delta_H(CD_2Cl_2)$ 2.99ppm(s) m/z(C.I+) 120(100%), 76(7), 46(86), 44(77), 35(56). When all of the colourless liquid had been transferred (no further change in mass of original Rotoflo) a red gum remained. Weight, 0.21g, ν max (contact film) 3310m, 3060m, 3030w, 2990w, 2940m, 2870m, 2800w, 1592vs, 1571vs, 1500w, 1482m, 1448s, 1414s, 1400s, 1290m, 1182s, 1142w, 1109w, 1062s, 1030m, 1004vw, 992vw, 958m, 925w, 896m, 810sh, 782vs, 710vs, 660m, 630m, 582vw, 560m cm^{-1}. $\delta_H(CD_2Cl_2)$ 2.56(s,2), 2.68(s,3), 2.84(s,14), 6.30(s,br,2), 7.33(m,12), m/z(C.I.+) 310(0.4%), 253(0.6), 239(0.9), 211(0.3), 185(0.5), 149(100), 121(5), 46(10), 44(7).

(c) Reaction with Trimethylamine

Trimethylamine (2.0g, 0.03mol) was condensed onto $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) in a Rotoflo ampoule at 77K. On warming to 21°C a deep red solution was observed. No change was observed after 5d and so the amine was pumped off and the i.r. of the purple-red residue recorded.

ν max 1225w, 1138w, 1068w, 1020w, 924vw, 902vw, 838w, 830w, 806m, 778s, 770m, 685m, 653s, 510m cm^{-1}. All bands can be assigned to $(PhCN_2S_2)_2$.[52]

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CHAPTER 6

THE REACTIONS OF PHENYL DITHIADIAZOLE WITH SOME ELECTROPHILIC AND FREE RADICAL REAGENTS

6.1 GENERAL INTRODUCTION

Most reported reactions of dithiadiazoles have involved electrophilic species and resulted in the formation of dithiadiazolium salts. Much of this work was carried out in Durham[1] where species of general formula $[PhCN_2S_2]X$ (X=Cl,Br,I,$SbCl_6$,AsF_6) were prepared from $(PhCN_2S_2)_2$, and SO_2Cl_2, $SOCl_2$, $(NSCl)_3$, Br_2, I_2, $SbCl_5$ and $S_8{}^{2+}$ or $Se_8{}^{2+}(AsF_6)_2{}^-$, respectively. The radicals $XCN_2S_2\cdot$ (X=F,Cl,Br,CF_3) have been prepared by Mews[2] and reacted with a variety of electrophilic and radical compounds. Reaction of the chloro- and bromo- derivatives with SO_2Cl_2 gave the corresponding chloride salts. Interestingly, the reaction of the chloro- and trifluoromethyl radicals with their chloride salts gave the novel compounds $[XCN_2S_2]_3Cl$ (X=Cl,CF_3). The structure of the latter is shown in Figure 1.4.

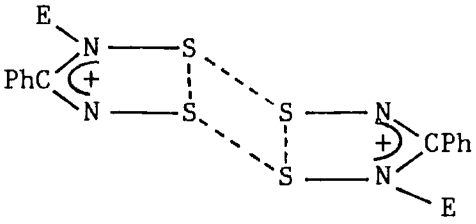
The action of $[ClCN_2S_2]SbCl_6$ upon $ClCN_2S_2\cdot$ gave only $[ClCN_2S_2]_2SbCl_5$ and $[ClCN_2S_2]Cl$. The reaction[2] of $ClCN_2S_2\cdot$ with the radicals O_2, NO and $(CF_3)_2NO$ led to isolation of the chloride salt, although in liquid SO_2 the latter gave the fluorosulphate and $CF_3N{=}CF_2$.

The work described in this chapter extends the use of electrophilic reagents to include those capable of protonation, methylation, acetylation and trimethylsilylation. Species used as radicals or potential sources of radicals include NO, N_2O_4, N_2F_4,$(Me_3Sn)_2$ and AgF_2. The reaction with the electron acceptor TCNQ (tetracyanoquinodimethane) is also discussed. Where appropriate, S_4N_4 is used as a 'model' compound (for comparison with $(PhCN_2S_2)_2$) as discussed in Chapter 1. Due to the nature of the experiments discussed in this chapter, the Results and Discussion section is divided into three parts: Section A deals with reactions involving species of general formula EX (E=Me,MeCO,Me_3Si,H; X=I,SO_2F,Cl,Br,BF_4), Section B deals with the radical species mentioned above and Section C is devoted to the reaction of $(PhCN_2S_2)_2$ with TCNQ.

6.2 RESULTS AND DISCUSSION

SECTION A: Reactions of $(PhCN_2S_2)_2$ with Electrophilic Reagents

The aim of this series of experiments, involving reaction of $(PhCN_2S_2)_2$ with species of general formula EX (E=Me,MeCO,Me_3Si,H; X=I,SO_2F,Cl,Br,BF_4), was to prepare compounds in which the electrophile (E) has attached itself to the ring via the lone pair on nitrogen. Such compounds might adopt a structure similar to that[3] of $S_6N_4Cl_2$ as shown below in I.



[I]

Attack at sulphur was thought less likely on electronegativity grounds and this is supported by MNDO calculations which show the atomic charge on nitrogen to be -0.24, whereas that on sulphur is +0.13 (Section 1.6).

6.2.1 Reaction of $(PhCN_2S_2)_2$ with HCl.

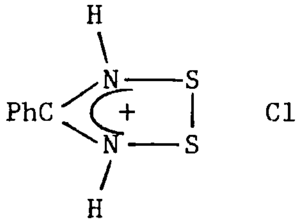
Although S_4N_4 reacts[4] with HCl to give S_4N_3Cl and NH_4Cl, the loss of a nitrogen atom was thought less likely to occur with $(PhCN_2S_2)_2$; cf. reactions of S_4N_4[5] and $(PhCN_2S_2)_2$[1] with bromine to give $[S_4N_3]Br_3$ and

[$PhCN_2S_2$]Br, respectively. However, the reaction is thought[4] to proceed via S_4N_4HCl, presumably protonated on nitrogen, and so it was hoped a compound with the structure shown in I (E=H, X=Cl) could be isolated.

The reaction (with dry HCl) in fact produced two products which separate incompletely on dichloromethane extraction (Section 6.4.1). I.r. spectroscopy identified one of the components of the mixture as [$PhCN_2S_2$]Cl. The i.r. spectrum of material rich in the other component showed some resemblance to that of [$PhC(NH_2)_2$]$Cl.H_2O$ (Section 6.4.1). Also, no e.s.r. signal was observed[6] from the mixture, indicating no free radical monomer from I was present (such a species would be expected to be partially dissociated in the solid state[7]). This evidence suggests the following reaction scheme:

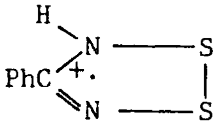
$$(PhCN_2S_2)_2 + 2HCl \longrightarrow [PhCN_2S_2]Cl + [PhC(NH)_2S_2]Cl$$

A suggested structure for [$PhC(NH)_2S_2$]Cl, II, is given below:

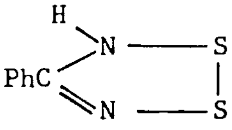


[II]

A plausible mechanism for this reaction invokes the initial formation of a short-lived radical cation intermediate, III, which, rather than dimerize to give I, accepts an electron from a dithiadiazole radical to form IV. The electron transfer reaction also results in the formation of the dithiadiazolium cation, $PhCN_2S_2^+$.



[III]



[IV]

Carbon based heterocycles containing an $HN^{+\cdot}$ unit are well-known.[8] Species IV can then accept a second proton from HCl to form II.

6.2.2 Reaction of $(PhCN_2S_2)_2$ with $HBF_4.OEt_2$: Preparation of $[PhC(NH)_2S_2]BF_4$

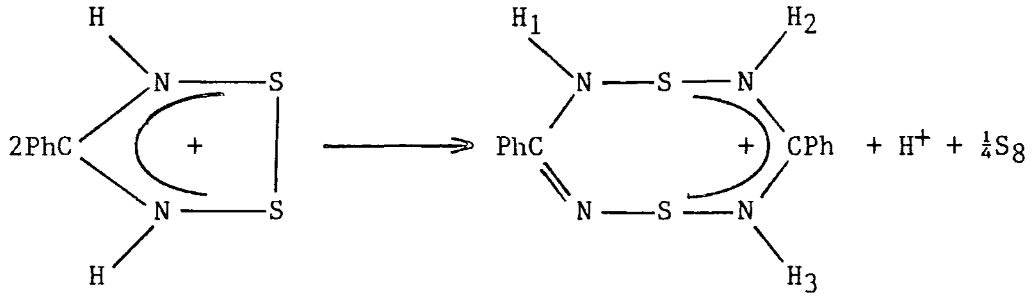
In order to achieve separation of the two species obtained in the reaction of $(PhCN_2S_2)_2$ with a protonic acid (HCl) it was decided to try tetrafluoroboric acid-diethyl etherate (usually formulated $Et_2OH^+BF_4^-$) as the source of H^+. It was hoped that the expected hydrogen-bonding between cation and anion in the protonated product would make the compound less soluble than the analogous chloride, in dichloromethane, whereas the $[PhCN_2S_2]BF_4$ should exhibit greater solubility in this solvent (BF_4^- is a harder, less interacting species than Cl^-).

Tetrafluoroboric acid-diethyl etherate is known[9] to protonate S_4N_4 on nitrogen, in dichloromethane, to give $S_4N_4H^+BF_4^-$ with hydrogen-bonding between the proton and the fluorine atoms of the anion.

In this work, the two products were indeed separated in dichloromethane giving orange, soluble $[PhCN_2S_2]BF_4$ and a white insoluble product analysing as $C_7H_7N_2BF_4S_2$ and presumed to be the tetrafluoroborate salt of the cation in II.

The mass and infrared spectra support this proposal (Section 6.4.2). The i.r. spectrum is quite similar to that of the material obtained in the reaction of $(PhCN_2S_2)_2$ with HCl and formulated as $[PhC(NH)_2S_2]Cl$; the additional strong band at $1040cm^{-1}$ can be assigned[10] to BF_4^-.

However, the ^1H n.m.r. data, obtained from acetonitrile solutions, are not consistent with the presence of $[PhC(NH)_2S_2]BF_4$. Three low field signals, at 8.67, 8.97 and 9.59ppm. (relative intensities 1:1:1), were observed and these are all assignable to NH protons.[11a] The signals at 8.67 and 8.97ppm. broaden on warming in 10K steps from 295K to 325K, whereas the signal at 9.59ppm. remains unchanged. Also, the white product $[PhC(NH)_2S_2]BF_4$ dissolves to give orange solutions from which a yellow solid precipitated. These results indicate that $[PhC(NH)_2S_2]BF_4$ decomposes in solution, perhaps as follows:



[V]

The observed signal broadening may then be due to H_1 flipping between the two nitrogen atoms on the l.h.s. of compound V, as a result of which the environments of H_2 and H_3 are averaged. After cooling back down to 295K an additional doublet was observed at 8.55ppm. (J=6.8Hz) and after 6 weeks at room temperature this was the only signal present in the NH region (Section 6.4.2). The origin of this signal is unknown. The liberated proton will be present as $MeCNH^+$ and was not observed possibly due to exchange broadening. The ^{13}C n.m.r. data support this proposal in that two low-field signals, at 166.27 and 168.58ppm., lie close to those observed for the carbon atoms bonded to nitrogen in amidinium chlorides.[12] The remaining signals may be assigned to two sets of phenyl groups.[11b] The ^{19}F n.m.r. spectrum shows a sharp singlet at -140ppm. immediately assignable[13] to BF_4^-.

Although the number of observed signals is adequately explained in the above discussion, the position of the H_1 peak relative to those for H_2 and H_3 is not as expected. Since H_2 and H_3 are more acidic than H_1, their n.m.r. signals should occur downfield of that due to H_1. Further work is justified, perhaps including a crystal structure of the compound recovered from the solution obtained on dissolving $[PhC(NH)_2S_2]BF_4$ in acetonitrile.

6.2.3 Attempted Reaction of $(PhCN_2S_2)_2$ with MeX (X=I,OSO2F)

The aim of these experiments was to prepare the methyl analogues of the protonic species discussed in the previous sections. However, the stirring of a solution of $(PhCN_2S_2)_2$ in neat iodomethane, in which the anticipated product was expected to be only partially soluble, at 45°C for five days did not lead to reaction. At higher temperatures, decomposition occurred to give an oil containing a high proportion of iodine (83.5%). The stronger methylating agent, methyl fluorosulphate, likewise did not react with $(PhCN_2S_2)_2$ in dichloromethane at 21°C (Section 6.4.3).

6.2.4 Reaction of $(PhCN_2S_2)_2$ with Me_3SiX (X=Cl,Br)

The object of these experiments was to prepare the trimethylsilyl derivatives of the species discussed in Section 6.2.1 and 6.2.2. However, treatment of $(PhCN_2S_2)_2$ with trimethylchlorosilane in toluene at 65°C for 12h gave only unreacted starting materials. Since the Si-Br ($330KJmol^{-1}$) is weaker than the Si-Cl bond ($410KJmol^{-1}$), a toluene solution of $(PhCN_2S_2)_2$ was stirred with trimethylbromosilane at 21°C. In this case reaction did occur, but only to give $[PhCN_2S_2]Br$ and, presumably, $(Me_3Si)_2$, although this was not detected (Section 6.4.4).

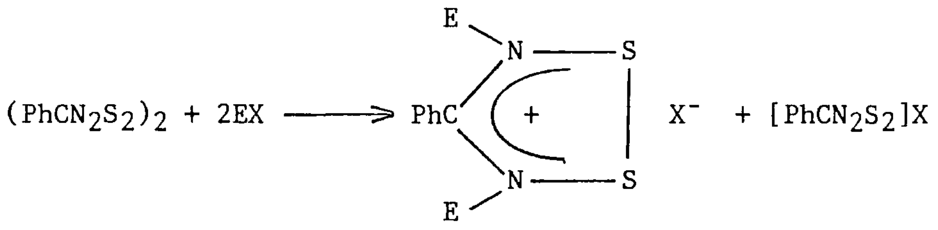
6.2.5 Reaction of $(PhCN_2S_2)_2$ with CH_3COBr

This reaction was performed to obtain the acetyl derivative of the species discussed in Sections 6.2.1 and 6.2.2. However, addition of acetyl bromide to a toluene solution of $(PhCN_2S_2)_2$ gave only $[PhCN_2S_2]Br$ and $(CH_3CO)_2$ (Section 6.4.5).

Diketones have been prepared[14] previously from acetyl halides using SmI_2 or pyrophoric lead.

6.2.6 A Brief Thermodynamic Discussion of the Reactions of $(PhCN_2S_2)_2$ with Electrophilic Reagents

The above results indicate that two pathways are available for the reaction of $(PhCN_2S_2)_2$ with an electrophile. These are given as reactions (1) and (2):



(1)

$$(PhCN_2S_2)_2 + 2EX \longrightarrow 2[PhCN_2S_2]X + E\text{-}E \qquad (2)$$

Reaction (1) occurs only for E=H, while reaction (2) occurs for E=CH_3CO and Me_3Si.

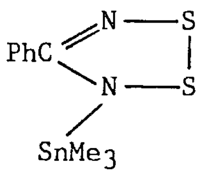
The thermodynamic parameters relevant to this discussion are (i) the ionization potential of $(PhCN_2S_2)_2$, (ii) the E-X bond energy, (iii) the lattice energy of the ionic products, (iv) the electron affinity of X, (v) the E-E bond energy, and (vi) for reaction (1) only, the E-N bond energy. The energy involved for the first two parameters must be supplied to the system whereas the remaining parameters represent energy recovered and provide the driving force for reaction to occur. The ionization potential of $(PhCN_2S_2)_2$ and the lattice energies mentioned above are not available but certain features may be noted.

For the reactions involving protonic acids (i.e. E=H), if we assume that the lattice energies of $[PhC(NH)_2S_2]X$ and $[PhCN_2S_2]X$ are approximately equal, then the driving force for reaction (1) compared with reaction (2) may be the strength of the two N-H bonds (2 x $391KJmol^{-1}$)[15] relative to that of the H-H bond ($435KJmol^{-1}$). Although reaction (1) is more favourable for $E=CH_3CO$ and Me_3Si on bond energy grounds (B.E.(Si-Br)=330; (C-Br)=290; (N-Si)=333; (N-C)=286; (Si-Si)=226; (C-C)=$347KJmol^{-1}$)[15], the lattice energy of $[PhC(NE)_2S_2]X$ will be slightly lower than that of $[PhCN_2S_2]Br$ (lattice energy is inversely proportional to ionic radius) and there will also be greater delocalisation energy in $PhCN_2S_2^+$. These factors, especially the latter (delocalisation energy) may well provide the driving force for reaction (2). $(PhCN_2S_2)_2$ did not react at all with MeI or $MeOSO_2F$ and this may be due to the low lattice energy of $[PhCN_2S_2]I$ and $[PhCN_2S_2]OSO_2F$.

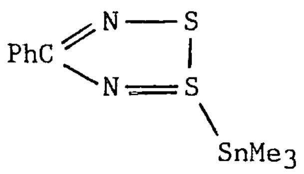
SECTION B: Reaction of $(PhCN_2S_2)_2$ with Radical Species

6.2.7 Attempted Reaction of $(PhCN_2S_2)_2$ with $(Me_3Sn)_2$

Hexamethyldistannane, $(Me_3Sn)_2$, is known to act as a source of $Me_3Sn\cdot$ radicals when photolysed[16] in the presence of di-tert-butyl peroxide $(^tBuO)_2$. However, photolysis of a mixture of $(PhCN_2S_2)_2$, $(Me_3Sn)_2$ and $(^tBuO)_2$ in thf at 21°C for 18h did not lead to reaction to give the desired monostannylated ring, V or VI.



[VI]

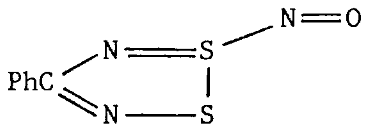


[VII]

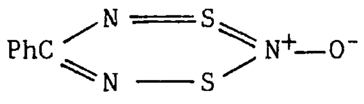
The bond energies involved^{17}, i.e. Sn-Sn at 151, Sn-N at 172 and Sn-S at 217KJmol^{-1}, suggest VII to be a more likely product than VI. The lack of reactivity may be due to other factors perhaps connected with loss of π-bond energy in the ring (Section 6.2.6).

6.2.8 Attempted Reaction of $(PhCN_2S_2)_2$ with NO

The aim of this work was to prepare species such as $NO^+PhCN_2S_2^-$, VIII or IX:



[VIII]



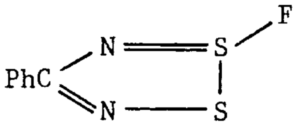
[IX]

However, reaction did not occur (Section 6.4.7).

The failure to generate $NO^+PhCN_2S_2^-$ most probably stems from the low oxidising ability of $PhCN_2S_2\cdot$ (Section 1.7.3). Species VIII and IX are perhaps not formed for reasons similar to those discussed in Sections 6.2.6 and 6.2.7. For example, bond energy considerations indicate compound VIII to be stable (B.E.(N O)^{15}=634; (N=O)^{15}=596; (S-N)^{18a} 247 KJmol^{-1} (the latter value is for $(SNH)_4$). The loss of delocalisation energy may account for the fact that VIII was not obtained.

6.2.9 Reaction of $(PhCN_2S_2)_2$ with AgF_2: Preparation of $[PhCN_2S_2]_3F$ and $PhCN_2S_2F$

The nucleophilic radical oxidising agent AgF_2 reacts[19] with S_4N_4 to give $S_4N_4F_2$ together with a little $(NSF)_3$ and $(NSF)_4$. The reaction is thought to proceed[20] via interaction of the high energy SOMO of the radical, in this case F·, and the low lying LUMO of S_4N_4. In this work it was hoped that AgF_2 would fluorinate $(PhCN_2S_2)_2$ to give X as a result of interaction of F· with the SOMO of $PhCN_2S_2\cdot$.



[X]

Reaction of $(PhCN_2S_2)_2$ wiith an excess of AgF_2 in carbon tetrachloride gave a yellow solution which, on pumping to dryness, yielded a dark green solid, the analysis (C,H,N) for which was in excellent agreement with that required for X. (Found: C,42.7; H,2.3; N,13.7%; $PhCN_2S_2F$ required C,42.0; H,2.5; N,14.0%.) However, sublimation of this material gave a purple sublimate of $(PhCN_2S_2)_2$ and a yellow-brown residue. This evidence, together with the i.r. spectrum which shows bands characteristic of both dithiadiazole- and dithiadiazolium species (Section 6.4.8)[1], although clearly not a simple mixture of both, suggests that either $[PhCN_2S_2]_2F$ or $[PhCN_2S_2]_3F$ have been prepared. Similar species are known in that $[PhCN_2S_2]_2Cl$ can be prepared[21] by simply grinding $(PhCN_2S_2)_2$ and $[PhCN_2S_2]Cl$ together in a mortar and pestle; crystals can be obtained by allowing saturated solutions of the two starting materials to diffuse together through a glass sinter[21], although none have been found suitable for X-ray analysis. Compounds of general formula $[XCN_2S_2]_3Cl$ (X=Cl,CF_3) have been reported by Mews[2] (Section 1.4) and the structure of the latter is given in Figure 1.4. The sublimation can now be represented by one of the processes given below:

$$2[PhCN_2S_2]_2F \longrightarrow (PhCN_2S_2)_2 + 2\ PhCN_2S_2F \qquad (1)$$

$$[PhCN_2S_2]_3F \longrightarrow (PhCN_2S_2)_2 + PhCN_2S_2F \qquad (2)$$

$$2[PhCN_2S_2]_3F \longrightarrow (PhCN_2S_2)_2 + [PhCN_2S_2]_2F \qquad (3)$$

Sublimation of 0.02g green compound gave 0.01g $(PhCN_2S_2)_2$ and 0.005g residue. These weight changes suggest that process (2) is proceeding since 0.02g $[PhCN_2S_2]_3F$ would give 0.013g $(PhCN_2S_2)_2$ and 0.007g $PhCN_2S_2F$, whereas in process (1) 0.01g $(PhCN_2S_2)_2$ and 0.01g $PhCN_2S_2F$, and in process (3) 0.006g $(PhCN_2S_2)_2$ and 0.014g $[PhCN_2S_2]_2F$ would be formed.

The mass spectrum gave a major peak at 181, as expected for a $PhCN_2S_2$ species, together with minor peaks at 200 for $PhCN_2S_2F$ and 381 for $[PhCN_2S_2]_2F$ (Section 6.4.8).

In accord with the paramagnetic nature of $[PhCN_2S_2]_3F$, n.m.r. spectra could not be obtained.

The isolation of $[PhCN_2S_2]_3F$ rather than $PhCN_2S_2F$ is most probably due to the reaction between $(PhCN_2S_2)_2$ and $PhCN_2S_2F$, formed as an intermediate, being faster than the heterogeneous reaction between $(PhCN_2S_2)_2$ and AgF_2.

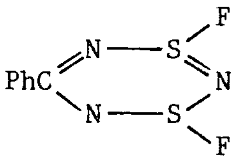
The mass and i.r. spectra (Section 6.4.8) of $PhCN_2S_2F$ suggest that it adopts the structure shown in X.

Although the covalent species, FCN_2S_2F, has been postulated[2] as an intermediate in the reaction of $[ClCN_2S_2]Cl$ with AgF_2, the compounds described in this section are the first examples of dithiadiazolium fluorides to be isolated.

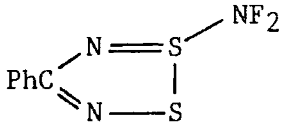
6.2.10 Reaction of $(PhCN_2S_2)_2$ with N_2F_4

(a) Reaction in Liquid Sulphur Dioxide: Preparation of $[PhCN_2S_2]SO_2F_3$.

Tetrafluorohydrazine is known to act as a source of $NF_2\cdot$ radicals[22] and in this work it was hoped that the nitrogen atom would insert into the S-S bond of $PhCN_2S_2\cdot$, to be followed by migration of fluorine from nitrogen to sulphur to give XI:



[XI]



[XII]

The related species $RCN_3S_2Cl_2$ ($R=CF_3$[2,23], NR'_2[24]; $R'=Me,Et,{}^iPr$) have been previously prepared from $(NSCl)_3$ and RCN. It was thought that XII would be less likely to form on thermodynamic grounds.

Addition of an excess of N_2F_4 to a stirred solution of $(PhCN_2S_2)_2$ in liquid sulphur dioxide resulted in an immediate reaction to give a yellow solid in a yellow solution. However, the mass spectrum of the recovered solid did not show a molecular ion at 233, as expected for XI, but rather gave a typical dithiadiazolium spectrum (Section 6.4.9a). Also, the analyses were incorrect for XI ($PhCN_3S_2F_2$ requires C,36.0; H,2.2; N,18.0%. Found: C,27.9; H,1.6; N,9.6%). In order to try to identify the species present, a single crystal was grown and an X-ray structure determination was attempted by Dr W Clegg of the University of Newcastle upon Tyne. Unfortunately, the crystal was disordered (R=14%) but enough data were obtained to be able to describe the species as the dithiadiazolium salt of a trigonal bipyramidal anion.[25] The anion contained a central sulphur atom but oxygen could not be distinguished from fluorine in the coordination sphere. However, the only possible combination that would give rise to a singly negative charged species is the previously unknown $SO_2F_3^-$

anion. The analyses are in excellent agreement with this formulation (Section 6.4.9a). The mechanism of the reaction is unclear. The obvious scheme would involve formation of $[PhCN_2S_2]F$ and SO_2F_2, but N_4F_4 only reacts with SO_2 at 120°C or under photolysis conditions[26], and then to give FSO_2NF_2 (which was not detected). Also sulphuryl fluoride is rather inert[27], although base hydrolysis is thought to proceed via a trigonal bipyramidal intermediate, $SO_2(OH)F_2^-$, which loses fluoride ion to give fluorosulphuric acid, $SO_2(OH)F$. It is possible that N_2F_4 fluorinates $(PhCN_2S_2)_2$ to give $[PhCN_2S_2]F$ which converts to $[PhCN_2S_2]SO_2F$ in liquid SO_2. The fluorosulphite might then be fluorinated by N_2F_4 to give the product. Further work in this area seems necessary.

Overall, the reaction may be represented as follows:

$$2(PhCN_2S_2)_2 + 3N_2F_4 + 4SO_2 \longrightarrow 4[PhCN_2S_2]SO_2F_3 + 3N_2$$

According to the valence shell electron pair repulsion approach of Gillespie and Nyholm[28], the apical positions in trigonal bypyramidal $SO_2F_3^-$ will be occupied by fluorine atoms.

(b) Reaction in Dichloromethane

In order to try and further elucidate the mechanism of the reaction between $(PhCN_2S_2)_2$ and N_2F_4, the latter was introduced to a dichloromethane solution of $(PhCN_2S_2)_2$. A yellow solution was again immediately observed but removal of solvent only gave a yellow sticky solid which darkened on standing. The washings from this solid were found to contain benzonitrile indicating some degree of ring fragmentation to have occurred. Interestingly, when only a slight excess of N_2F_4 was used, a purple-pink solution was obtained. This was not due to the presence of an intermediate since reaction with a further excess of N_2F_4 did not occur. Removal of solvent from this solution again gave a sticky solid which contained a nitrile group (Section 6.4.9b).

The similarity between the i.r. spectra of the sticky solids mentioned above and that of $(PhCN_2S_2)_3F$ suggest that the latter compound may be formed in this reaction. However, this species is best prepared using AgF_2 (Section 6.3.9) and the above products were not investigated further.

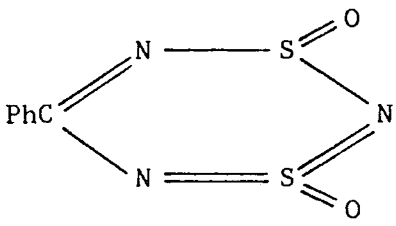
6.2.11 Reaction of $(PhCN_2S_2)_2$ with N_2O_4

Dinitrogen tetroxide is used extensively[29] as a non-aqueous solvent in inorganic chemistry, usually involving the preparation of anhydrous metal nitrates. These reactions depend on equilibrium (1). However, the $NO_2\cdot$ radical, formed according to equilibrium (2), is important in reactions of N_2O_4 with unsaturated organic compounds.

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^- \qquad (1)$$

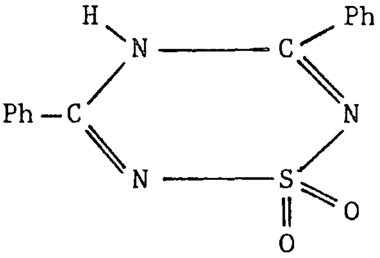
$$N_2O_4 \rightleftharpoons 2NO_2\cdot \qquad (2)$$

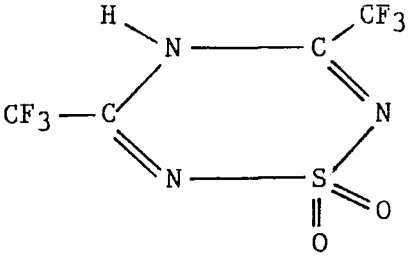
The aim of the present work was to utilise equilibrium (2), which gives ca. 0.1% $NO_2\cdot$ at 21.15°C[30], to try and prepare species XIII.



[XIII]

The action of N_2O_4 on $(PhCN_2S_2)_2$ produced a pale yellow material which could be extracted with dichloromethane to give a lemon-yellow soluble substance and a white insoluble species. The analytical data on the former substance still (Section 6.4.10) indicated a mixture to be present as did the i.r. and mass spectra. However, the latter did suggest the identity of the major component of the mixture. In particular, the intense peak at 285 together with other peaks at 220 (loss of SO_2 + H) and 117 ($PhCN_2$) suggest the structure shown as XIV.


[XIV]


[XV]

The related 1,2,4,6-thiatriazine, XV, has been prepared[31a] previously from CF_3COOH and $ClSO_2N{=}PCl_3$.

The i.r. bands at 1174 or 1212 and 1422 or 1465cm^{-1} may then be assigned to the SO_2 group.[31b] However, the existence of XIV remains highly speculative, and further attempts at purification are required before the compounds present can be fully characterised. The insoluble material is also a mixture and possibly contains NO_2^+. The S:N ratio is close to 1:1 (0.81:0.76).

An alternative pathway for reaction would involve the formation of a nitrate according to:

$$(PhCN_2S_2)_2 + 2N_2O_4 \longrightarrow 2[PhCN_2S_2]NO_3 + 2NO$$

Such a reaction would explain the appearance of NO in the gas phase i.r. spectra (as would the formation of XIV) and, possibly, the i.r. bands near 690 and 1410 cm^{-1} which may be due[31c] to NO_3^-.

Section C: Reaction of $(PhCN_2S_2)_2$ with TCNQ

6.2.12 Preparation of $[PhCN_2S_2](TCNQ)_2$

Tetracyanoquinodimethane (TCNQ) is the ubiquitous electron-acceptor in the chemistry of charge-transfer (C.T.) complexes (materials formed by partial transfer of charge from a donor to an acceptor) and as such features prominently in the design and synthesis of organic metals.[32] For a C.T. complex to exhibit the electronic properties of a metal (for a discussion of organic magnets, see Appendix 3) it seems necessary to meet several criteria:

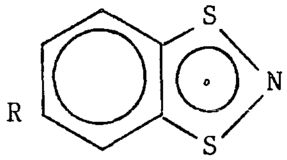
(1) The ionization potential of the donor and the electron affinity of the acceptor should favour incomplete charge transfer (i.e. the ionization potential should be relatively low, and the electron affinity relatively high).

(2) The donor and acceptor should be planar species of similar size with a high degree of symmetry and π-delocalisation.

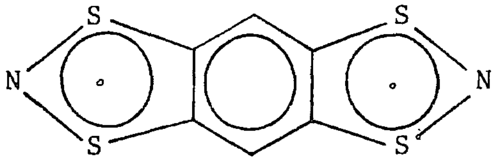
(3) The donor and acceptor should form segregated stacks within the structure (i.e. each participant in the charge transfer process should be equally associated with identical near neighbours).

These properties combine to produce a highly uniform lattice with maximum orbital overlap along the stacks, each of which contributes approximately equally to the conduction, which, of course, occurs predominantly along the stacks. The most widely studied C.T. complex, formed between TCNQ and tetrathiafulvalene (TTF), has a room temperature, single crystal conductivity of $2 \times 10^{3} \Omega^{-1}$ cm^{-1} (cf. $(SN)_x$[33] $1\text{-}3 \times 10^{3}$, Bi 8.6×10^{3}, Hg 10^{4}, Cu $6 \times 10^{5} \Omega^{-1}$ cm^{-1}).[34] It has been shown that 0.59e is transferred from TTF to TCNQ. $(PhCN_2S_2)_2$ seems ideally suited to meet these criteria since it is a planar, delocalised system, and, in common with other SN and CSN species, will undoubtedly possess a relatively low ionisation potential. A stack of dithiadiazole rings has already been discussed as a potential molecular metal.[35]

The only reports of CSN rings forming C.T. complexes with TCNQ are those of Wölmershäuser[36], who employed the free-radical donors shown below (R=H,Me).



[XVI]



[XVII]

The pressed powder conductivity of XVI.TCNQ was found to be 1.1 (R=H) and 3.0 (R=Me)Ω^{-1} cm^{-1}, while that of XVII.$(TCNQ)_2$ was 1.6 x $10^{-3}\Omega^{-1}$ cm^{-1}. The radical cation of XVII, isolated as an intermediate in the reduction of the dication, formed a 1:1 complex with TCNQ which possessed a conductivity of 3.18 x $10^{-4}\Omega^{-1}$ cm^{-1}. These values should be compared with the pressed powder conductivity[36] of TTF-TCNQ at $10\,\Omega^{-1}$ cm^{-1}.

In the present work, $(PhCN_2S_2)_2$ was found to react with four equivalents of TCNQ to form the dark green C.T. complex $[PhCN_2S_2](TCNQ)_2$. The stoichiometry is not unusual; for example Cp_2^*Fe[37a], and CpFeAr[37b] (Ar = 2,4,6-$Me_3C_6H_3$,C_6Me_6) form 1:2 complexes with TCNQ, with each of the latter accepting half of the transferred charge. Both the Cp_2^*Fe complex and the arene-containing complexes (actually salts rather than C.T. complexes) were semiconductors.

The conductivity of a compressed pellet of $[PhCN_2S_2](TCNQ)_2$ was found[38] to be < 6 x $10^{-8}\Omega^{-1}$ cm^{-1} at r.t. This value suggests that the structure of the complex consists of alternating units of $PhCN_2S_2\cdot$ and $(TCNQ)_2$.

Interestingly, the complex did not melt up to 360°C, but a weak exotherm was observed at <u>ca</u>. 265°C. The residue was a blue-black material, the i.r. spectrum of which showed a broad band in the nitrile region and an extremely broad band between 1650 and 1000cm^{-1} (Section 6.4.11). This suggests a phase transition having occurred to give a material in which charge transfer is occurring to a much greater extent than in the original complex.

6.3 CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

$(PhCN_2S_2)_2$ has been found to react with $HBF_4.OEt_2$, CH_3COBr, Me_3SiBr, AgF_2, N_2F_4, N_2O_4 and TCNQ and the following new species have been prepared: $[PhC(NH)_2S_2]BF_4$, $[PhCN_2S_2]_3F$, $PhCN_2S_2F$, $[PhCN_2S_2]SO_2F_3$ and $[PhCN_2S_2](TCNQ)_2$.

The behaviour of $[PhC(NH)_2S_2]BF_4$ in solution merits further investigation since rearrangement obviously occurs (Section 6.2.2). The structure of $[PhCN_2S_2]_3F$ may well be interesting (see Section 1.5) and the growing of a single crystal containing the $SO_2F_3^-$ anion, say as the Cs^+ salt, (prepared via metathesis of the $[PhCN_2S_2]^+$ salt with CsCl) is well worth attempting. Although the TCNQ complex did not conduct, its magnetic properties certainly warrant attention (see Appendix 3) as does the phase transition. It should be noted that the structural requirement for conductivity (segregated stacks) is different from that required for ferromagnetism (mixed stacks).

One possibility for further work in this area is the reaction of $(PhCN_2S_2)_2$ with $(CF_3)_2NO$. This reagent is, like AgF_2, a nucleophilic radical oxidising species[20] and reacts[39] with S_4N_4 to give $S_4N_4(CF_3NO)_2$ and $S_4N_4(CF_3NO)_4$.

6.4 EXPERIMENTAL

6.4.1 Reaction of $(PhCN_2S_2)_2$ with HCl

A large excess (approx. 0.1mol) of gaseous HCl was condensed onto $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) at 77k. The mixture was then allowed to warm up to 21°C. When the HCl liquefied (m.pt. -84°C) an orange solution containing an orange solid was observed. The HCl was pumped off leaving an orange-yellow solid, 0.21g; Found: Cl,16.7; N,13.3; S,28.6%. $PhCN_2S_2HCl$ requires Cl,16.3; N,12.9; S,29.4%. ν max 3200m,bd (NH), 2750sh, 1675m, 1600w, 1506m, 1400s, 1298w, 1266w, 1157m, 1072m, 1031m, 926w, 898s, 850s, 800m, 794m, 788m, 703vs, 550s cm^{-1}. (cf. $PhC(NH)_2Cl$: 3420s,bd, 3200s,vbd, 2750sh, 1685s,bd, 1630m, 1606m, 1562m, 1520w, 1478m, 1445m, 1350sh, 1300w, 1178m, 1160w, 1118m, 1096m, 1026w, 926m, 838m, 781s, 774w, 757s, 687s, 600w, 550sh, 530s, 408m, 390s cm^{-1}). m/z (C.I.+) 300(3%), 299(12), 279(3), 258(9), 257(9), 253(7), 252(3), 224(2), 202(8), 196(2), 192(5), 184(24), 183(34), 182(92), 181(95), 168(1), 160(8), 149(8), 144(7), 138(22), 135(11), 134(16), 128(3), 122(6), 121(10), 117(2), 104(35), 103(91), 96(2), 89(9), 87(7), 77(12), 64(12).

Extraction of '$PhCN_2S_2.HCl$' with Liquid SO_2 and Dichloromethane

A sample of the product of the reaction between $(PhCN_2S_2)_2$ and HCl, formulated as $PhCN_2S_2.HCl$ (1.4g) was placed in one limb of a dog (Figure 7.2) and SO_2 (~$10cm^3$) condensed into the other limb at 77K. The sample was then repeatedly washed with liquid SO_2 with the solid contained in the washings being collected into one limb of the dog and the solid not dissolving in SO_2 remaining in the other limb. This procedure was found to give two solid samples; a less-soluble orange product which was not extracted into liquid SO_2, 0.7g, ν max 1665w,bd, 1580w,bd, 1460sh, 1385vs, 1315s, 1295sh, 1212w, 1170w, *1150s*, 1138s, *1070w*, *1030m*, *1002w*, *926s*, *900vs*, *847vs*, *790vs*, *700vs*, *550s*, *522s* cm^{-1}, and a lemon-yellow solid, 0.6g, ν max 3100vs,bd (NH), 2750sh, 1655vs, *1600w*, 1580w, 1515m, 1460sh, *1395sh*, 1314m, 1295m, 1210vw, 1170vw, *1150m*, 1136m, 1108s, 1090sh, 1039m, *1002m*, *926s*, *898s*, *848s*, 797sh, *789s*, 723s, *695vs*, 662s, 618m, *550m*, *522m*, 409m cm^{-1}.

Further washing of this second component with dichloromethane in an extractor (Figure 7.1) yielded two products. The first component, soluble in dichloromethane, was a yellow crystalline compound νmax 1678m, *1602m*, 1484sh, 1465sh, *1400vs*, 1293w, 1220w, 1173w, *1152s*, *1072w*, *1031m*, *1004w*, *928s*, *898vs*, *849vs*, 799m, *788s*, 732s, *702vs*, 668w, *552s* cm^{-1}. The second product, insoluble in dichloromethane, was a pale yellow solid, νmax ~3200vs,bd (NH), 2750m, 1675vs, 1610m, 1590m, 1530s, 1487s, 1466s, *1400m*, 1300w, 1203w, 1112s, *1090m*, *1034w*, *1002w*, 972w, *930m*, *897w*, *850w*, 798s, *790s*, 728vs, *700vs*, 670vs, 621w, 538m, 412m, 398m cm^{-1}. Underlined bands are due[1] to $PhCN_2S_2Cl$.

6.4.2 Reaction of $(PhCN_2S_2)_2$ with $HBF_4.OEt_2$

$HBF_4.OEt_2$ (54% HBF_4, 0.3cm^3, 1.8mmol) was added dropwise to a stirred solution of $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) in dichloromethane (20cm^3) at 21°C. The red solution immediately turned orange and an orange-yellow solid was precipitated. Stirring was continued for 1h when the mixture was pumped to dryness and the solid washed with diethyl ether (2 x 5cm^3) and dried *in vacuo*. Yield 0.23g. νmax 3360m,bd, 3240m,bd, 1672s, 1598m, 1515m, 1470sh, 1404s, 1392s, 1370sh, 1340sh, 1302w, 1285w, 1200w, 1190w, 1170m, 1125sh, 1090vs,bd, 1030sh, 1008sh, 990vs, 945m, 930s, 852m, 822w, 791s, 769s, 708vs, 690sh, 668w, 620vw, 568s, 530sh, 523s, cm^{-1}. This material was extracted (Figure 7.1) with dichloromethane for 24h giving an orange-red soluble compound, 0.1g. ν max 1602s, 1520w, 1508m, 1470sh, 1405vs, 1305m, 1292m, 1205m, 1192w, 1172s, 1125sh, 1075vs,bd, 1030vs,bd, 1008vs,bd, 948m, 932s, 854s, 794s, 772s, 710vs, 692m, 671m, 569s, 528s cm^{-1}. These bands can all be assigned[40] to $[PhCN_2S_2]BF_4$. A white, insoluble material was also obtained. Yield 0.08g. Found: C,32.1; H,2.9; N,10.4; S,24.1%. $C_7H_7N_2BF_4S_2$ requires C,31.1; H,2.6; N,10.4, S,23.8%. ν max 3380s,bd, 3250s,bd, 1675vs, 1600m, 1590m, 1518s, 1483s, 1448sh, 1338w, 1298w, 1290sh, 1263w, 1197m, 1169m, 1040vs,vbd, 978sh, 950m, 940sh, 823m, 798m, 782w, 768w, 706s, 524w, 509w cm^{-1}. δ_H (CD_3CN): 9.59 (1H,br,s,NH), 8.97 (1H,br,s,NH), 8.67 (1H,br,s,NH), 7.75 (7H,m,Ph); after 6 weeks: 8.55 (1H,br,d,NH), 7.74 (18H,m,Ph). δ_C (CD_3CN) 168.58, 166.27, 135.17, 134.22, 130.41, 129.93, 129.22, 128.89, 128.15, 127.57. δ_F (CD_3CN): -140.04ppm. m/z (C.I.+) 256(8%), 224(2), 202(4), 192(1), 184(8), 183(16), 182(80), 181(100), 160(5), 138(4), 136(3), 121(21), 103(2), 77(2). The D.S.C. trace showed melting to occur at 146.7°C, followed by decomposition at 216.0°C.

6.4.3 Attempted Reaction of $(PhCN_2S_2)_2$ with MeX ($X=I,OSO_2F$)

(a) X=I. $(PhCN_2S_2)_2$ (0.1g, 0.28mmol) was dissolved in iodomethane (5cm^3, previously dried over P_2O_5) and the resulting deep red solution was stirred in a sealed Rotoflo vessel for 7d at 21°C. No reaction was observed and so the solution was heated to 45°C (b.pt. CH_3I=43°C) for 5d. After cooling to 21°C the iodomethane was pumped off leaving a red solid, 0.08g, ν max 1324w, 1242w, 1228w, 1141m, 1079w, 1030m, 927m, 904m, 841m, 835m, 783vs, 773s, 692s, 658s, 510s cm^{-1}. All bands can be assigned[1] to $(PhCN_2S_2)_2$. The experiment was repeated in a sealed tube which was heated to 80°C for 5d, but no change was observed, then to 110°C for 3d which resulted in the formation of a red oil. The tube was opened under an atmosphere of dry nitrogen and the oil transferred to a Schlenk via a syringe. It was found to be insoluble in toluene but slightly soluble in dichloromethane. However, no solid products could be obtained. Found: S,5.0; I,83.5%. ν max 3300m,bd, 3000s, 2915m, 2800w, 1635sh, 1612s, 1580w, 1530m, 1490w, 1470sh, 1458m, 1429s, 1414s, 1400s, 1348m, 1312m, 1292w, 1212m, 1173m, 1162w, 1078w, 1044s, 940m, 920w, 882m, 773s, 738w, 714s, 701m, 650w, 472w cm^{-1}.

(b) X=OSO_2F. $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) was dissolved in dichloromethane (10cm^3) and methyl fluorosulphate (0.46cm^3, 0.65g, 5.7mmol) was added via automatic pipette. The mixture was stirred at 21°C for 12h in a sealed Rotoflo vessel but no change was observed and so stirring was continued at 50°C for 12h. However, no change was observed and the mixture was pumped to dryness to give a purple solid, 0.14g, νmax 1140m, 1070m, 1028m, 924w, 902w, 839m, 808s, 780s, 770m, 692s, 657s, 514s cm^{-1}. All bands can be assigned[1] to $(PhCN_2S_2)_2$.

6.4.4 Reaction of $(PhCN_2S_2)_2$ with Me_3SiX (X=Cl,Br)

X=Cl. $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) was dissolved in toluene (15cm^3) and Me_3SiCl (0.25cm^3, 0.21g, 2mmol) was added via automatic pipette. The mixture was stirred at 21°C for 12h but no change was observed, and so the temperature was raised to 65°C for 12h, but with no effect. The mixture was pumped dry to give a red solid, 0.15g. νmax 1222m, 1135m, 1070m, 1023m, 924w, 898w, 835s, 802s, 778s, 770s, 684s, 656s, 510s cm^{-1}. All bands can be assigned[1] to $(PhCN_2S_2)_2$.

(b) X=Br. $(PhCN_2S_2)_2$ (0.36g, 1mmol) was dissolved in toluene (20cm^3) and Me_3SiBr (1cm^3, 1.16g, 7.6mmol) added via automatic pipette. A flocculent red solid was immediately precipitated. Stirring was continued for 24h, when the solvent was pumped off and the remaining solid sublimed in vacuo to remove excess $(PhCN_2S_2)_2$, 0.23g; V max 1324w, 1240w, 1228w, 1187vw, 1179vw, 1152vw, 1141s, 1079m, 1030m, 927m, 903m, 893m, 842s, 832m, 809s, 784vs, 773s, 730w, 692s, 658s, 545w, 512s cm^{-1}. The residue was a red solid, 0.09g. Found: C,33.2; H,2.5; N,10.3, Si,0.2; S,24.0%; $C_7H_5N_2BrS_2$ requires C,32.2; H,1.9; N,10.7; Br,30.6; S,24.6%. V max 1412s, 1390s, 1162w, 932w, 903m, 854m, 805w, 796w, 710s, 558 cm^{-1}. These bands can be assigned[1] to $[PhCN_2S_2]Br$.

6.4.5 Reaction of $(PhCN_2S_2)_2$ with CH_3COBr

$(PhCN_2S_2)_2$ (0.18g, 0.5mmol) was dissolved in toluene ($20cm^3$) and acetyl bromide ($0.25cm^3$, 0.43g, 3.5mmol) added via syringe. A red solid was immediately precipitated and stirring was continued for 24h when the liquid phase was condensed into a trap at -196°C, leaving a dark red solid, 0.2g; V max 1452s, 1402s, 1390sh, 1300w, 1225m,bd, 1172w, 1153m, 1105m, 1070w, 1030s, 922m, 892s, 843s, 794m, 782m, 730w, 712w, 700vs, 547m cm^{-1}. These bands can be assigned[1] to $[PhCN_2S_2]Br$. The contents of the trap were allowed to warm to 21°C and investigated by gas chromatography-mass spectrometry (Section 7.2.4) which showed 2,3-butanedione as a reaction product (86.29%).

6.4.6 Attempted Reaction of $(PhCN_2S_2)_2$ with $(Me_3Sn)_2$

$(PhCN_2S_2)_2$ (0.09g, 0.25mmol) together with $(Me_3Sn)_2$ ($0.1cm^3$, 0.16g, 0.49mmol) and $(^tBuO)_2$ (5 drops) were stirred in thf ($15cm^3$) at 21°C in front of a medium pressure mercury lamp (ca. 300nm, 1kW) for 18h. The mixture was then pumped dry leaving a red solid, 0.07g. V max 1212w, 1070w, 1028w, 927w, 903w, 842m, 808m, 782s, 772m, 693s, 659s, 513s cm^{-1}. All bands can be assigned[1] to $(PhCN_2S_2)_2$.

6.4.7 Attempted Reaction of $(PhCN_2S_2)_2$ with NO

$(PhCN_2S_2)_2$ (0.22g, 0.61mmol) was dissolved in thf ($15cm^3$) in a dog (Figure 7.2). The solution was then stirred under 2Ats. NO for 18h at 21°C. No change was observed and the gas and solvent were pumped away leaving a red solid, 0.2g. ν max 1322w, 1240w, 1228w, 1141m, 1069m, 1028m, 923w, 902w, 840m, 808s, 781vs, 772s, 692s, 658s, 512s cm^{-1}. All of these bands are assigned[1] to $(PhCN_2S_2)_2$.

6.4.8 Reaction between $(PhCN_2S_2)_2$ and AgF_2

$(PhCN_2S_2)_2$ (0.18g, 0.5mmol) and AgF_2 (0.3g, 2.05mmol) were stirred in carbon tetrachloride ($15cm^3$) in one limb of a dog (Figure 7.2) for 24h. The mixture was then filtered to give a yellow solution and a green residue which was washed with carbon tetrachloride (2 x $5cm^3$). The solvent was pumped off from the yellow solution to give dark green $(PhCN_2S_2)_3F$, 0.10g, 53%. Found: C,44.4; H,3.0; N,14.4%. $C_{21}H_{15}N_6FS_6$ requires C,44.8; H,2.7; N,14.9%; ν max 1602vw, 1442sh, 1320m, 1300sh, 1273s, 1250sh, 1172m, 1140m, 1120s, 1071w, 1030s, 977m, 939vw, 929w, 910vw, 878m, 850w, 805vs, 787sh, 778s, 740w, 690vs, 674s, 664m, 658sh, 562s, 520vw, 480sh, 462s cm^{-1}. m/z (C.I.+) 381(13%), 252(8), 241(6), 224(2), 197(2), 181(100). The mass spectrum was recorded at ca. 100°C since the compound melted at 62.3°C and decomposed at ca. 96°C.

Sublimation of $(PhCN_2S_2)_3F$ (0.02g) at 50°C (cold finger -10°C) gave a purple sublimate, 0.01g, νmax 1322vw, 1228m, 1138m, 1074m, 1022m, 920vw, 898vw, 836w, 830w, 802m, 778s, 769m, 687s, 652s, 510m cm^{-1}. The residue was a brown yellow solid, 0.0044g. Found: C,41.6; H,2.7; N,14.1%. $C_7H_5N_2FS_2$ requires C,42.0; H,2.5; N,14.0%. ν max 1230w, 1175m, 1140m, 1020m, 800m, 778m, 720m, 684s, 648s cm^{-1}. m/z (E.I.) 200(4%), 185(3), 181(100), 149(3), 135(62), 128(3), 120(3), 117(3), 103(18), 91(4), 77(12), 68(5), 64(3), 54(3), 51(7), 46(4). The i.r. bands of the sublimate can all be assigned[1] to $(PhCN_2S_2)_2$.

6.4.9 Reaction of $(PhCN_2S_2)_2$ with N_2F_4

(a) Reaction in Liquid Sulphur Dioxide: $(PhCN_2S_2)_2$ (0.22g, 0.61mmol) was dissolved in liquid SO_2 in one limb of a dog (Figure 7.2), and N_2F_4 (ca. 0.5g, 4.8mmol) was condensed into the other limb at 77K (the limb containing the SO_2 was sealed off for this stage). As soon as the stirred solution was exposed to N_2F_4, immediate reaction occurred to give a yellow precipitate in a yellow solution. Stirring was continued for 30 min. when the solution was filtered through the frit. The solid was washed with SO_2 (2 x 5cm^3) which was then pumped out of the dog to leave a yellow solid on the frit, 0.08g, and a yellow solid, previously dissolved in SO_2 which was washed with diethyl ether and pumped dry, 0.14g. These solids were shown to be identical by i.r. spectroscopy, both being $[PhCN_2S_2]SO_2F_3$, making a total yield of 0.22g, 73%, m.pt. 116.3°C (decomp. ca. 200°C). Found: C,27.9; H,1.6; N,9.6%. $C_7H_5N_2F_3O_2S_3$ requires C,27.9; H,1.7; N,9.3%, ν max 1590w, 1498w, 1392vs, 1410sh, 1298m, 1248m, 1175m, 1160m, 1060w, 1021m, 930sh, 918s, 850m, 786sh, 777m, 750sh, 730vs,bd, 702s, 693vs, 665s, 653m, 640sh, 603w, 528w, 556s, 318m cm^{-1}. δ_F (liquid SO_2) -137.8ppm. m/z (E.I.) 181(100%), 160(3), 135(24), 117(3), 108(4), 103(22), 91(4), 85(15), 78(54), 77(14), 64(9). The spectrum was recorded at ca. 150°C.

(b) Reaction in Dichloromethane: $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) was dissolved in dichloromethane (15cm^3) in one limb of a dog, which was sealed off. N_2F_4 (ca. 0.5g, 4.8mmol) was condensed into the other limb at 77K. As soon as the solution was exposed to the N_2F_4, it immediately turned yellow and this colour persisted on stirring for 1h. Removal of solvent gave a sticky yellow gum, ν max 1648m, 1598w, 1492w, 1402s, 1392s, 1301w, 1270m, 1261w, 1245vw, 1208vw, 1170w, 1162w, 1070sh, 1043m, 1032s, 1003w, 946w, 924m, 869vw, 853sh, 850w, 808s, 800m, 793sh, 770m, 740s,bd, 704s, 690m, 668w, 659w, 640m,bd, 563m, 482m, 473m, 469m, 452vw cm^{-1}. After 12h a brown-black gum was observed, ν max 1645s, 1598w, 1580w, 1500sh, 1490m, 1450m, 1440sh, 1420w, 1400sh, 1315w, 1275s, 1250sh, 1180m, 1160w, 1140m, 1118m, 1070w, 1030m, 1021s, 1002w, 980m, 940sh, 923m, 909m, 882w, 872w, 852m, 830m, 800s, 770s, 740s, 688s, 671w, 659s, 620w, 559m, 540sh, 520m, 491w, 470m, 459m cm^{-1}. Washing the gum with pentane did not give a tractable product but removal of the pentane from the washings, in vacuo, left a minute quantity of a less volatile liquid, νmax 2226m, 1598w, 1490s, 1449s, 1180m, 923m, 759s, 686s, 549s cm^{-1}. The bands were all assigned to benzonitrile by comparison with the spectrum of an authentic sample.

Addition of ca. 0.15g (1.4mmol) N_2F_4 to a solution of $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) in dichloromethane ($10cm^3$) gave a purple-pink solution which did not react with N_2F_4. Removal of the solvent gave a purple-pink solid, ν max 2285w, 2230vw (CN), 1790w,bd, 1735sh, 1692m, 1600vw, 1504vw, 1448s, 1409s, 1332s, 1290sh, 1282m, 1260m, 1245sh, 1213w, 1172w,bd, 1142w, 1110w, 1088vw, 1072w, 1048m, 1020w,bd, 1000w, 931m, 923w, 858m, 850vw, 790sh, 780m, 768w, 712w, 694s, 672w, 573m,bd, 512w, 450m cm^{-1}.

For the reactions in both liquid sulphur dioxide and dichloromethane, the i.r. spectra of the volatile phase, removed in vacuo, was recorded. However, only N_2F_4 and solvent bands were observed: in sulphur dioxide; νmax 2510m, 2495m, 1350vs,bd, 1168s, 1140s $(SO_2)^{41a}$, 1030sh, 1018vs, 1010vs, 970vs,bd, 738s, 587m $(N_2F_4)^{41b}$, 532s, 508s (SO_2), 468m (N_2F_4) cm^{-1}: in dichloromethane; ν max 3000s, 2904s, 1460m,bd, 1272vs, 1260vs (CH_2Cl_2), 1029s, 1023s, 1008s, 996sh, 975sh, 960s, 945s, 930s (N_2F_4), 893m, 750vs,bd (CH_2Cl_2), 725vs (N_2F_4), 705s (CH_2Cl_2), 590m (N_2F_4) cm^{-1}.

6.4.10 Reaction of $(PhCN_2S_2)_2$ with N_2O_4

Dinitrogen tetroxide (ca. 5cm^3, 7.50g, 0.08mol) previously dried over P_2O_5, was condensed onto $(PhCN_2S_2)_2$ (0.18g, 0.5mmol) in a dog (Figure 7.2) at 77K. The mixture was allowed to warm to r.t. and the N_2O_4 was pumped off from a solution containing a very small amount of white solid. This was then washed with dichloromethane (ca. 5cm^3) to give a yellow crystalline solid (0.06g). Found: C,58.2; H,3.65; N,9.9%. ν max 3055w, 1790m, 1730m, 1690m, 1600w, 1490w, 1465m, 1422m, 1410m, 1332m, 1283w, 1237w, 1212m, 1174m, 1162w, 1072w, 1035m, 1018m, 998m, 930w, 856w, 772m, 709s, 700s, 690s, 670w, 650s, 625w, 525m cm^{-1}. m/z (E.I.) 285(91%), 220(36), 192(4), 181(3), 165(2), 135(2), 129(3), 117(41), 104(100), 103(77), 91(14), 89(9), 77(50), 76(25), 64(13), 51(28), 50(16), 48(7), 46(2), 39(12), 32(6). A white solid, insoluble in dichloromethane, was also obtained (0.03g). Found: C,0.5; H,0.5; N,10.7; S,25.9%. ν max 3060sh, 2300s (NO_2^+)[42a], 1798m, 1692s, 1603w, 1582w, 1420w, 1364w, 1250vbd.vs, 1088s, 1040s, 934w, 888w, 840sh, 780bd,s, 740s, 711m, 682w, 667w, 648m, 580bd.s (NO_2^+)[42a], 521s, 460m cm^{-1}. m/z (E.I.) 257(3%), 256(2), 229(2), 221(2), 213(2), 199(2), 185(2), 181(6), 171(2), 167(2), 155(2), 149(34), 147(6), 135(3), 129(9), 120(18), 115(5), 104(34), 103(11), 97(18), 95(11), 91(4), 85(17), 83(34), 77(8). This compound is obtained alone if N_2O_4 is reacted with $(PhCN_2S_2)_2$ at r.t. (the reaction is highly exothermic). Repeat prep: Yellow material: Analysis C,53.6; H,3.7; N,14.0%. ν max 3200vbd.w, 1795w, 1690m, 1602w, 1510w, 1450sh, 1412s, 1333s, 1295sh, 1285m, 1214w, 1175w, 1142w, 1110w, 1074w, 1030w, 1000w, 932m, 859m, 770m, 710s, 694s, 672m, 620w, 608w, 450w cm^{-1}. m/z (C.I.+) 420(22%), 386(2), 341(4), 309(16), 302(22), 297(12), 285(5), 282(6), 254(10), 224(23), 181(9), 178(13), 165(3), 149(4), 139(12), 135(4), 121(32), 104(63), 92(2), 77(2). White material: νmax 3100bd,sh, 2295m, 2285m, 1800w, 1250vbd.s, 1080bd,m, 1030s, 870m, 780bd.s, 735s, 570bd,s, 515w, 460w, 445w cm^{-1}. m/z (C.I.+) 319(3%), 311(2), 302(9), 294(2), 285(4), 278(5), 266(23), 264(5), 245(17), 226(8), 225(5), 220(24), 217(4), 205(10), 202(5), 189(16), 174(37), 162(2), 160(4), 146(7), 139(6), 121(13), 117(3), 104(66), 91(2), 46(2).

Species present in the gas phase were detected by i.r. spectroscopy, ν max 3060sh, 3022m, 2910m, 2870sh, 2230m, 2200m, 1895m, 1872m, 1810s, 1784s, 1738vs, 1610vs, 1388w, 1370vs, 1355sh, 1342vs, 1358m, 1340m, 1260vs, 1160m, 1138m, 1028s, 750vs, 690m, 588m, 528w, 500sh cm^{-1}. The bands at 2230 and 2220 cm^{-1} are assigned[42c] to CO_2; those at 1895 and 1872 cm^{-1} are due[42b] to NO and those underlined are due[41a] to SO_2. The remainder are assigned[43] to N_2O_4, apart from the bands above 3000 cm^{-1} and that at 1028 cm^{-1} which remain unassigned.

6.4.11 Reaction of $(PhCN_2S_2)_2$ with TCNQ

$(PhCN_2S_2)_2$ (0.20g, 0.55mmol) and TCNQ (0.2g, 1mmol) were stirred together in acetonitrile solution (15cm^3) at 80°C for 24h. The solvent was then pumped off leaving a very dark green solid which was extracted (Figure 7.1) with petroleum ether for 18h to give a green $PhCN_2S_2$.2TCNQ, 0.15g, 47%. Found: C,64.3; H,2.6; N,25.4%; $C_{31}H_{13}N_{10}S_2$ requires C,63.2; H,2,2; N,23.8%. νmax 2210m (CN), 1650m, 1592w, 1535m, 1350w, 1320w, 1170w, 858s, 826w, 798w, 771w, 762w, 712w, 682m, 648w, 470m cm^{-1}. δ_H (CD_3CN) 7.77ppm. (br m). m/z (E.I.) 204(100%), 177(24), 152(12), 141(81), 135(2), 124(6), 114(11), 103(27), 89(11), 75(24), 63(14), 57(10), 50(22), 45(16), 41(15). The D.S.C. showed an exothermic phase change to occur at ca. 265°C. The i.r. spectrum of the D.S.C. residue was recorded. ν max 2180br.m, 2050sh, 1600vbr,s, 820sh, 800w, 770w, 718w, 690sh cm^{-1}. This material was coloured dark blue-black.

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CHAPTER 7

GENERAL EXPERIMENTAL TECHNIQUES

7.1 Manipulation of Air- and Moisture-Sensitive Materials

Since many of the compounds discussed in this thesis are both air- and moisture-sensitive, all manipulations were carried out under an atmosphere of dry nitrogen. At the bench, standard Schlenk techniques[1] were used on a double manifold vacuum line fitted with double oblique taps so that apparatus could either be evacuated or purged with nitrogen. The vacuum was provided by an Edwards (No.2) two-stage rotary oil-pump, backed, when necessary, by a Jencons mercury diffusion pump. A pressure less than 10^{-3}mm Hg was easily achieved. The nitrogen was supplied as 'boil-off' from a central liquid nitrogen reservoir and was rated at less than 6ppm. oxygen and 10ppm. water. Primary deoxygenation was carried out before the gas entered the departmental line by passage over hot copper. Further drying and deoxygenation was carried out in the laboratory by a molecular sieve column (BDH Grade 4A), two columns of phosphorus (V) oxide dispersed on glass wool and a hot copper column. Sample handling was carried out in a Vacuum Atmosphere glove box (Type HE43-2) equipped with a recirculating pump and a drying/deoxygenating column (HE493 Dritrain). The water content was typically 2ppm. The pressure in the box was regulated using a Pedatrol HE-63-P regulator and the nitrogen was supplied from a cylinder (BOC White Spot grade). The box was entered through a port which was evacuated for ca. 20 minutes using an Edwards No.8 pump and then filled with dry nitrogen.

All glassware was dried in an oven at ca. 100°C for at least 24 hours or flame dried with a hand torch (approx. 500°C) in a flow of nitrogen before use. Two items of special glassware designed by Dr Z.V.

Hauptman were used in the work viz. an enclosed extractor[2] shown in Figure 7.1 and a 'dog'[3] shown in Figure 7.2.

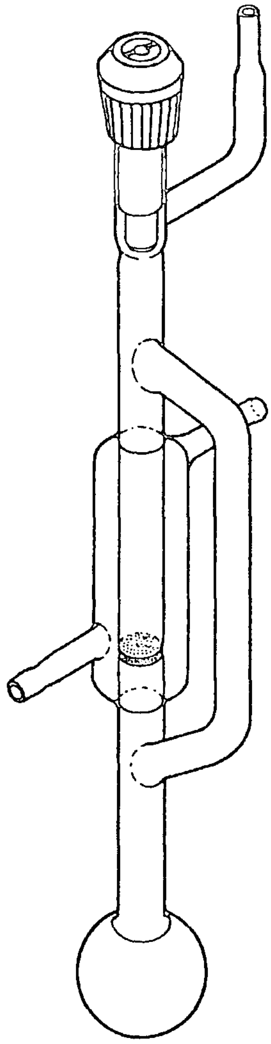

Figure 7.1

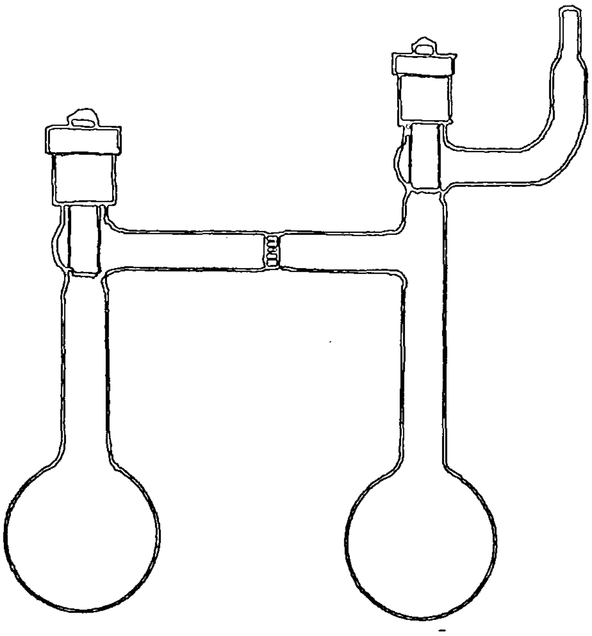

Figure 7.2

Transfer of more volatile materials such as sulphur dioxide, ammonia, hydrogen chloride, dinitrogen tetroxide, nitric oxide, and tetrafluorohydrazine, were carried out on a Monel vacuum line, fitted with stainless steel Whitey valves (IKS4). Apparatus was attached to the line via Swagelok Teflon compression fittings (1/4 inch O.D.). The pressure was measured using a Budenberg pressure gauge.

7.2 Spectroscopic and Other Analytical Techniques

1. Infrared spectra were recorded on either a Perkin Elmer 457 or 577 grating spectrophotometer. Solids were recorded as Nujol mulls between KBr, CsI or KRS-5 (TlCl-TlBr, for N_2F_4 and AgF_2 reaction products). Gas phase spectra were recorded in either a Pyrex gas cell fitted with KBr windows or, for the N_2F_4 reaction, a stainless steel cell fitted with AgCl windows. Solution phase spectra were recorded in a solution cell (path length 0.01mm) fitted with CaF_2 windows.

2. Raman spectra were recorded on a Cary 82 spectrophotometer using a Spectra Physics 164 argon ion laser operating at 514.5nm. Samples were sealed in glass capillaries.

3. Nuclear magnetic resonance spectra were obtained by Dr R.S. Matthews, Mr J.W. Banks or Mr V.J. McNeilly. They were recorded on a Bruker AC250 spectrometer at 22°C unless otherwise stated. Operating frequencies and standards (internal for ^1H, external for the remainder) are listed in Table 7.1. The upfield direction was taken as positive. The ^1H and ^{19}F spectra samples were sealed up in 5mm O.D. tubes; the remainder in 10mm O.D. tubes supplied by the Wilmad Glass Co. Deuterated solvents (Aldrich) were used to provide a ^2H lock.

Table 7.1 N.M.R. Operating Frequencies and Standards

NUCLEUS	FREQUENCY (MHz)	STANDARD
^1H	250.133	Me_4Si
^{13}C	62.896	Me_4Si
^{19}F	235.342	CCl_3F
^{31}P	101.256	H_3PO_4

4. Mass spectra were obtained by Dr M. Jones and Mr V.J. McNeilly. They were recorded on a V.G. Analytical 7070E spectrometer at 70eV and 250°C with an accelerating potential of 6KV. Samples were introduced

by direct insertion into the ion source. Certain samples discussed in Chapter 3 (the non-polymeric products) were found to decompose before reaching the ion chamber and so these were introduced in capillaries which contained a glass plug about one third of the way along their length. In this way the sample could be pushed closer to the electron beam in order to minimise thermal decomposition before ionisation. This procedure approximates to the use of Desorption Chemical Ionisation (D.C.I.)[4] which could not be carried out on these samples due to their air sensitivity. Electron ionisation (E.I.), Chemical Ionisation (C.I.) using iso-butane or ammonia as carrier gases, or Fast Atom Bombardment (F.A.B.) modes were used. Glycerol or thioglycerol were used as the F.A.B. matrix. Gas chromatography-mass spectra were recorded on a Pye Series 104 Gas Chromatograph linked to a V.G. Micromass 12B spectrometer.

5. Ultraviolet-visible spectra were recorded on a Philips PU 8720 uv/vis. scanning spectrophotometer. Samples of $(PhCN_2S_2)_2$ together with ammonia or amine were sealed up in silica ampoules (60mm long, 8mm O.D.) which were placed inside an ordinary u.v. cell for the recording of spectra. Since the path length through the sample was not accurately known, it was not possible to obtain the concentrations of the absorbing species. The spectra were only used to identify the species present.

6. Differential scanning calorimetry (D.S.C.) was carried out using a Mettler FP80 control unit linked to a Mettler FP85 thermal analysis cell and a Fisons y-t chart recorder. Charts were calibrated using an indium standard and samples were cold sealed in aluminium capsules. All melting points and decomposition temperatures were determined using this method.

7. X-Ray oscillation photographs were recorded on potential single crystals mounted in Lindemann glass or quartz capillaries. Samples

were mounted on an Enraf-Nonius integrating Weissenberg camera. X-rays were obtained from a Philips PW 1009/30 X-ray generator using copper K_α radiation and a nickel filter. These photographs were recorded on Agfa-Gevaert Osray film.

8. X-ray structure determinations were carried out by Dr W. Clegg at the University of Newcastle upon Tyne (unless otherwise stated) on a Siemens AED2 diffractometer with a graphite monochrometer and using either copper K_α (1.54184Å) or molybdenum K_α (0.71073Å) radiation. The SHELXTL suite of programs was used for structure solution.

9. Elemental Analyses. Carbon, hydrogen, and nitrogen analyses were determined by Mrs M. Cocks on a Carlo Erba 1106 or a Perkin-Elmer 240 Elemental Analyser. All other analyses were carried out by Mr R. Coult or Mrs J. Dostal. Sulphur was determined by oxygen flask combustion followed by titration of sulphate using $BaClO_4$ with Sulphanazo III as indicator. Phosphorus was measured by colourimetric determination of orthophosphate as the vanadomolybdophosphate complex following decomposition with equal volumes of concentrated sulphuric and perchloric acids. Chlorine was determined potentiometrically against 0.01M $AgNO_3$ solution using Ag,AgCl electrodes in an acetone medium, following oxygen flask combustion. Bromine and iodine were determined using iodometric methods^5 also following oxygen flask combustion. All other elements were determined by atomic absorption using a Perkin-Elmer 5000 atomic absorption spectrophotometer.

7.3 Temperature control was achieved using a Haake F2 circulator with methylated spirits as coolant. Temperature rippling for crystal growth was carried out using a Haake PC10 programmer and a 'home-made' timer switch built by Mr G. Rowe. Typically, the temperature was cycled between 0 and -10°C at 0.4°C min^{-1}. The dwell time at the start and end of each cycle was 5 minutes.

7.4 Photolyses were carried out using a Rayonet reactor fitted with four 350nm mercury discharge lamps (400W).

7.5 Solvents were handled under an atmosphere of dry nitrogen or *in vacuo*. Petroleum ether (b.pt. 40-60°C) and toluene were supplied by May and Baker Ltd and were dried by refluxing over sodium-potassium alloy. Dichloromethane was supplied by May and Baker Ltd and was dried by refluxing over calcium hydride. Carbon tetrachloride (Aldrich) was refluxed over P_2O_5 and then distilled and stored over molecular sieve (B.D.H. grade 4A). Acetonitrile (H.P.L.C. grade, Aldrich) was also dried by refluxing over calcium hydride. Ether was supplied by May and Baker Ltd. and was dried by refluxing over lithiuim aluminium hydride. Tetrahydrofuran (thf) was supplied by the Aldrich Chemical Company and was dried over potassium hydroxide pellets for ca. 1 week followed by refluxing over potassium-benzophenone. Sulphur dioxide (B.D.H. Ltd.) was kept over phosphorus pentoxide for ca. 2d and then vacuum transferred on to calcium hydride for storage.

7.6 Starting Materials

1. $PhCN_2S_2Cl$ was prepared from NH_4Cl, SCl_2 and PhCN using the literature procedure.[5] Yield 24.6g 32%. Analysis: Cl,16.2; S,29.8%; $PhCN_2S_2Cl$ requires Cl,16.4; S,29.6%.

2. $(PhCN_2S_2)_2$ was prepared from $PhCN_2S_2Cl$ using the literature method[6], except that a reduced excess of zinc-copper couple was used (7.0g, 32.3mmol $PhCN_2S_2Cl$ and 2.5g, 34.9mmol Zn. Zn-Cu:91.3% Zn, 5.1% Cu) and the pentane extraction was omitted. Yield 5.1g 87.3%. Analysis: C,46.1; H,2.8; N,15.4; S,35.2%; $(PhCN_2S_2)_2$ requires C,46.4;

H,2.8; N,15.5; S,35.4%.

3. $M(CO)_3(RCN)_3$ $(M{=}Mo, R{=}CH_3;\ M{=}W, R{=}{}^iPr)$. $Mo(CO)_3(CH_3CN)_3$ was prepared from $Mo(CO)_6$ (1.0g) using the published method.[7a] The reaction was monitored by i.r. spectroscopy[7b]. ν max 2020s, 1900vs, 1820vs, 1780vs. ($Mo(CO)_4(CH_3CN)_2$ also present. Yield 1.2g. $W(CO)_3({}^iPrCN)_3$ was also prepared from $W(CO)_6$ (1.0g) using a published procedure[8]. Yield 0.85g. ν max 2085m, 2005s, 1820vbr,vs.

4. $(Ph_3P)_4Pt$ was prepared according to literature methods[9] using 8.8g (33.6mmol) Ph_3P, 0.8g (14.3mmol) KOH and 7.0g (7.2mmol) K_2PtCl_4. Yield 7.0g,77.8%. Analysis: P,9.9; Pt,15.8%. $(PPh_3)_4Pt$ requires P,10.0, Pt,15.7%.

5. $Mo_2(OAc)_4$ was kindly provided by Mr T.P. Kee (Ph.D. student) and was prepared according to the literature method.[10]

6. $MoCl_4(CH_3CN)_2$ was kindly provided by Mr D N Williams (Ph.D. student) and was prepared using the published procedure.[11]

7. Me_4NN_3 was kindly provided by Dr C J Ludman, and was obtained from the metathetical reaction between Me_4NI and AgN_3 (prepared from $AgNO_3$ and NaN_3) in aqueous ammmonia. The Me_4NI (4.36g,19.95mmol) was dissolved in a mixture of aqueous ammonia ($60cm^3$) and ethanol ($30cm^3$). A solution of AgN_3 in aqueous ammonia ($50cm^3$ ammonia + $50cm^3$ water) was added to the iodide solution to give a white precipitate of $AgI.NH_3$. This was filtered off and washed with ethanol. The filtrate was evaporated to give, first, a small amount of a grey solid, assumed to be $AgI.NH_3$, making the total weight of this compound to be 4.71g (100.35% recovery). Further evaporation of the original filtrate gave a white crystalline solid, which was dried to constant mass *in vacuo*. Yield 2.26g, 98.1%.

8. Me_3P was kindly provided by Mr T.P. Kee (Ph.D. student) and was prepared using the literature method.[12]

9. Na amalgam was kindly provided by Mr J W Hayes (Ph.D. student) and

was prepared using the published procedure.[13] (2.5% Na)

10. $[CpNi(CO)]_2$ was kindly provided by Mr N. Mason (Ph.D. student) and was prepared according to the literature.[14]

11. HCl was obtained from B.O.C. Ltd. The gas was stored in a 10dm^3 bulb fitted with a cold finger. When HCl was required the cold finger was cooled to 77K and allowed to slowly warm up to room temperature. The gas used for reaction was taken while liquid HCl was still present in the cold finger thus ensuring a dry sample.

12. Me_3SiCl was obtained from the Aldrich Chemical Co. and was distilled before use.

13. N_2O_4 was obtained from B.D.H. Ltd. and was stored over P_2O_5.

14. Me_3NO was obtained from the Aldrich Chemical Company as the dihydrate. It was dried by heating to 50°C *in vacuo* for 12h followed by double sublimation.

15. R_nNH_{3-n} (n=0-3) were all dried by storage over sodium for at least 24h before use. Ammonia was supplied by B.O.C. Ltd., the remainder by B.D.H. Ltd.

16. NaH was obtained from B.D.H. Ltd. as an 80% dispersion in white oil. The latter was removed by washing with petroleum ether.

17. 18-crown-6 ether was obtained from Fluka AG and was dried by dissolving in benzene and distilling off the benzene-water azeotrope.

18. Other chemicals were obtained from the suppliers indicated and were used as received.

JOHNSON MATTHEY LTD:	K_2PtCl_4, $PdCl_2$
BDH LTD:	$Mo(CO)_6$, $W(CO)_6$, NO, CH_3COBr, S_8, $HBF_4.OEt_2$(~54% HBF_4) Ph_3As, SCl_2, $TiCl_4$, Mg (stored at 110°C), $NiCl_2$, $CoCl_2$, KOH
STREM CHEMICALS LTD:	$V(CO)_6$, $CpV(CO)_4$, $Co_2(CO)_8$, $(Ph_3P)_3RhCl$, $Fe_3(CO)_{12}$, $Re_2(CO)_{10}$, $[CpMo(CO)_3]_2$, $CpMn(CO)_3$, $CpCo(CO)_2$, $CuCl_2$
FLUKA AG:	$Fe(CO)_5$, Cp_2TiCl_2

VENTRON ALFA PRODUCTS: $Mn_2(CO)_{10}$, $[CpFe(CO)_2]_2$ $MeOSO_2F$, Zn-Cu, $CrCl_2$, $FeBr_2$, AgF_2

ALDRICH CHEMICAL CO: Ph_3P, MeI, CuCl, $(Me_3Sn)_2$, Me_3SiBr, $(Ph_3P)_4Pd$, NH_4Cl, PhCN, TCNQ, $MnCl_2$

K & K LABORATORIES INC: N_2F_4 (research grade)

19. $Fe_2(CO)_9$ was supplied by Strem Chemicals Inc. It was found to be contaminated with pyrophoric iron and was purified by exhaustive extraction with conc. HCl followed by washing with diethyl ether.

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APPENDIX 1

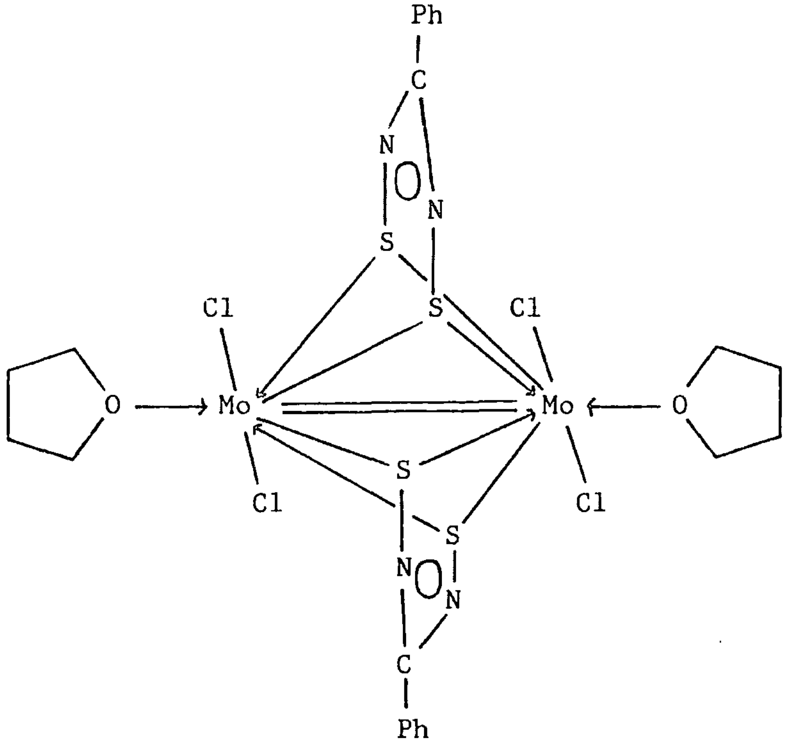
REACTION OF PHENYL DITHIADIAZOLE WITH MOLYBDENUM (II) ACETATE IN THE PRESENCE OF TRIMETHYCHLOROSILANE: PREPARATION OF $[MoCl_2(PhCN_2S_2)(thf)]_2$

A1.1 Introduction

The dimer $[Mo(\mu\text{-}OCOMe)_2]_2$ which contains a Mo-Mo quadruple bond, has been shown to act[1] as a convenient starting material for a wide variety of binuclear molybdenum derivatives, both with and without oxidation of the Mo_2^{4+} core. An important advance was made in this area when it was discovered[2] that trimethylchlorosilane can be used to replace acetate by chlorine, together with other ligands, under mild conditions (r.t. for 24h). More forcing conditions (thf reflux for 24h) have been found to give[3] tetranuclear compounds. The strength of the silicon-oxygen bond (in Me_3SiOAc) relative to that of the silicon-chlorine bond (443 and 410KJmol^{-1} respectively)[4] was thought to provide at least part of the driving force for these reactions.

A1.2 Results and Discussion

Treatment of $[Mo(\mu\text{-}OCOMe)_2]_2$ with $(PhCN_2S_2)_2$ in the presence of an excess of Me_3SiCl gave a shiny black compound formulated, on the basis of analysis and spectrosopic evidence, as $[MoCl_2(PhCN_2S_2)(thf)]_2$. The i.r. spectra indicated acetate groups to be absent with no bands appearing in the range 1400-1450 or 1590-1620cm^{-1} (bridging acetate groups) or at ~1710cm^{-1} (monodentate acetate groups).[2] The bands below 400cm^{-1} agree well with those previously reported[5] for species containing the Mo_2Cl_4 unit. The proton n.m.r spectra exhibited signals due to phenyl groups in the range 7.2-7.7ppm. and signals at 1.81 and 3.65ppm. due to uncoordinated thf.[6] The signals at 2.17 and 2.32 ppm. may be due to replacement of coordinated thf by acetonitrile solvent. Such behaviour has been noted previously.[2] The mass spectrum was of low quality due to the low volatility of the species (Section A1.3). These results point to the structure shown below:



The reaction involves a double oxidative addition of disulphide linkages to the Mo-Mo quadruple bond with a consequent reduction in bond order. Reactions of disulphides with a variety of molybdenum-molybdenum quadruply bonded species have been reported by Cotton[7], who prepared compounds such as [Mo(μ-SPh)Cl_2(dmpe)$]_2$ (dmpe = dimethlyphosphinoethane, $Me_2PCH_2CH_2PMe_2$) from [MoCl_2(dmpe)$]_2$ and Ph_2S_2. Although the structure above is given with a metal-metal double bond linking two (18 electron) molybdenum (IV) centres, the bridging ligand orbitals may well interact with metal orbitals in such as way as to reduce the bond order even further.[7b] Obviously, the growth of a single crystal for X-ray analysis would clarify the situation.

Finally, an electrochemical study[8] of the compound may prove interesting. Investigations on Re_2Cl_4(μ-SePh$)_2$(μ-dppm$)_2$ (dppm = diphenylphosphinomethane, $Ph_2PCH_2PPh_2$) have led to the observation of redox processes involving Re_2^{4+} - Re_2^{8+}.

A1.3 Experimental

$[Mo_2(\mu\text{-}OCOMe)_2]_2$ (0.4g, 0.9mmol) and $(PhCN_2S_2)_2$ (0.36g, 1mmol) were stirred together in thf ($25cm^3$) at 21°C to give a deep red solution containing undissolved acetate. Me_3SiCl ($2cm^3$, 1.8mmol) was added via syringe and stirring was continued. Within 20 minutes the acetate had dissolved and after 12h the deep red solution was pumped to dryness. Toluene ($20cm^3$) was added and a black solid was filtered off, washed with toluene (2 x $5cm^3$) and hexane ($5cm^3$) and dried in vacuo. Yield 0.54g, 71%. Found: Cl, 17.3; Mo, 22.9; N, 6.6; S, 13.0%. $C_{22}H_{26}Cl_4Mo_2N_4O_2S_4$ requires Cl, 16.9; Mo, 22.8; N, 6.7; S, 13.0% ν_{max} 1250w.br, 1180w, 1150w, 1028w, 1000w, 978w, 920w.br, 850m, 812w, 770m, 730m, 695s, 470w, 370sh, 340s, br.cm^{-1}. $\delta_H(CD_3CN)$ 7.7-7.2 (multiplet), 3.65, 2.32, 2.17, 1.81ppm. m/z(C.I+) 515 (0.3, $C_7H_5N_2S_2Mo_2Cl_4^+$), 469 (0.3, $C_7H_5N_5Mo_2Cl_4^+$),

426 (1.3, $N_2S_2Mo_2Cl_4^+$), 103 (100, $PhCN^+$), 72(80, $C_4H_8O^+$). The D.S.C. trace showed a broad exotherm centred near 165°C due to either loss of coordinated thf or decomposition, and an endotherm, due to melting, at 225.2°C. The compound was found to be insoluble in hydrocarbons and dichloromethane but soluble in thf and acetonitrile.

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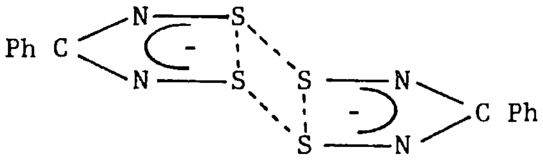
APPENDIX 2

REACTION OF PHENYL DITHIADIAZOLE WITH SODIUM AMALGAM IN THE PRESENCE OF 18-CROWN-6 ETHER: PREPARATION OF $[Na(C_{12}H_{24}O_6)]^+[PhCN_2S_2]^-$

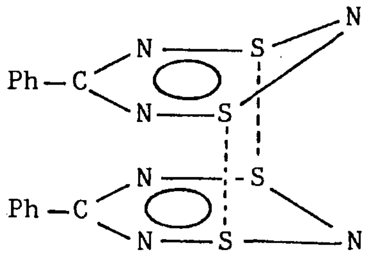
A2.1 Introduction

The drastic structural rearrangements usually undergone by binary sulphur-nitrogen species on oxidation or reduction has made the redox chemistry of carbon sulphur nitrogen systems an area of current interest.[1] It has been argued[1] that the introduction of carbon should render these systems more stable towards rearrangement and hence increase their potential for applications in, for example, the electronics industry. Since the conditions for the reduction of $[PhCN_2S_2]^+$ are well known (Section 1.3) it was decided to investigate the possibility of further reduction. The expected product, $[PhCN_2S_2]^-$, would be of interest for several reasons:

(1) The anion is an 8π species and so may dimerise to give I in a manner analogous[2] to the isoelectronic compound $PhCN_3S_2\cdot$ as shown in II (it will probably be staggered due to charge repulsion).



[I]



[II]

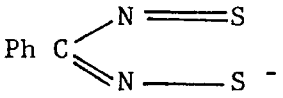
(2) Preliminary ab initio (4-31G) calculations suggest reduced S-S bonding in the anion[3] (d(S-S)=2.281Å, cf. 2.09Å in $(PhCN_2S_2)_2$). This is to be expected since the $PhCN_2S_2\cdot$ SOMO is antibonding with respect to S-S. The S-N bonds, also antibonding in the HOMO, are predicted to be lengthened (d(S-N)=1.779Å, cf. 1.63Å in $(PhCN_2S_2)_2$).

(3) Such a species could be a useful starting material for metathetical reaction with halogen containing compounds. Although

$PhCN_2S_2\cdot$ itself can act as a dehalogenating agent (Sections 6.2.4 and 6.2.5), the lattice energy of sodium halide (in the absence of crown ether) should make the anion a more versatile reagent. The object of the crown ether was to aid the formation of crystals[4] (thf-coordinated cations are often disordered). Although no crystals suitable for X-ray analysis were obtained, a microcrystalline solid was isolated.

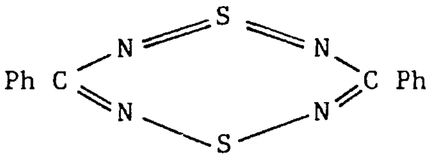
A2.2 Results and Discussion

Sodium amalgam was found to reduce $(PhCN_2S_2)_2$ in the presence of 18-crown-6 ether to give the crown-ether coordinated sodium salt of the new anion $[PhCN_2S_2]^-$. Elemental analysis on the bright yellow crystals agrees with the stoichiometry $Na(C_{12}H_{24}O_6)C_6H_5CN_2S_2$ and so the structure adopted could well be that of compound I. A localised structure, as shown in III,

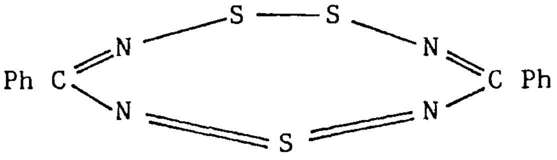


[III]

would be less likely as terminal -N=S units are unstable, immediately decomposing to give sulphur and a sulphur-diimide unit.[5] Compound III would therefore most probably give sulphur, S^{2-} and IV, first prepared by Woodward[6], or V and S^{2-}.



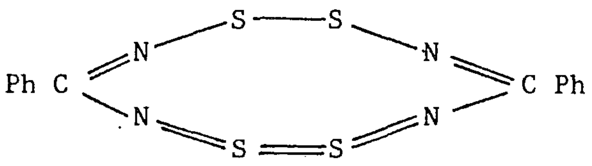
[IV]



[V]

I.r. spectra gave no indication of such compounds.

Cyclic voltammetry of $(PhCN_2S_2)_2$ gave[7] an irreversible reduction peak at -0.7V, indicating that the reduction product is not oxidised back to $PhCN_2S_2\cdot$. This can be explained by postulating the formation of a planar Hückel 14 π-electron ring shown as VI, on addition of two electrons to I. Alternatively, ring opening could occur to give polymeric products.



[VI]

The product may be of limited synthetic utility because of (i) low yield (much remains in solution - with a red gum) and (ii) it slowly decomposes in solution. However, the fact of its isolation indicates that it may be of use when generated by electrochemical reduction.

A2.3 Experimental

A solution of $(PhCN_2S_2)_2$ (0.18g,0.5mmol) and 18-crown-6 ether (0.26g,1mmol) in thf (25cm^3) containing sodium amalgam (2.5% Na, 2g, 2.2mmol Na) was stirred for 2h at 21°C. The resulting yellow brown solution was removed via syringe and the solvent pumped off leaving a yellow gum. Tetrahydrofuran (5cm^3) was added and the solution kept at -30°C for 12h during which time a yellow solid appeared. The supernatant liquor was removed via syringe and the solid washed with cold thf (2 x 2cm^3) and pumped dry. Yield 0.08g,17%. Found: C,49.8; H,6.0; N,6.5; Na,5.0; S,14.7%. $C_{19}H_{29}N_2O_6NaS_2$ requires C,48.7; H,6.2; N,6.0; Na,4.9; S,13.7%. ν max 3040sh, 1503s, 1482s, 1455s, 1414w, 1372m, 1349m, 1320w, 1301s, 1288s, 1247m, 1168w, 1110vs, 1067m, 1055m, 1021m, 961s, 937s, 914sh, 826m, 782w, 768s, 748w, 708s, 696m, 659w, 648w, 612s, 552m, 511m cm^{-1}. Underlined bands are assigned to coordinated 18-crown-6 ether.[8]

The solvent was pumped off from the supernatant liquor to give a red gum from which no i.r. spectra could be obtained. Warming with a hot-air blower gave a dichroic blue-carmine red gum which was washed with diethyl ether (2 x $5cm^3$). The gum was then dissolved in thf ($5cm^3$) and diethyl ether ($15cm^3$) was added. The mixture was left at -30°C for 12h but no solid was obtained. Similar results[7] were given by the material isolated from electrochemical reduction of $(PhCN_2S_2)_2$.

Although quite stable in the solid state, the product was found to decompose in solution at 21°C, in ca. 12h, to give metallic sodium and presumably crown ether and some decomposition product such as VI or polymer. Consequently, solutions had to be stored at -30°C.

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8. Data obtained from an authentic sample.

APPENDIX 3

THE MAGNETIC PROPERTIES OF SOME PHENYLDITHIADIAZOLE COMPLEXES OF TRANSITION METALS

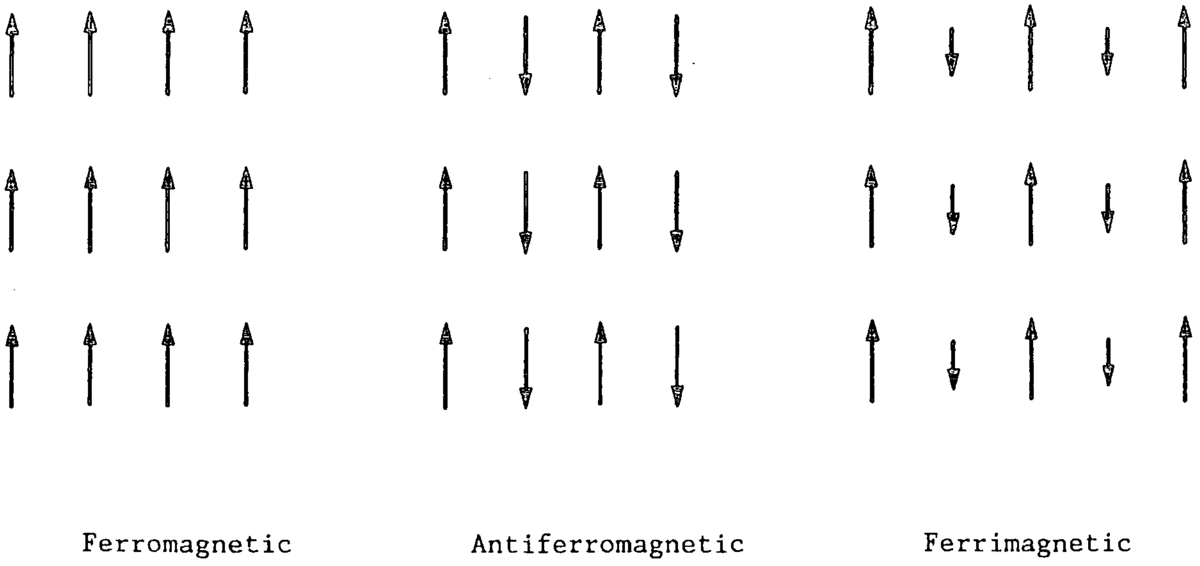
The magnetic measurements described in this Appendix were carried out by Dr D B Lambrick of the Department of Physics. What follows is a brief introduction to some basic magnetic properties[1-3] and to molecular ferromagnets, and then a discussion of the results obtained from compounds presented in this thesis followed by some suggestions for further work.

A3.1 INTRODUCTION

All matter responds to the application of a magnetic field, due to the motion of its electrons. This motion generates magnetic moments, the sum of which, for each electron, gives rise to a resultant atomic moment. It is these atomic moments which determine the magnetic properties of bulk matter.

In closed shell systems the resultant atomic magnetic moment is zero, but in an applied magnetic field a net resultant atomic magnetic moment is induced. This induced moment is very small and opposes the applied field. Such behaviour is known as diamagnetism. In some materials the atoms possess free, unpaired electrons which give rise to a resultant magnetic moment. Normally, these moments are aligned randomly, because of thermal motion, giving a zero magnetic moment for the sample as a whole. However, when an external field is applied, partial alignment of the atomic moments takes place (opposed by thermal effects) resulting in an overall net magnetic moment for the sample. This behaviour is known as paramagnetism. It should be noted that paramagnetic substances also contain a diamagnetic contribution to their magnetic moments, due to the paired-up core electrons, but since this is 1 - 3 orders of magnitude less than the paramagnetic effect, it is treated as a minor correction, if at all.

Diamagnetism and paramagnetism do not occur in the absence of an applied field and disappear when the field is removed. However, in certain paramagnetic materials, spontaneous ordering (alignment) of atomic magnetic moments takes place, even in the absence of an external field. Three arrangements of moments are commonly observed. If the moments are all aligned in the same direction, then a <u>ferromagnetic</u> state is obtained; if the moments are aligned in an antiparallel fashion, then an <u>antiferromagnetic</u> state is obtained; and finally, if the moments are antiparallel but of unequal magnitude, then a <u>ferrimagnetic</u> state is obtained. These states are illustrated in Figure A3.1 in which the arrows represent atomic moments.



<u>Figure A3.1</u>

The properties of ordered magnetic materials (ferro-, antiferro-, and ferrimagnetic) are described with reference to regions, called <u>domains</u>. Within each domain of, for example, a ferromagnetic material, there is parallel alignment of the atomic moments. The orientation of domains, however, is random, resulting in a zero net moment in the absence of an external field. When a field is applied the domains that are aligned or nearly aligned with the field direction, grow at the expense of the others and the sample acquires a net magnetisation. Domains are formed so that the potential energy associated with the magnetised sample (magnetostatic self-energy) is minimised. This occurs when the decrease in energy due to domain formation exceeds the energy required to form the domain boundaries.

A quantitative measure of the response of a material to an external magnetic field is given by the magnetic susceptibility, χ . It is defined by the expression given below:

$$\chi = \frac{M}{H}$$

where M is the magnetisation (magnetic moment per unit volume) and H is the strength of the external field. The total magnetic flux density (magnetic induction), B, is made up from the contributions of H and M, and is given by:

$$\begin{aligned} B &= \mu_0(H+M) \\ &= B_0 + \mu_0 M \end{aligned}$$

where μ_0 is the permeability of free space. We can now redefine the susceptibility as follows:

$$\chi = \frac{M}{B_0}$$

Since it is easier to accurately measure mass, rather than volume, the magnetisation per unit mass, σ, is usually quoted:

$$\chi = \frac{\sigma}{B_0} \qquad (\mathrm{JT^{-2}Kg^{-1}})$$

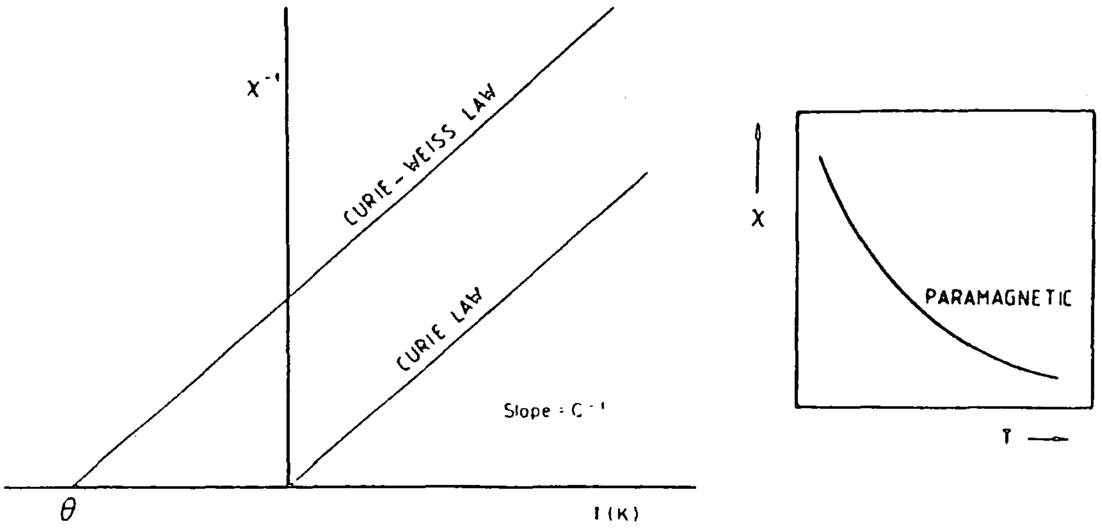
The susceptibility is thus given by the gradient of a σ-B_0 curve. The types of magnetic behaviour discussed above can be distinguished by the different ways in which the susceptibility varies with applied magnetic field, H, and with temperature, T. Diamagnetic substances have a small negative susceptibility (-1 to -10^{-4} emu mol^{-1}) which is independent of field strength and temperature. Paramagnetic susceptibilities (10^{-4} to 10^{-2} emu mol^{-1}) are also independent of field strength (at normal field strengths) but do vary with temperature according to:

$$\chi = \frac{C}{T}$$

which is the Curie Law, where C is the Curie constant for the material in question. For some materials, a more accurate representation, especially at lower temperatures, is given by the Curie-Weiss Law:

$$\chi = \frac{C}{T+\theta}$$

where θ is the Curie-Weiss constant. This behaviour is shown in Figure A3.2a. The normal temperature-susceptibility curve is shown in Figure A3.2b.



a

b

Figure A3.2

The temperature dependence of the initial susceptibility of a ferromagnetic substance (10^{-2} to 10^{6} emu mol^{-1}) is more complicated as shown in Figure A3.3.

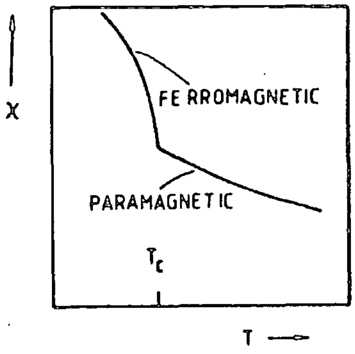


Figure A3.3

Starting from temperatures below T_C, the Curie temperature, the alignment of the moments is gradually reduced as the temperature (thermal motion) is increased, resulting in a fall in the susceptibility. When the Curie temperature is reached the spontaneous magnetisation becomes zero, the domain structure breaks down and the material exhibits ordinary paramagnetism. The susceptibilities of ferromagnetic materials are also field-dependent and there is therefore a different value of χ at each point in the magnetisation curve.

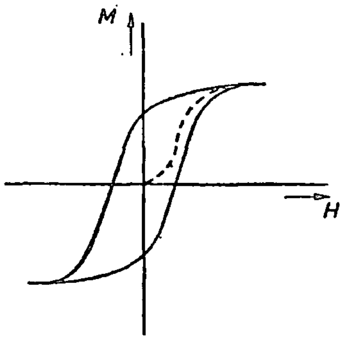


Figure A3.4

As the applied field, H, is increased from zero (broken line), the magnetisation, M, increases (reversibly) as the domains that are aligned with the field, expand in size. At higher fields the domains become locked, due to the presence of lattice defects, and so further increase in magnetisation (irreversible) is due to alignment of individual moments. This is a higher energy process (than domain expansion) and so the increase in magnetisation falls off, until a saturation level is reached. If the field is reversed, the magnetisation falls but since energy is required to overcome the locking action of the lattice defects, the magnetisation does not fall back to zero and a hysteresis curve is obtained.

The effect of temperature on antiferromagnetic susceptibility (0 to 10^2 emu mol^{-1}) is shown in Figure A3.5.

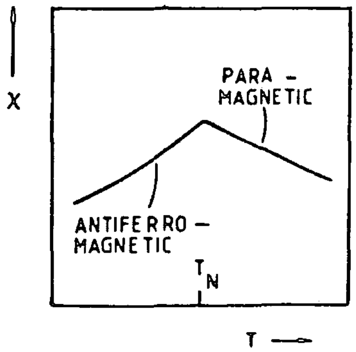


Figure A3.5

At temperatures below T_N, the Néel temperature, the susceptibility increases with increasing temperature since the number of paired-up antiparallel moments will decrease and the number of free moments will increase, until usual paramagnetic behaviour is followed above the Néel temperature. The field-dependence of antiferromagnetic susceptibilities is beyond the scope of this work, as are the temperature and field dependencies of ferrimagnetic susceptibilities.

The design and synthesis of molecular ferromagnets is the subject of much current research.[4,5] Such systems hold promise for applications such as electro-magnetic devices and may also point the way toward advances in fundamental magnetic theory which holds a central position in condensed matter physics. A further advantage is that organic based ferromagnets provide opportunity for modification of physical properties via structural changes, made using conventional synthetic organic chemistry. However, the commercial potential of these species will only be realised if the temperature at which ferromagnetic ordering occurs, lies at or close to room temperature. This condition has not yet been met, although some important results have been obtained, as discussed below.

The first material to be confirmed as a true molecular ferromagnet was the decamethylferrocinium salt[4] of TCNE (the TCNQ salt[4] was only ferromagnetic above 1.6KG and an earlier report[6] of the occasional exhibition of ferromagnetic behaviour by a polymer, of variable composition, isolated from the reaction of triaminobenzene with iodine has not been substantiated). At about the same time[7], the compound $MnCu(pbaOH)(H_2O)_3$ (pbaOH is 2-hydroxy-1,3 propylenebis (oxamato)-) was shown to order ferromagnetically. The ordering (Curie) temperatures for the above species were 4-5K. Later, MnCu (obbz).H_2O ((obbz is oxamido bis (benzoato)-) was found[8] to order, in a manner similar to the pbaOH complex, at 14K while $[TmTTF]_3[\{(MeCp)VCl_2\}_2(\mu\text{-}O)]_2$ (TmTTF is tetramethyl-tetrathiafulvalene) underwent a ferromagnetic transition at 20K[9].

Several models have been proposed[4] for ferromagnetic coupling in molecular solids (i.e. those without extensive intermolecular covalent bonding in the solid state), and one of these has been adapted to explain bulk (3D) ferromagnetism - this approach invokes configuration mixing of a virtual triplet excited state with the ground state, for a $--D^{\cdot+}A^{\cdot-}D^{\cdot+}A^{\cdot-}--$ chain, which leads to ground state stabilisation for ferromagnetic coupling. The relevance to the $Cp_2{}^{*}Fe$-TCNE system is clear as is shown below:

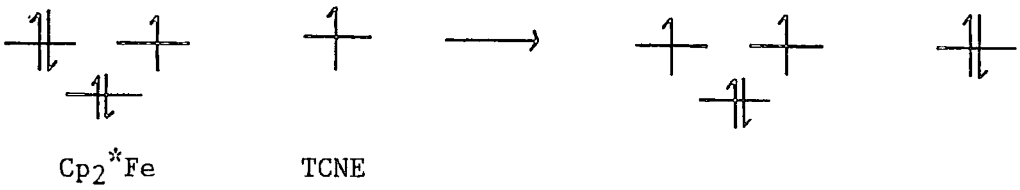


Figure A3.6

The other models[4] are (1) Heitler-London spin exchange between radicals with large positive and negative atomic π spin-densities, (2) high spin multiplicity molecules and polymers which might form ferromagnetic domains and (3) superexchange via a degenerate orbital on a closed-shell ion. A different approach[10] has been used for the MnCu complexes mentioned above. Here, the Mn^{2+} spins (S=5/2) have been polarised along the same direction through antiferromagnetic coupling to Cu^{2+} (S=1/2). The Mn^{2+} spins can then exhibit 3D ferromagnetism below a critical temperature. The spin arrangement is shown below.

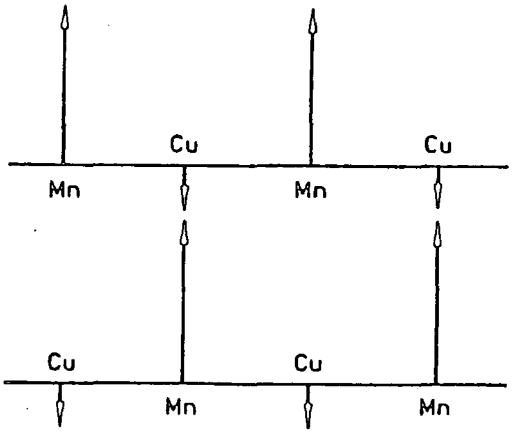


Figure A3.7

It should be noted that ionic ferromagnets are well-known[11], but these have relatively low ordering temperatures (up to 80K) and lack the versatility of modification of organic-based materials.

A3.2 RESULTS AND DISCUSSION

Magnetisation curves (σ-B_0 plots) for some of the solids described in this thesis are given in Figure A3.8. Plot A shows the curve for the glass bulb used to contain the sample and is a typical diamagnetic response. Plot B shows the curve of the starting material $(PhCN_2S_2)_2$ which gives a typical paramagnetic response. Plots C,D and E for $Mn_2(CO)_8PhCN_2S_2$, $Cp_2Ni_2PhCN_2S_2$ and the $Co_2(CO)_8$-$(PhCN_2S_2)_2$ product, respectively, also exhibit this behaviour. The susceptibilities are given in Table A3.1.

Table A3.1 Magnetic Susceptibilities of Some $PhCN_2S_2$ Complexes

COMPOUND	$(JT^{-2}Kg^{-1})$
$Mn_2(CO)_8PhCN_2S_2$	0.375
$Cp_2Ni_2PhCN_2S_2$	0.022
$Co_2(CO)_8$-$(PhCN_2S_2)_2$	0.048

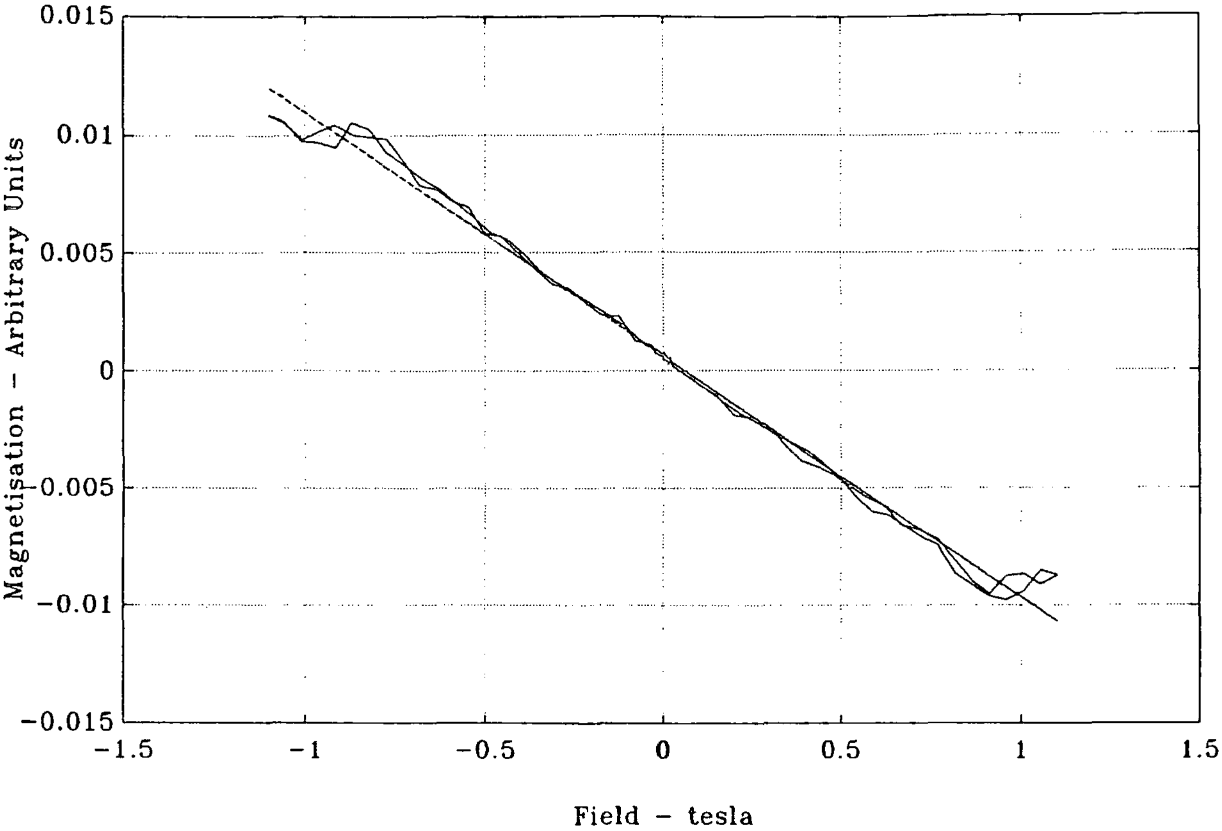
Curves F,G and H show a very weak paramagnetic response and can be considered to be essentially diamagnetic.

The remaining plots show behaviour similar to that (see Figure A3.9) of fine-particle ferrofluid systems[12] (based on the ferromagnetic metals iron, cobalt and nickel) and suggest that some form of magnetic ordering is occurring at room temperature.

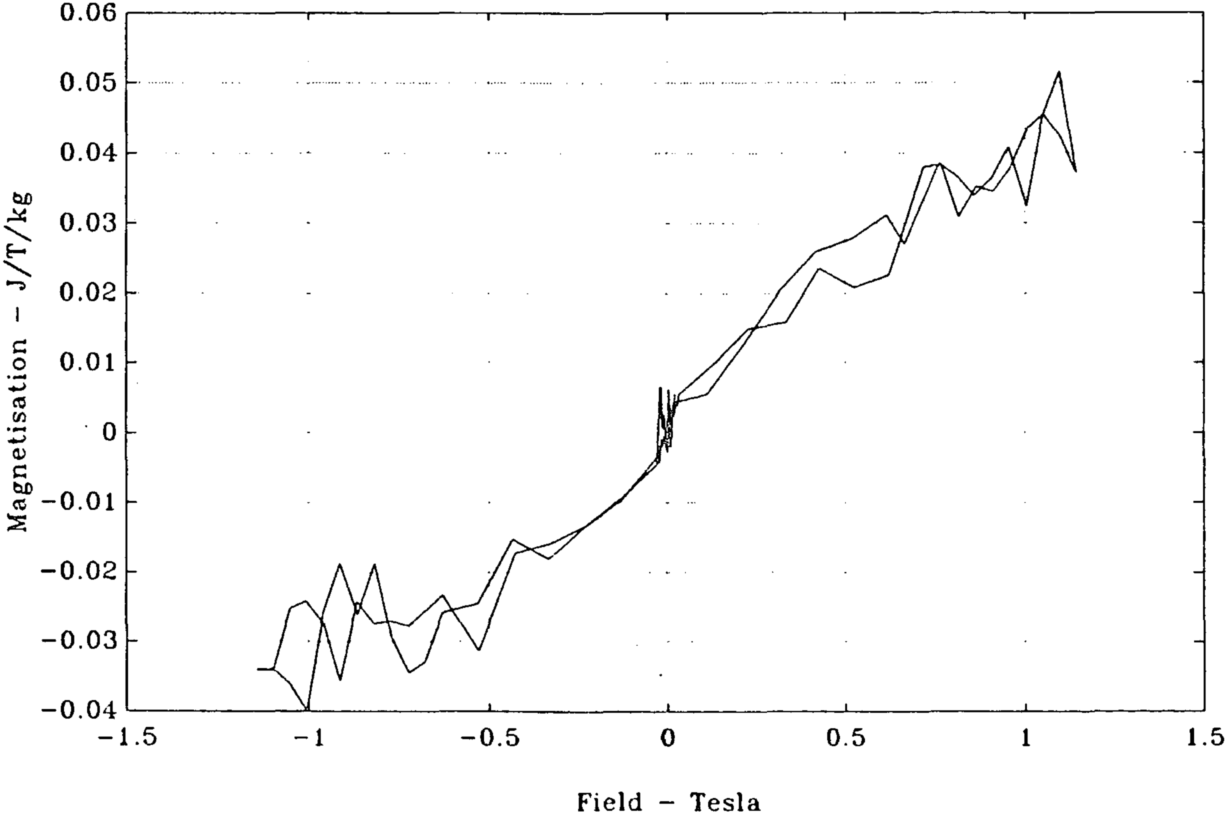
This behaviour for intrinsically ferromagnetic systems, can be explained as follows.[1] In a very small magnetic body, the relative contribution of the domain wall energy to the magnetostatic self-energy increases and eventually it becomes unfavourable for a domain wall to form. The body then behaves as a single domain. The resultant magnetic moment of a crystalline material usually lies along some preferred crystal axis. This tendency, known as

A. Glass Bulb

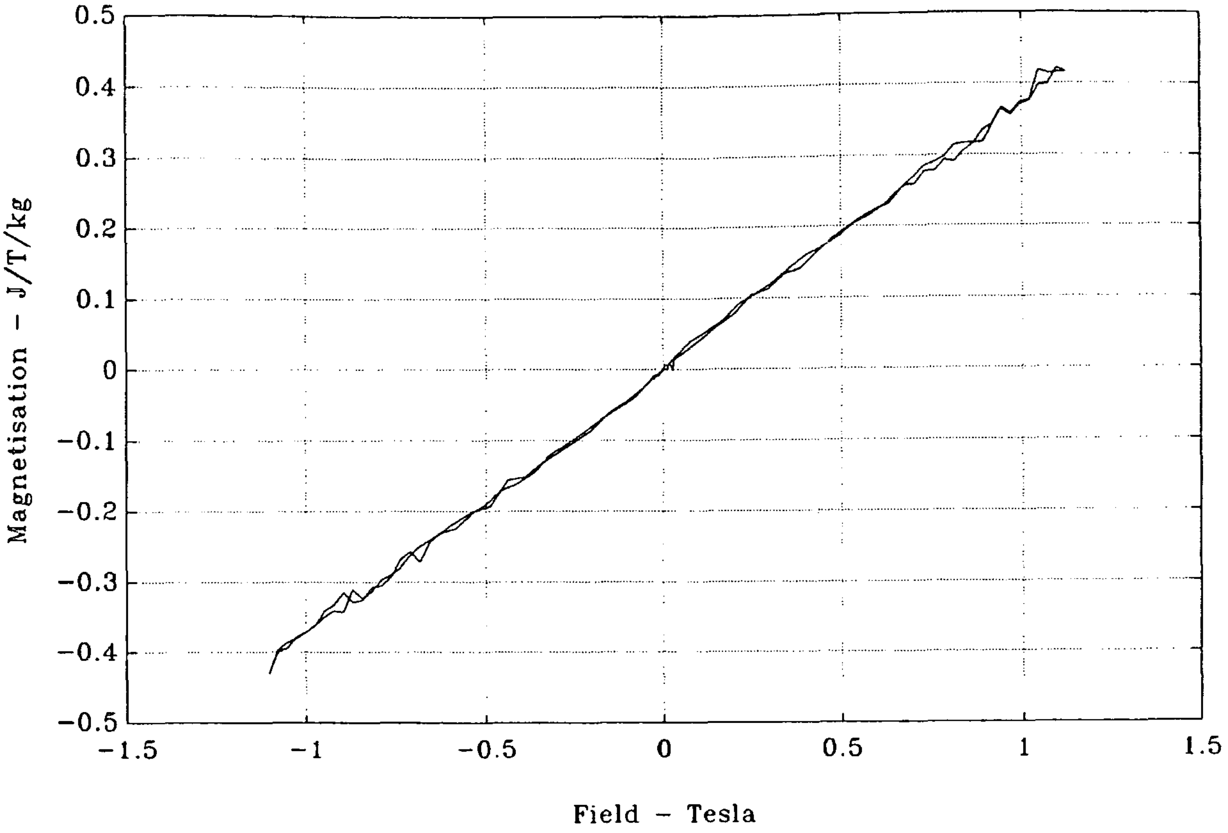
Figure A3.8.



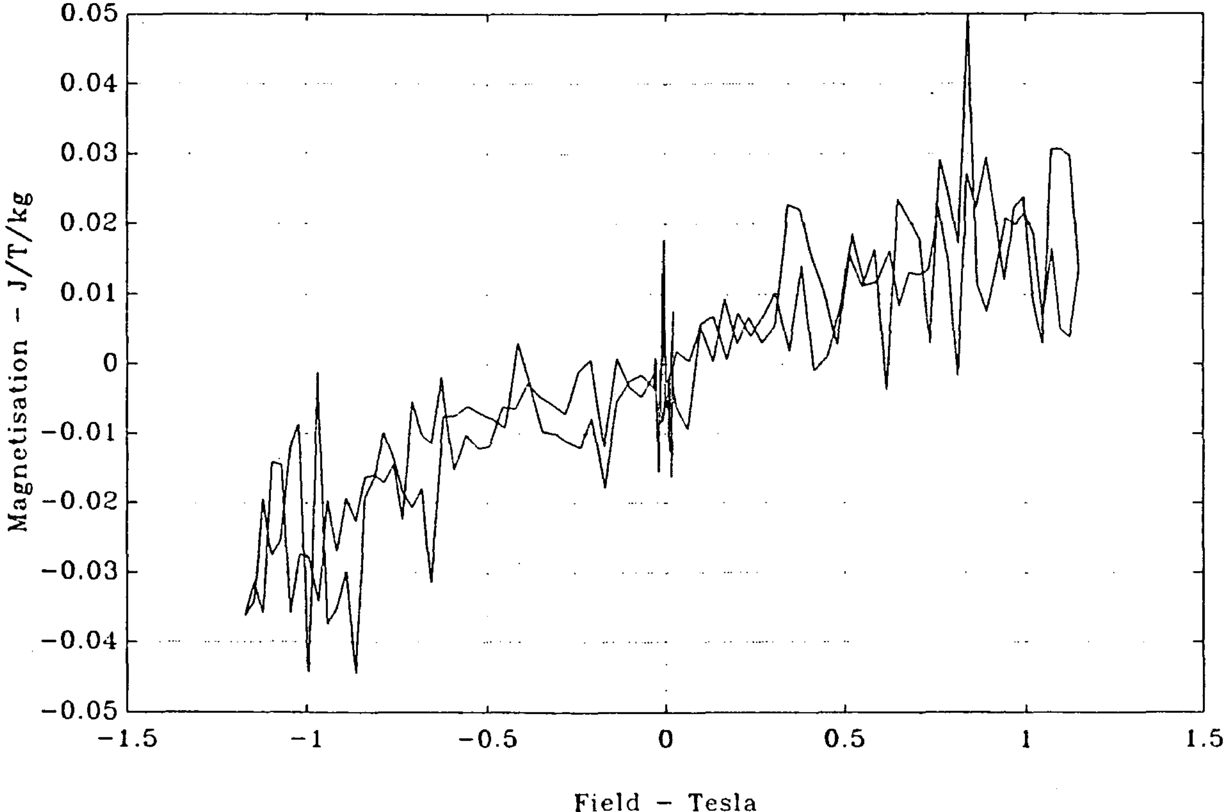
B. $(PhCN_2S_2)_2$



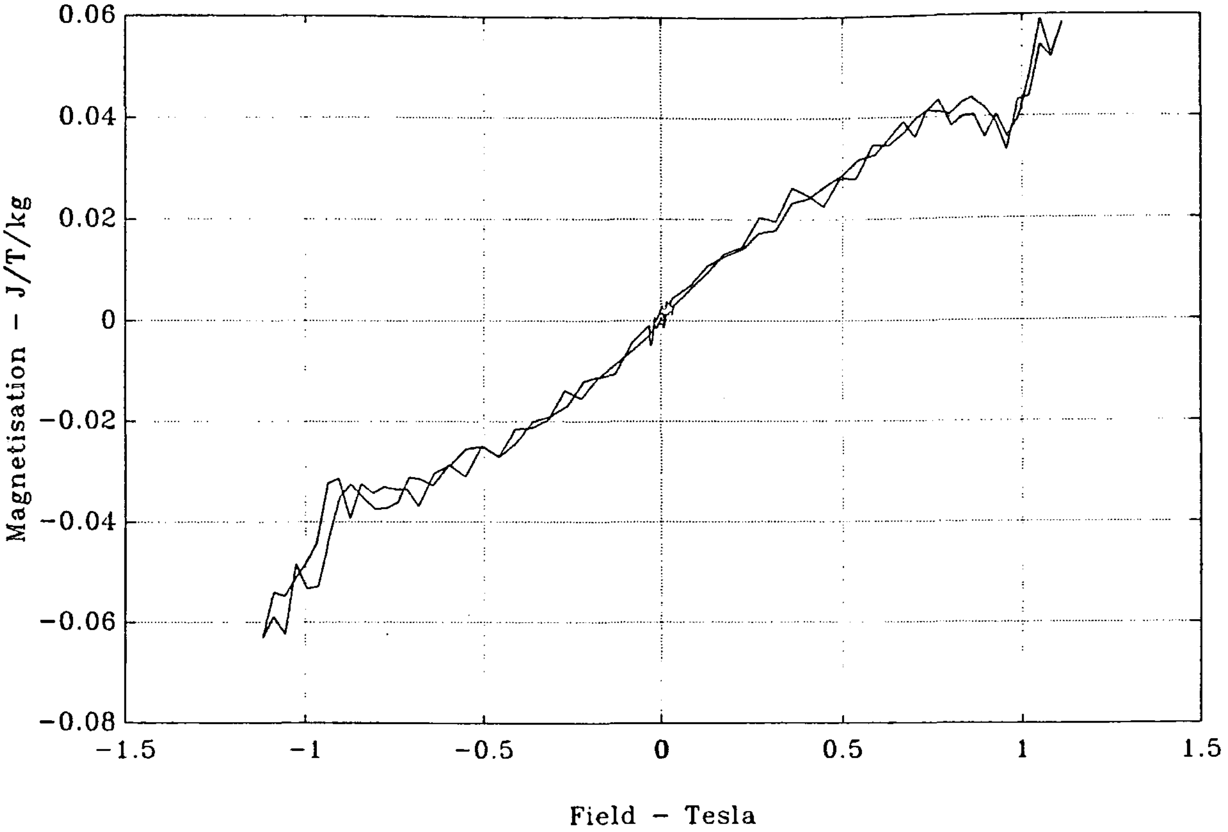
C. $Mn_2(CO)_8PhCN_2S_2$



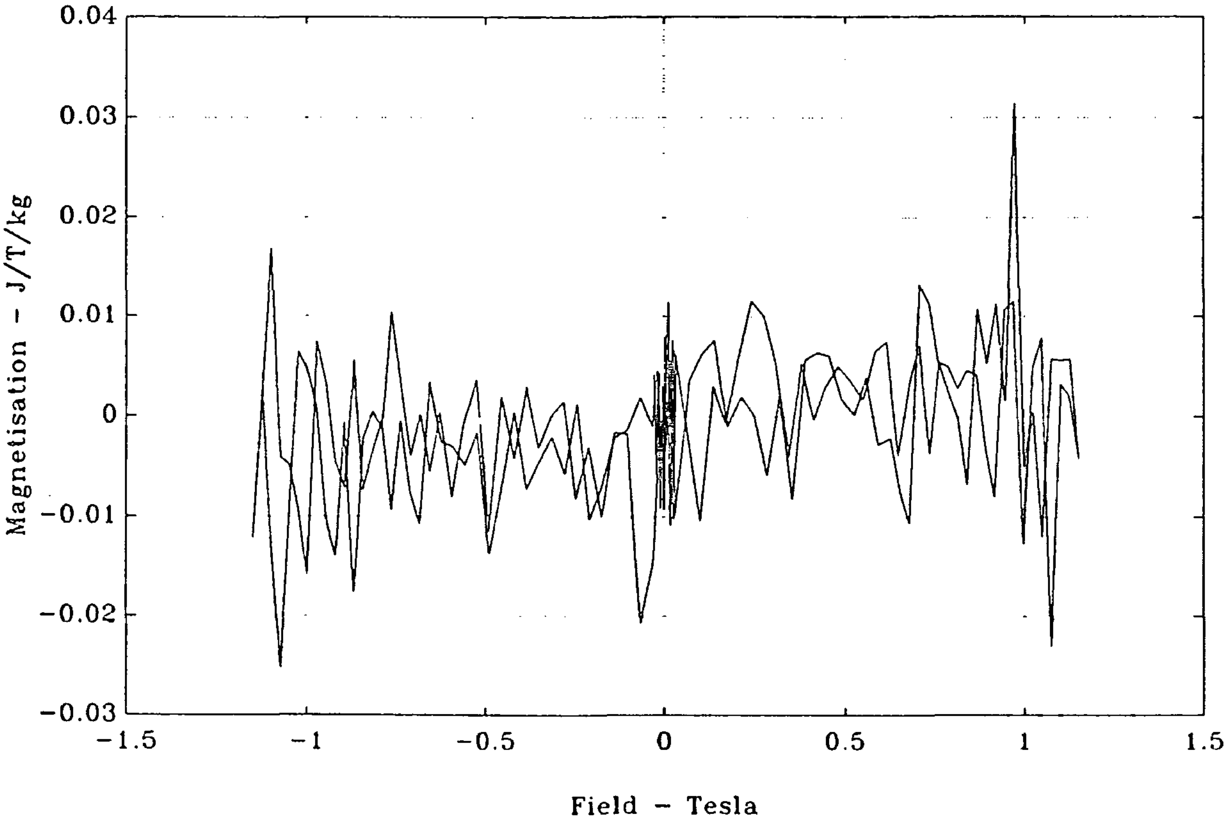
D. $Cp_2Ni_2(PhCN_2S_2)$



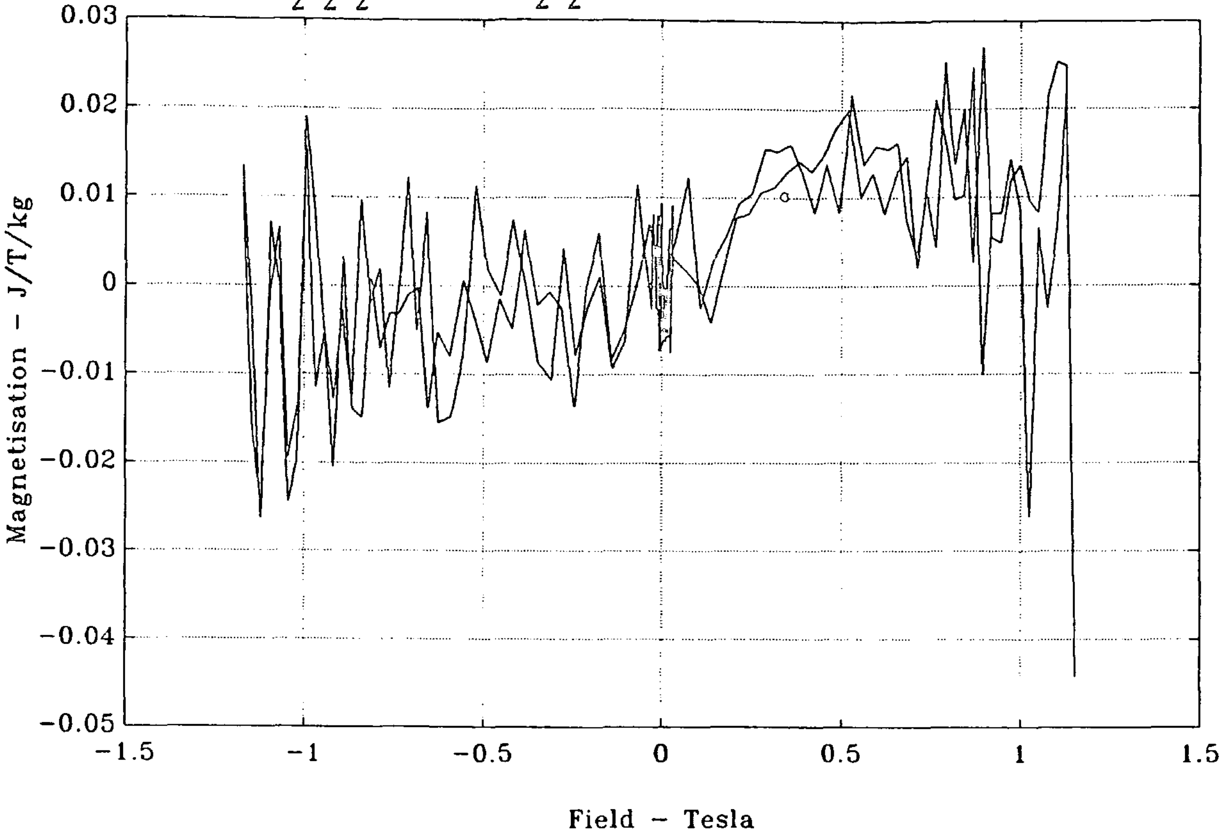
E. $(PhCN_2S_2)_2$-$Co_2(CO)_8$



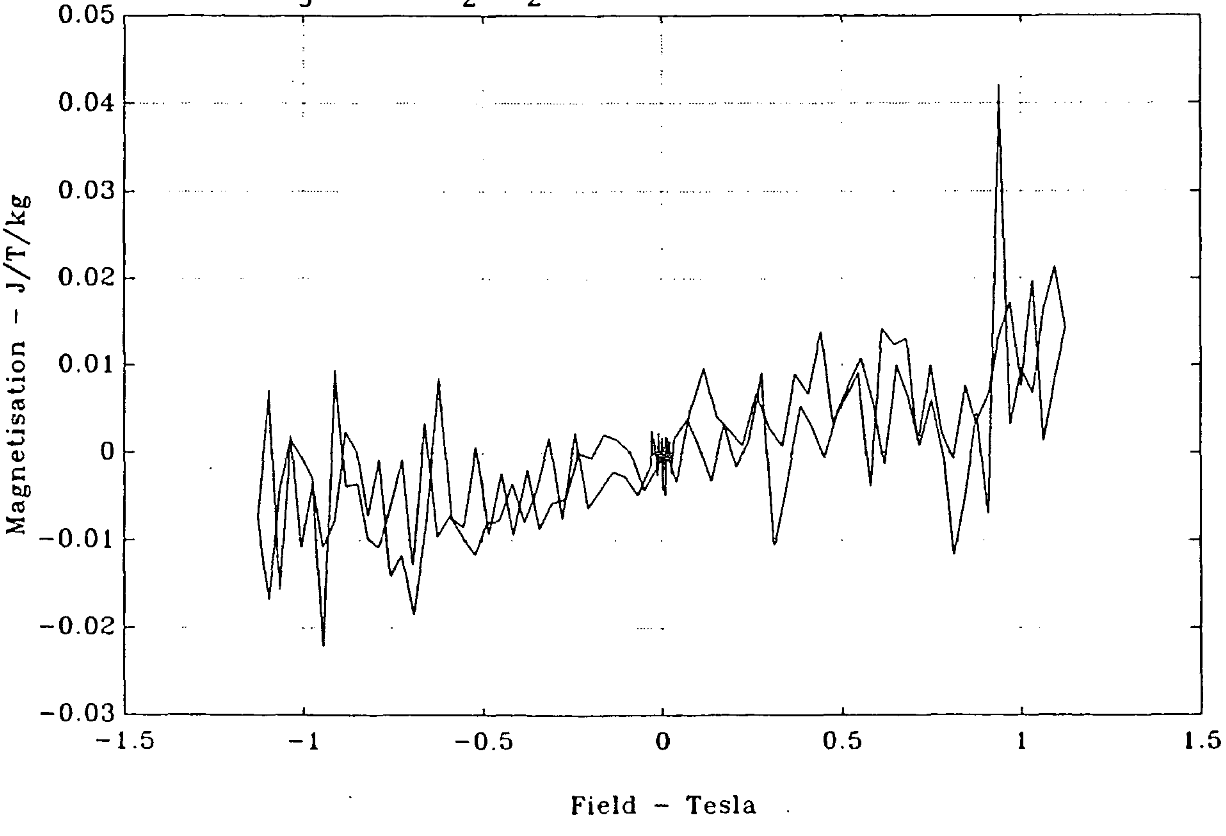
F. $[CpCo(PhCN_2S)]_2$



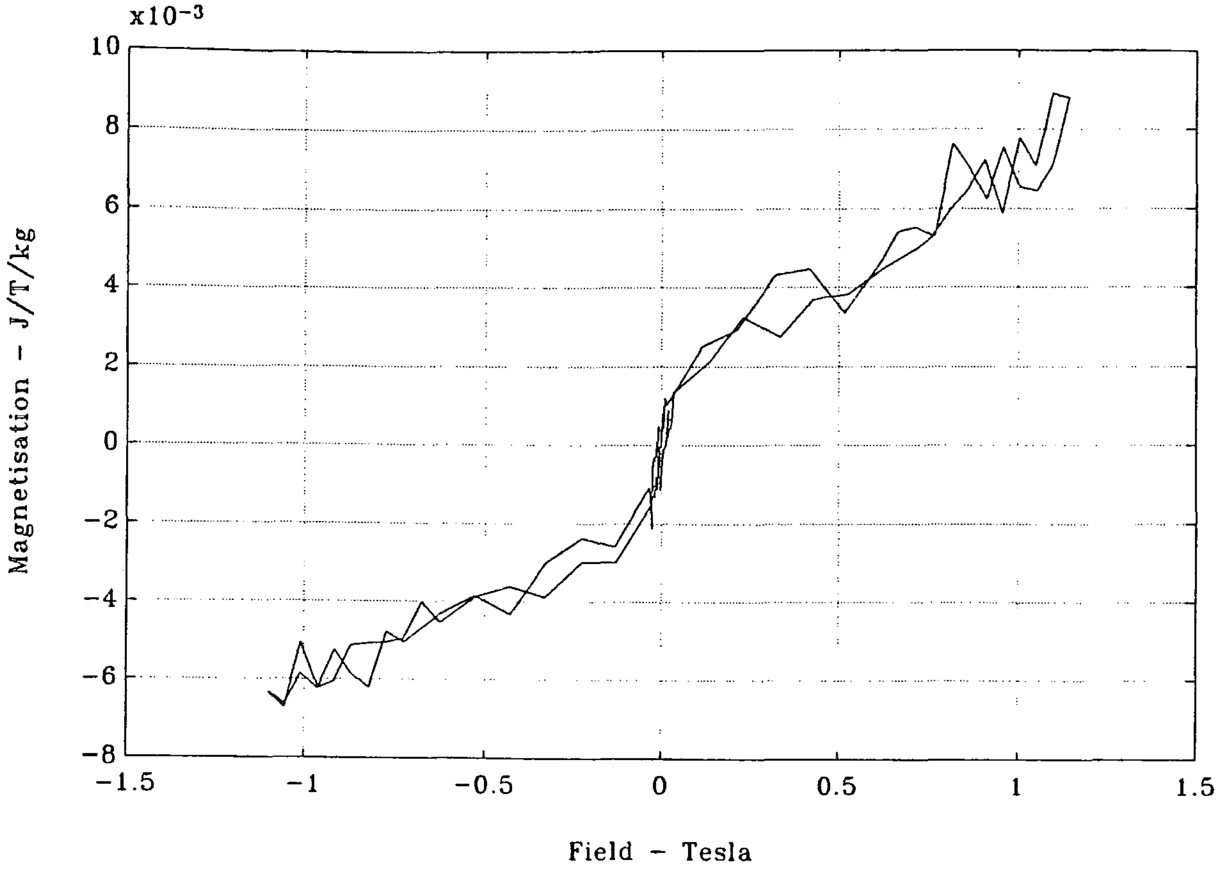
G. $(PhCN_2S_2)_2$-$[CpFe(CO)_2]_2$



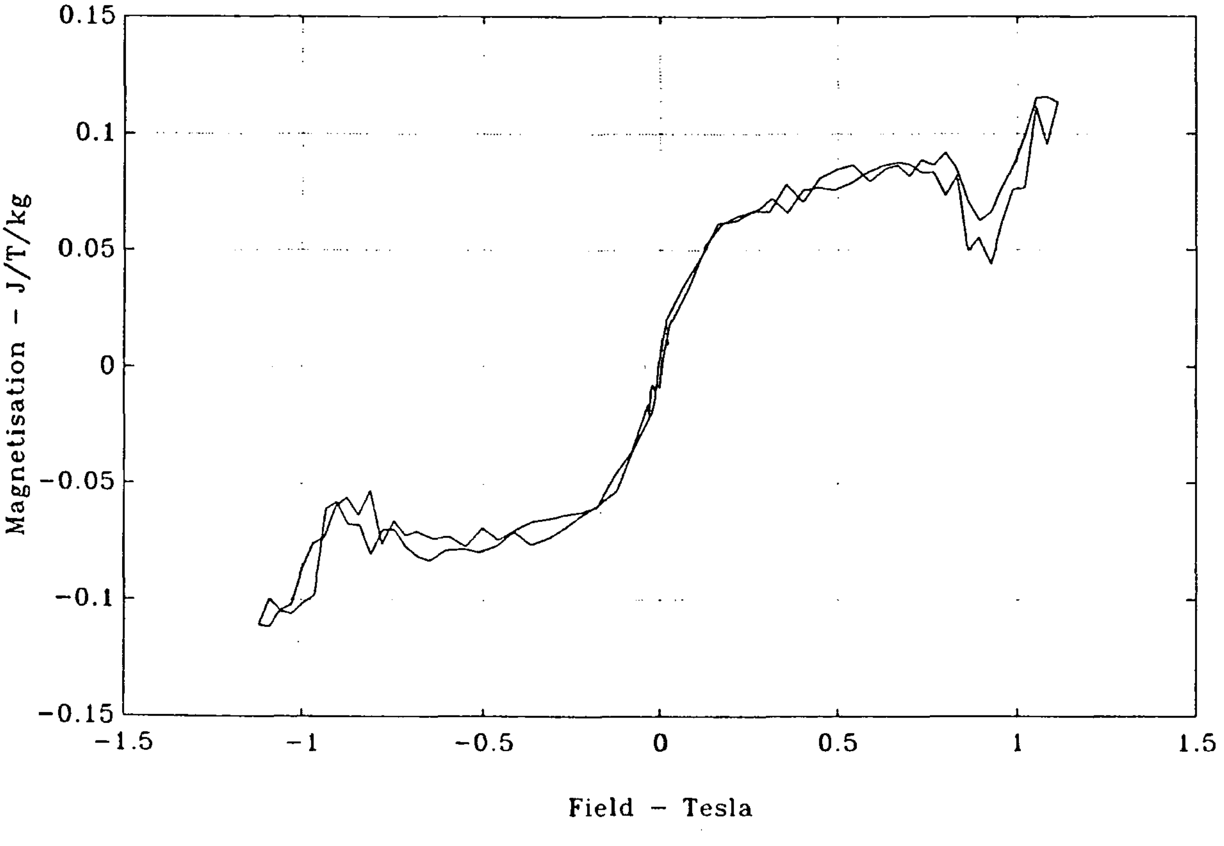
H. $[(Ph_3P)Pt(PhCN_2S)]_2$



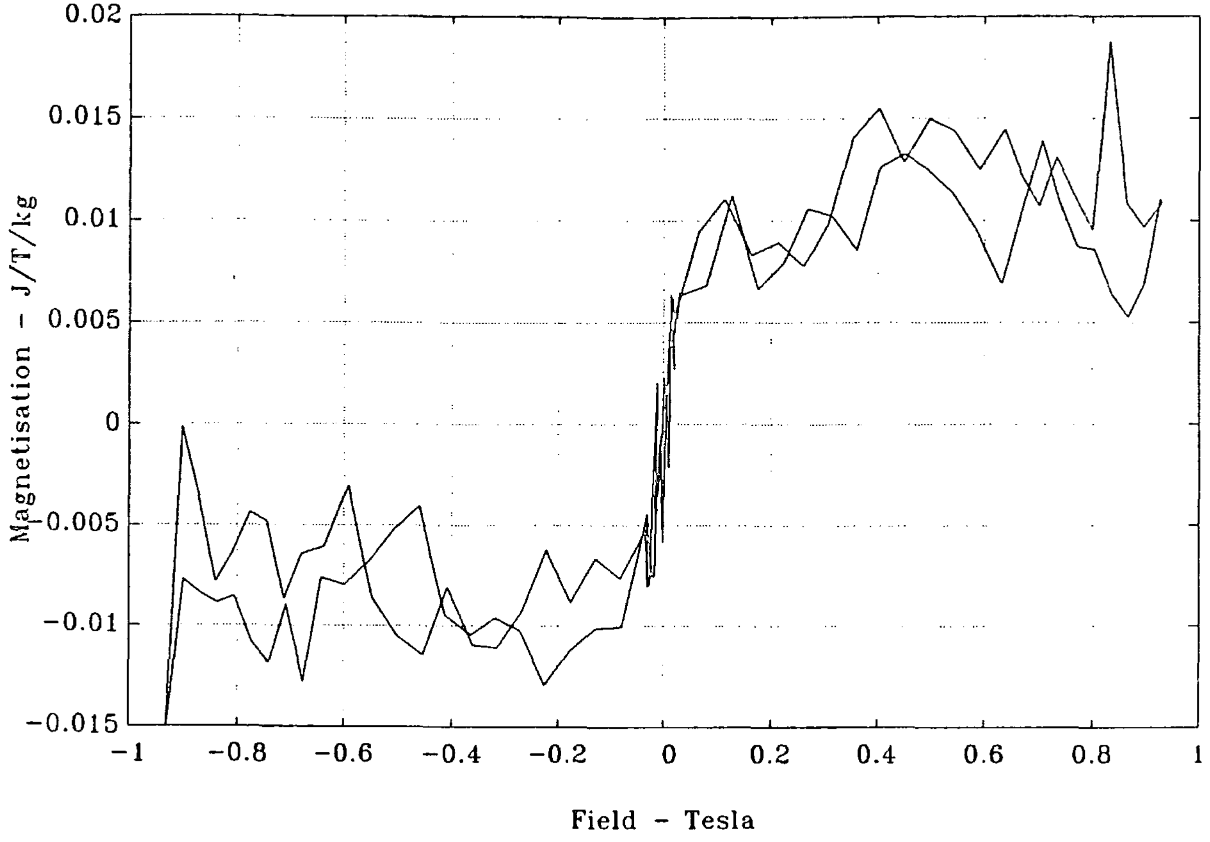
I. $Fe_2(CO)_6PhCN_2S_2$



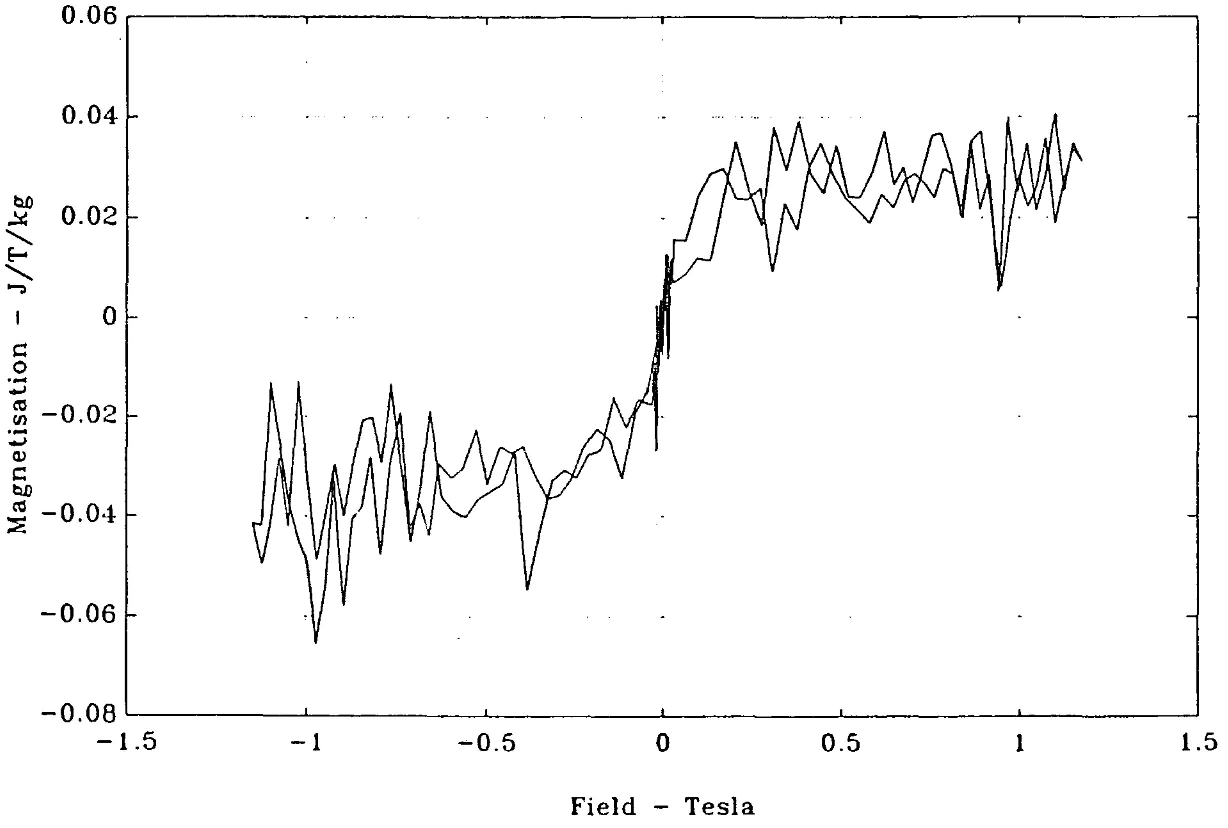
J. $[CpV(PhCN_2S_2)]_2$



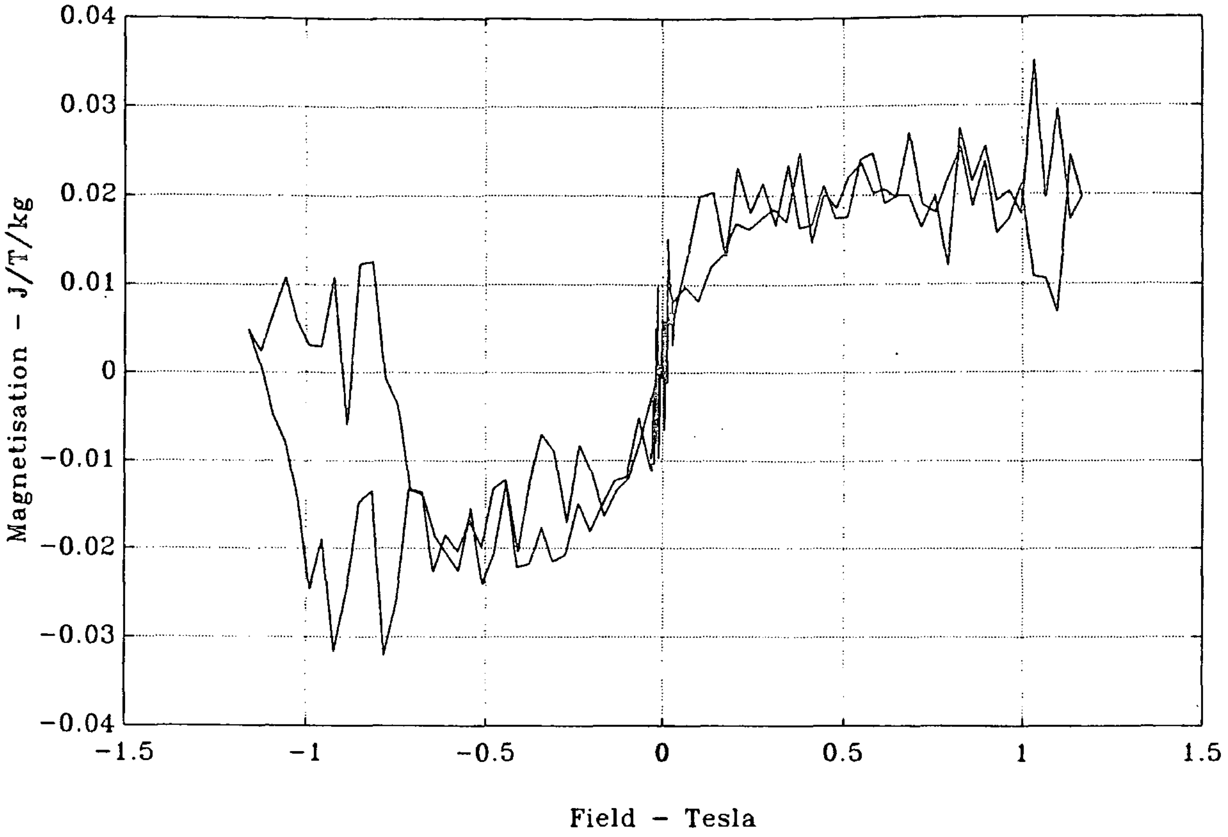
K. $(PhCN_2S_2)_2$-$Re_2(CO)_{10}$



L. $(PhCN_2S_2)_2$-$[CpMo(CO)_3]_2$



M. $(PhCN_2S_2)MoCO$



magnetocrystalline anisotropy, is dependent upon the volume of the particle. The anisotropy energy (KV) will be small for a single domain particle and for even smaller bodies can become smaller than the thermal energy; the magnetic moment of the particle will then fluctuate in a manner analogous to Brownian motion; i.e. $kT \approx KV$. This behaviour resembles that of a paramagnetic system except that the resultant magnetic moment in question consists of 10^4-10^5 atomic moments. Hence, this phenonenon is known as superparamagnetism. However, since the individual atomic moments still exhibit cooperative (ferromagnetic) behaviour within the particle these materials are not paramagnetic.

A typical magnetisation curve for a superparamagnetic system is given below in Figure A3.9. There is no hysteresis and saturation is reached in fields that are 10^4 less than those required for paramagnetic materials. The resemblance to curves I-M is clear, suggesting that some form of magnetic ordering is occurring in these systems.

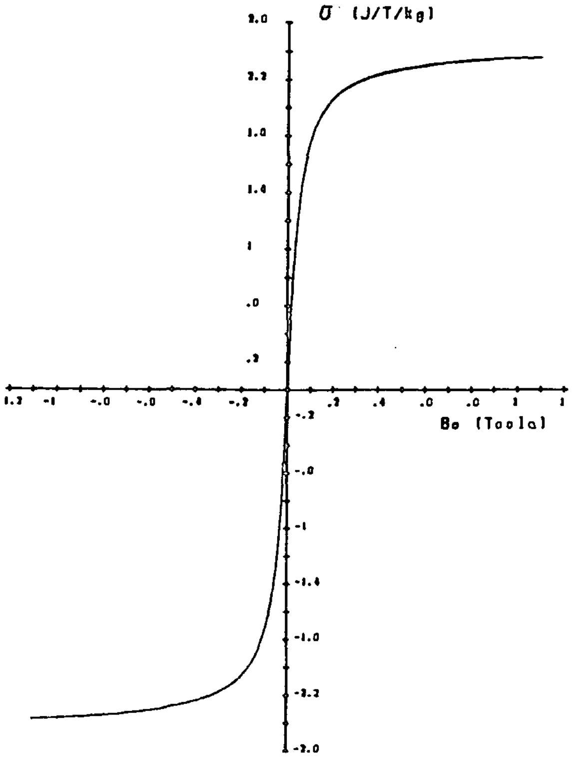


Figure A3.9

X-ray structure determinations have thus far been carried out on $Fe_2(CO)_6PhCN_2S_2$ and $Cp_2Ni_2PhCN_2S_2$. The iron compound, which behaves as a superparamagnetic material, was found to form chains, linked through ring nitrogen atoms (Section 2.5.2) whereas the nickel complex showed no intermolecular interactions (Section 3.7.2) and behaved as a normal paramagnet. This obviously suggests that intermolecular contacts may be responsible for the superparamagnetic behaviour.

A3.3 CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

The preliminary studies discussed in this appendix show that the magnetic properties of transition metal dithiadiazole complexes merit further investigation. At the present time, some of the magnetisation curves indicative of superparamagnetic behaviour are not fully reproducible and so the degree of sample purity will require attention, possibly using methods such as chromatography or slow recrystallisation. Less soluble compounds are usually more difficult to purify (most purifications are more easily carried out on solutions) and so changes in the ligands of the transition metal starting materials could be made to increase solubility e.g. the use of pentamethylcyclopentadiene complexes. Other dithiadiazoles[13] could also be used e.g. 1,3-dithiadiazoles or different substituents at the ring carbon. Also, different radical rings could be investigated[13], such as dithiazoles and different transition metals. These changes should enable the steric and electronic environments at the metal centre and on the CSN ligand to be probed. The relationship between these environments and the magnetic properties of the bulk solid will, hopefully, become apparent.

The measurements described here were made using a vibrating sample magnetometer.[14] Further measurements could be made using a much more sensitive instrument known as a SQUID (superconducting quantum interference device).[14] Low temperature measurements would also be useful. Mossbauer spectroscopy[15], which can give information on magnetic structure via Zeeman splitting, could be applied to complexes containing a suitable isotope (γ-ray emitter). Also, polarised neutron diffraction[16] can be used to determine the locations, magnitudes and directions of the magnetic moments present in magnetic materials.

Clearly, much further work needs to be done before the exchange mechanism responsible for the unusual magnetic behaviour of these complexes can be identified. However, the mechanism put forward[4] for the Cp_2^*Fe-TCNE system does not seem to be responsible for the effects observed in this work (viz no hysteresis observed, no donor-acceptor pairs). Interestingly, a strategy based on 'bringing into interaction metal ions and stable organic radicals which can act as ligands' has been reported[17] recently. Ferro- and ferrimagnetic chains have been prepared, but 3D order has not yet been achieved by these workers.

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CLARK, Prof. D.T. (ICI New Science Group) 'Structure, Bonding, Reactivity and Synthesis as Revealed by ESCA'	22nd November 1984
OATES, Prof. G.E. (formerly of University of Wyoming, U.S.A.) 'Chemical Education in Britain and America: Successes and Deficiencies'	7th May 1985
OVINGTON, Dr. A.K. (University of Newcastle-upon-Tyne) 'Chemistry with Chips'	24th January 1985
ILLON, Dr. K.B. (University of Durham) '^{31}P NMR Studies of Some Anionic Phosphorus Complexes'	12th December 1984
VERALL, Mr. N. (University of Durham) 'Picosecond Pulsed Laser Raman Spectroscopy'	21st November 1984
EAST, Dr. W.J. (University of Durham) 'Syntheses of Conjugated Polymers. Why and How?'	25th October 1984
EAST, Dr. W.J. (University of Durham) 'A Plain Man's Guide to Polymeric Organic Metals'	27th November 1984
LEET, Dr. G.W.J. (University of Oxford) 'Syntheses of some Alkaloids from Carbohydrates'	13th February 1985
ERMAIN, Dr. A. (Université du Languedoc, Montpellier) 'Anodic Oxidation of Perfluoro Organic Compounds in Perfluoroalkane Sulphonic Acids'	19th October 1984
IBSON, Dr. H.W. (Signal UOP Research Centre, Des Plaines, llinois) Isomerization of Polyacetylene'	21st September 1984

OLDING, Prof. B.T. (University of Newcastle-upon-Tyne) 15th November 1984
The Vitamin B_{12} Mystery'

REEN, Dr. M.L.H. (University of Oxford) 31st January 1985
Naked Atoms and Negligée Ligands'

RIMMETT, Dr. R. (University of Otago, Dunedin, New Zealand) 22nd May 1985
Some Aspects of Nucleophilic Substitution in Imidazoles'

ROSSEL, Dr. M.C. (Bedford College, University of London) 24th April 1985
Hydroxypyridone Dyes - Bleachable One-Dimensional Metals?'

ARRIS, Prof. R.K. (University of Durham) 24th October 1984
NMR of Solid Polymers'

ARRIS, Prof. R.K. (University of Durham) 9th May 1985
Chemistry in a Spin: Nuclear Magnetic Resonance'

UDLICKY, Dr. M. (Virginia State University, Blacksburg) 22nd May 1985
Preferential Elimination of Hydrogen Fluoride from
Vicinal Bromofluorocompounds'

ATRITZKY, Prof. A.R., FRS (University of Florida) 14th March 1985
Some Adventures in Heterocyclic Chemistry'

AALI, Dr. K. (Hydrocarbon Research Institute, University of 12th July 1985
outhern California)
'Recent Developments in Superacid Chemistry and Mechanistic
Considerations in Electrophilic Aromatic Substitutions; a
Progress Report'

EDWITH, Prof. A. (Pilkington Bros.) 7th February 1985
Glass as a High Technology Material'

OGAN, Dr. N. (University of Nottingham) 18th October 1984
N_2O_4 and Rocket Fuels'

UX, Mr. P.J. (University of Durham) 5th December 1984
IR and GC Studies of the Interaction of CH_3OH with High
Silica Zeolites'

AITLIS, Prof. P.M., FRS (University of Sheffield) 21st February 1985
What Use is Rhodium?'

INCHER, Dr. D.J. (University of Durham) 19th February 1985
Stereoselective Syntheses of Some Novel Anthracyclinones
Related to the Anti-Cancer Drug Adriamycin and to the
Steffimycin Antibiotics'

ITCHELL, Dr. T.N. (University of Dortmund) 19th June 1985
Some Synthetic and NMR-Spectroscopic Studies of Organotin
Compounds'

ULVEY, Dr. R.E. (University of Durham) 27th February 1985
Some Unusual Lithium Complexes'

UNRO, Dr. H.S. (University of Durham) 7th November 1984
New Information from ESCA Data'

ACKER, Dr. J.E. (University of Auckland, New Zealand) 15th May 1985
tudies of Free Radical Reactions in Aqueous Solution
sing Ionising Radiation'

*PACKER, Prof. K.J. (B.P. Research Centre) 'NMR Investigations of the Structure of Solid Polymers'	12th March 1985
PARKER, Dr. D. (ICI plc, Petrochemical & Plastics Division, Wilton) 'Applications of Radioisotopes in Industrial Research'	1st May 1985
*PASSMORE, Prof. J. (University of New Brunswick) 'The Synthesis and Characterisation of some Novel Selenium-Iodine Cations, Aided by ^{77}Se NMR Spectroscopy'	14th May 1985
*POLIAKOFF, Dr. M. (University of Nottingham) 'New Methods for Detecting Organometallic Intermediates in Solution'	21st March 1985
*PORTERFIELD, Prof. W.W. (Hampden-Sydney College, U.S.A.) 'There is No Borane Chemistry (Only Geometry)'	7th November 1984
RAPPOPORT, Prof. Z. (The Hebrew University, Jerusalem) 'The Rich Mechanistic World of Nucleophilic Vinylic Substitution'	14th June 1985
RINGSDORF, Prof. H. (Organic Chemistry Institute, University of Mainz) 'Polymeric Liposomes as Models for Biomembranes and Cells?'	28th March 1985
RODGERS, Dr. P.J. (ICI plc, Agricultural Division, Billingham) 'Industrial Polymers from Bacteria'	7th March 1985
*SALTHOUSE, Dr. J.A. (University of Manchester) 'Son et Lumiere' (A Chemical Energy Show)	14th February 1985
SHAW, Prof. G. (University of Bradford) 'Synthetic Studies on Imidazole Nucleosides and the Antibiotic Coformycin'	26th June 1985
*STEPHENSON, Dr. T.A. (University of Edinburgh) 'Some Recent Studies in Platinum Metals Chemistry'	28th November 1984
STIRLING, Prof. C.J.M. (University College of North Wales) 'Molecules Taking the Strain'	29th November 1984
*SUSCHITZKY, Emeritus Prof. H. (University of Salford) 'Fruitful Fissions of Benzofuroxanes and Isobenzimadazoles (umpolung of *o*-phenylenediamine)'	11th January 1985
*TUCK, Prof. D. (University of Windsor, Ontario) 'Lower Oxidation State Chemistry of Indium'	8th May 1985
WILLIAMS, Dr. D.L.H. (University of Durham) 'Chemistry in Colour'	21st May 1985
WILLIAMS, Prof. G. (University College of Wales, Aberystwyth) 'Liquid Crystalline Polymers'	8th May 1985
WOOLLINS, Dr. D. (Imperial College, University of London) 'Metal-Sulphur-Nitrogen Complexes'	13th June 1985

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COLLOQUIA, LECTURES AND SEMINARS GIVEN BY INVITED SPEAKERS:
1st AUGUST 1985 to 31st JULY 1986

*BARNARD, Dr. C.J.F. (Johnson Matthey Group) 'Platinum Anti-Cancer Drug Development'	20th February 1986
*BROWN, Dr. J.M. (University of Oxford) 'Chelate Control in Homogeneous Catalysis'	12th March 1986
*CLARK, Dr. B.A.J. (Kodak Ltd.) 'Chemistry and Principles of Colour Photography'	28th November 1985
*CLARK, Dr. J.H. (University of York) 'Novel Fluoride Ion Reagents'	29th January 1986
*DAVIES, Dr. S.G. (University of Oxford) 'Chirality Control and Molecular Recognition'	14th November 1985
*DEWING, Dr. J. (U.M.I.S.T.) 'Zeolites - Small Holes, Big Opportunities'	24th October 1985
ERTL, Prof. G. (University of Munich) 'Heterogeneous Catalysis'	7th November 1985
GRIGG, Prof. R. (Queen's University, Belfast) 'Thermal Generation of 1,3-Dipoles"	13th February 1986
*HARRIS, Prof. R.K. (University of Durham) 'The Magic of Solid State NMR'	27th February 1986
HATHWAY, Dr. D. (University of Durham) 'Herbicide Selectivity'	5th March 1986
*IDDON, Dr. B. (University of Salford) 'The Magic of Chemistry'	6th March 1986
*JACK, Prof. K.H. (University of Newcastle) 'Chemistry of Si-Al-O-N Engineering Ceramics'	21st November 1985
*LANGRIDGE-SMITH, Dr. P.R.R. (University of Edinburgh) 'Naked Metal Clusters - Synthesis, Characterisation and Chemistry'	14th May 1986
*LEWIS, Prof. Sir Jack (University of Cambridge) 'Some more Recent Aspects in the Cluster Chemistry of Ruthenium and Osmium Carbonyls'	23rd January 1986
*LUDMAN, Dr. C.J. (University of Durham) 'Some Thermochemical Aspects of Explosions'	17th October 1985
MACBRIDE, Dr. J.A.H. (Sunderland Polytechnic) 'A Heterocyclic Tour on a Distorted Tricycle - Biphenylene'	20th November 1985

O'DONNELL, Prof. M.J. (Indiana-Purdue University) 'New Methodology for the Synthesis of Amino Acids'	5th November 1985
PARMAR, Dr. V.S. (University of Delhi) 'Enzyme Assisted ERC Synthesis'	13th September 1985
PHILLIPS, Dr. N.J. (University of Technology, Loughborough) 'Laser Holography'	30th January 1986
PROCTER, Prof. G. (University of Salford) 'Approaches to the Synthesis of some Natural Products'	19th February 1986
*SCHMUTZLER, Prof. R. (University of Braunschweig) 'Mixed Valence Diphosphorous Compounds'	9th June 1986
SCHRODER, Dr. M. (University of Edinburgh) 'Studies on Macrocycle Complexes'	5th March 1986
SHEPPARD, Prof. N. (University of East Anglia) 'Vibrational and Spectroscopic Determinations of the Structures of Molecules Chemisorbed on Metal Surfaces'	15th January 1986
TEE, Prof. O.S. (Concordia University, Montreal) 'Bromination of Phenols'	12th February 1986
TILL, Miss C. (University of Durham) 'ESCA and Optical Emission Studies of the Plasma Polymerisation of Perfluoroaromatics'	26th February 1986
*TIMMS, Dr. P. (University of Bristol) 'Some Chemistry of Fireworks'	31st October 1985
WADDINGTON, Prof. D.J. (University of York) 'Resources for the Chemistry Teacher'	28th November 1985
*WHITTLETON, Dr. S.N. (University of Durham) 'An Investigation of a Reaction Window'	30th October 1985
WILDE, Prof. R.E. (Texas Technical University) 'Molecular Dynamic Processes from Vibrational Bandshapes'	23rd June 1986
YARWOOD, Dr. J. (University of Durham) 'The Structure of Water in Liquid Crystals'	12th February 1986

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COLLOQUIA, LECTURES AND SEMINARS GIVEN BY INVITED SPEAKERS
1ST AUGUST 1986 TO 31ST JULY 1987

*ALLEN, Prof. Sir G. (Unilever Research) Biotechnology and the Future of the Chemical Industry	13th November 1986
BARTSCH, Dr. R. (University of Sussex) Low Co-ordinated Phosphorus Compounds	6th May 1987
BLACKBURN, Dr. M. (University of Sheffield) Phosphonates as Analogues of Biological Phosphate Esters	27th May 1987
BORDWELL, Prof. F.G. (Northeastern University, U.S.A.) Carbon Anions, Radicals, Radical Anions and Radical Cations	9th March 1987
*CANNING, Dr. N.D.S. (University of Durham) Surface Adsorption Studies of Relevance to Heterogeneous Ammonia Synthesis	26th November 1986
*CANNON, Dr. R.D. (University of East Anglia) Electron Transfer in Polynuclear Complexes	11th March 1987
*CLEGG, Dr. W. (University of Newcastle-upon-Tyne) Carboxylate Complexes of Zinc; Charting a Structural Jungle	28th January 1987
DÖPP, Prof. D. (University of Duisburg) Cyclo-additions and Cyclo-reversions Involving Captodative Alkenes	5th November 1986
DORFMÜLLER, Prof. T. (University of Bielefeld) Rotational Dynamics in Liquids and Polymers	8th December 1986
*GOODGER, Dr. E.M. (Cranfield Institute of Technology) Alternative Fuels for Transport	12th March 1987
*GREENWOOD, Prof. N.N. (University of Leeds) Glorious Gaffes in Chemistry	16th October 1986
*HARMER, Dr. M. (I.C.I. Chemicals & Polymer Group) The Role of Organometallics in Advanced Materials	7th May 1987
*HUBBERSTEY, Dr. P. (University of Nottingham) Demonstration Lecture on Various Aspects of Alkali Metal Chemistry	5th February 1987
HUDSON, Prof. R.F. (University of Kent) Aspects of Organophosphorus Chemistry	17th March 1987
HUDSON, Prof. R.F. (University of Kent) Homolytic Rearrangements of Free Radical Stability	18th March 1987

JARMAN, Dr. M. (Institute of Cancer Research) The Design of Anti Cancer Drugs	19th February 1987
KRESPAN, Dr. C. (E.I. Dupont de Nemours) Nickel(0) and Iron(0) as Reagents in Organofluorine Chemistry	26th June 1987
*KROTO, Prof. H.W. (University of Sussex) Chemistry in Stars, between Stars and in the Laboratory	23rd October 1986
*LEY, Prof. S.V. (Imperial College) Fact and Fantasy in Organic Synthesis	5th March 1987
*MILLER, Dr. J. (Dupont Central Research, U.S.A.) Molecular Ferromagnets; Chemistry and Physical Properties	3rd December 1986
*MILNE/CHRISTIE, Dr. A./Mr. S. (International Paints) Chemical Serendipity - A Real Life Case Study	20th November 1986
NEWMAN, Dr. R. (University of Oxford) Change and Decay: A Carbon-13 CP/MAS NMR Study of Humification and Coalification Processes	4th March 1987
*OTTEWILL, Prof. R.H. (University of Bristol) Colloid Science a Challenging Subject	22nd January 1987
*PASYNKIEWICZ, Prof. S. (Technical University, Warsaw) Thermal Decomposition of Methyl Copper and its Reactions with Trialkylaluminium	11th May 1987
ROBERTS, Prof. S.M. (University of Exeter) Synthesis of Novel Antiviral Agents	24th June 1987
RODGERS, Dr. P.J. (I.C.I. Billingham) Industrial Polymers from Bacteria	12th February 1987
*SCROWSTON, Dr. R.M. (University of Hull) From Myth and Magic to Modern Medicine	6th November 1986
SHEPHERD, Dr. T. (University of Durham) Pteridine Natural Products; Synthesis and Use in Chemotherapy	11th February 1987
THOMSON, Prof. A. (University of East Anglia) Metalloproteins and Magnetooptics	4th February 1987
*WILLIAMS, Prof. R.L. (Metropolitan Police Forensic Science) Science and Crime	27th November 1987
*WONG, Prof. E.H. (University of New Hampshire, U.S.A.) Coordination Chemistry of P-O-P Ligands	29th October 1986
*WONG, Prof. E.H. (University of New Hampshire, U.S.A.) Symmetrical Shapes from Molecules to Art and Nature	17th February 1987

Research conferences attended:

'North-East Region Graduate Symposium', Durham University, 11th April 1984.

'North-East Region Graduate Symposium', Durham University, 29th March 1985.

'Spring Meeting', Dalton Division, Royal Society of Chemistry, Strathclyde University, 19th February 1986.

'North-East Region Graduate Symposium', Durham University, 16th April 1986.

'Molecules, Clusters and Networks in the Solid State', Royal Society of Chemistry (Dalton Division), Birmingham University, 8th-11th July 1986.

'Spring Meeting', Dalton Division, Royal Society of Chemistry, Heriot-Watt University, 11th March 1987.

'North-East Region Graduate Symposium', Durham University, 27th March 1987.

'Annual Chemical Congress', Royal Society of Chemistry, University of Kent at Canterbury, 12th-15th April 1988.

'University of Strathclyde Inorganic Chemistry Conference', Strathclyde University, 27th-28th June 1988.