METAL COMPLEXES OF HETEROCYCLIC CARBOTHIALDEHYDES

being a Thesis presented by

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to the

University of St. Andrews

in application for the degree of M.Sc.

September, 1984.

TO

KARIN AND FIONA

DECLARATION

I hereby declare that the following thesis is based on the results of experiments carried out by me, that it is of my own composition, and that it has not been submitted previously in application for a higher degree.

Peter James Pogorzelec

CERTIFICATE

I hereby certify that Peter James Pogorzelec has spent eight terms conducting research under my supervision, has fulfilled the conditions of the Resolution of the University Court 1974 No. 2, and is qualified to submit the accompanying thesis in application for the degree of Master of Science.

Professor D.H. Reid
Director of Research

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to Professor D.H. Reid for his advice, guidance and continued interest in my work.

I would like to thank Professor Lord Tedder and Professor P.A.H. Wyatt for making available the laboratory facilities in the Department of Chemistry, University of St. Andrews and to the academic and technical staff for their invaluable assistance.

Thanks are also due to Mr. Richard Speirs and Miss Jane Rhodes for their help in reading the typescript.

Finally, I am deeply indebted to my wife Wilma who prepared the typescript for this thesis.

EXPLANATORY NOTE

This thesis is divided into three sections, Parts 1, 2 and 3. Each part is divided into a number of principal sections, each prefixed by a capital letter.

Part 1 consists of a review of the relevant background literature.

Part 2 consists of a discussion of the results obtained.

Part 3 consists of the experimental details of the results discussed in Part 2, and is complementary to Part 2.

Where reference is made to the chemical literature, this is indicated by a number in superscript, a key to which can be found at the end of this thesis. The structural formulae which have been reproduced for illustrative purposes have been assigned Arabic numerals, which correspond to the numbers which have been assigned to the relevant compounds in the text. The structure keys to Parts 1 and 2 are distinct. The structure key to Part 3 is the same as that for Part 2.

CONTENTS

Page

INTRODUCTION

DISCUSSION

C./

SUMMARY

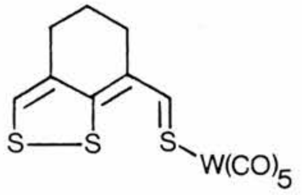
A series of mono-, di-, and trialkylpyrrole-2-carbothialdehydes and 3-carbothialdehydes was prepared, using a novel variation of the Vilsmeier reaction. Pyrrole-2-carbothialdehyde could not be isolated but could be obtained pure in ether solution.

The reaction of pyrrole-2-carbothialdehydes with metal acetates $[M(MeCO_2)_2; M = Co, Ni, Cu, Zn, Pd, Cd]$ was investigated. The acetates of Ni, Cu, Zn, Pd and Cd gave bis bidentate complexes with pyrrole-2-carbothialdehydes. The copper complexes were paramagnetic in solution, whereas the nickel, zinc, palladium and cadmium complexes were diamagnetic in solution. Cobalt(II)acetate gave, in the presence of air, tris bidentate complexes which were shown to be the *mer* isomer. However, with 4,5-dimethylpyrrole-2-carbothialdehyde as ligand, a trace of the *fac* isomer was also isolated.

Pyrrole-2-carbothialdehydes, pyrrole-3-carbothialdehydes and indolizine carbothialdehydes reacted with tetraethylammonium pentacarbonyliodotungstate (0) $\{Et_4\overset{+}{N}[W(CO)_5I]^-\}$ in the presence of aqueous silver nitrate to give the corresponding pyrrole carbothialdehyde (pentacarbonyl) tungsten (0) complexes.

1,6,6a λ^4-Trithiapentalenes, behaving as masked carbothialdehydes or carbothioketones, reacted with tetra-alkylammonium pentacarbonylhalogenometallate (0) salts $\{Et_4\overset{+}{N}[M(CO)_5I]^-; M = W, Cr, Mo\}$ in the presence of aqueous silver nitrate to give pentacarbonyl (group VIA)

metal complexes of the previously unknown thiocarbonyl valence isomers of 1, 6, 6a λ^4-trithiapentalenes. The metal complexes obtained from symmetrical 1, 6, 6a λ^4-trithiapentalenes were shown by ^{1}H nmr spectroscopy to be fluxional in solution. In contrast, the corresponding metal complexes prepared from unsymmetrical 1, 6, 6a λ^4-trithiapentalenes did not shown fluxional behaviour in solution. An X-ray crystallographic study of the (pentacarbonyl)-tungsten (0) complex of 4, 5-dihydro-3H-benzo[c, d]1, 6, 6a λ^4-trithiapentalene showed it to have structure (1) in the solid state.



(1)

The unstable pyrrole-2-carbothialdehyde is stabilised by metal complex formation, and the relative efficiencies of the metal acetates [$M(MeCO_2)_2$; M=Co, Ni, Cu, Pd, Cd] and the tungstate $Et_4\overset{+}{N}[W(CO)_5I]^-$ for this purpose were compared.

INTRODUCTION

The aim of the work described in this thesis was to extend the work of Reid and his co-workers. Novel carbothialdehydes were prepared and their reactions with some metal acetates to form metal complexes were studied. The reactions of some carbothialdehydes and trithiapentalenes with Group VI iodopentacarbonyl metallates were also studied.

A. THIOCARBONYL COMPOUNDS

The instability of thiocarbonyl compounds with respect to oligomerisation and polymerisation, depends on the reluctance of sulphur to participate in multiple bond formation. The formation of a thiocarbonyl function (Fig. 1) requires the overlap of the carbon 2p and sulphur 3p orbitals to form a π bond. Such a bond will be weakened because of the repulsion produced when one lobe of the 2p orbital interacts with a lobe of opposite sign on the 3p orbital (Fig. 2). In addition the difference in size between the 2p and 3p orbitals reduces the extent of their interaction, thus further weakening the bond.

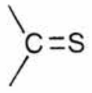


Fig. 1

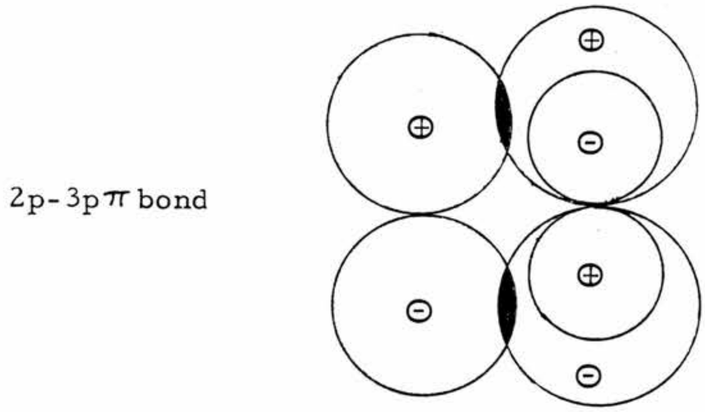


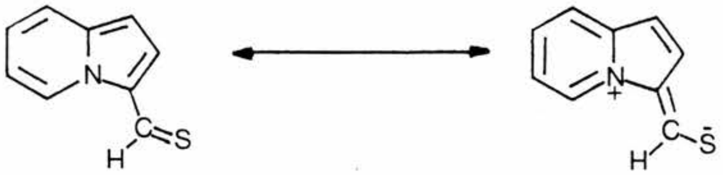
Fig. 2

The stability of thiocarbonyl compounds is greatly affected by the nature of the groups attached to the thiocarbonyl carbon atom.

The more effective these attached groups are in polarising C=S to the more stable singly bonded form $\overset{+}{C}-\overset{-}{S}$, and in delocalising the resultant positive charge, the more resistant will be the thiocarbonyl compound to oligomerisation and polymerisation.

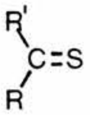
The most stable compounds have been found to be those in which the thiocarbonyl function is directly bonded to, or is conjugated with, a hetero atom which has an available lone pair. Interaction of the lone pair with the thiocarbonyl function gives rise to the more stable polarised form, e.g. (1) and (2).

(1)



(2)

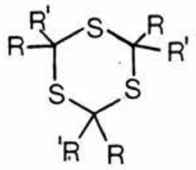
The least stable are those in which the thiocarbonyl function is attached to alkyl groups or hydrogen atoms (3), the inductive effect of these groups not being great enough to polarise the thiocarbonyl function sufficiently to confer stability. In these



R' = alkyl   R = alkyl, H

(3)

cases oligomers and polymers are the usual result (4) or, if an α-hydrogen is present, enethiolisation may take place (5).



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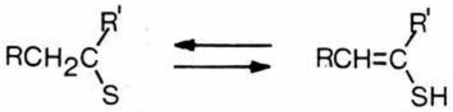
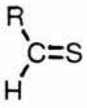


(5)

Further discussion of thiocarbonyl compounds will be limited to carbothialdehydes, in particular to compounds of general formula (6), where R may represent an alky, aryl or heterocyclic group.



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B. CARBOTHIALDEHYDES

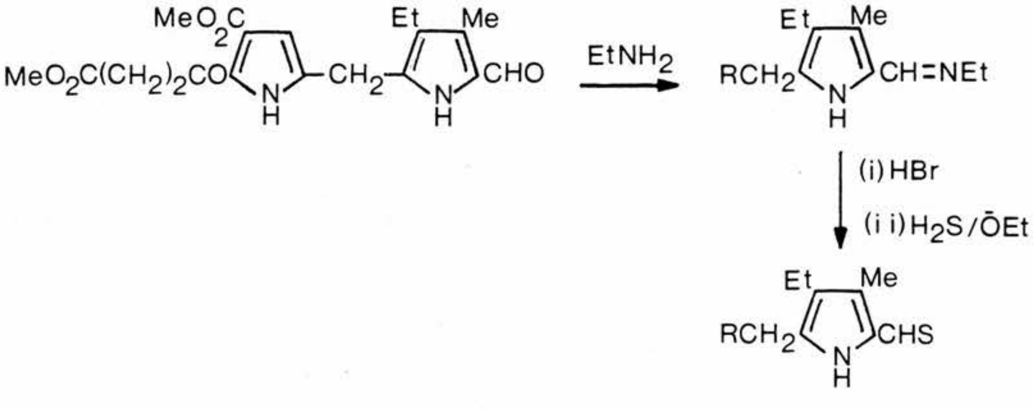
The fact that carbothialdehydes have a wide range of stabilities with respect to oligomerisation and polymerisation (from 6 minutes at 0.01-0.05 torr for thioformaldehyde[20], to over 5 years at normal temperatures and pressures for indolizine carbothialdehydes[61]) leads to their ready classification into two groups.

In this Introduction carbothialdehydes that can be readily prepared and isolated are classified as stable and those carbothialdehydes that are best described as transient intermediates and whose existence can only be deduced by spectral evidence or by a study of their reaction products are classified as unstable.

1. Stable Carbothialdehydes

a) Preparation of Carbothialdehydes Stabilised by Conjugative Effects

The first stable carbothialdehyde (7) was reported by Woodward and his co-workers[8] as an important intermediate in the synthesis of chlorophyll a (Scheme 1). No physical data apart from a melting point were given for this compound.



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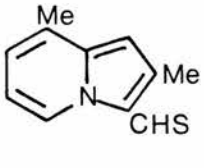
Scheme 1

A whole series of stable heterocyclic carbothialdehydes e.g. (8) - (14), have been prepared by Reid and his co-workers[9-12] using a novel variation of the Vilsmeier reaction, solvolysis of



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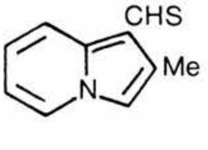

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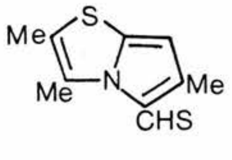

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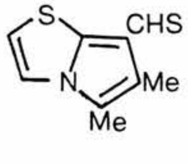

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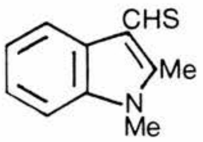

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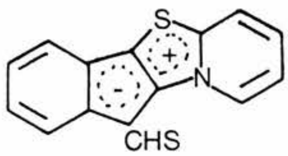

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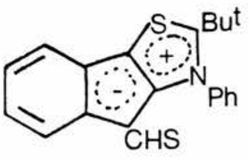
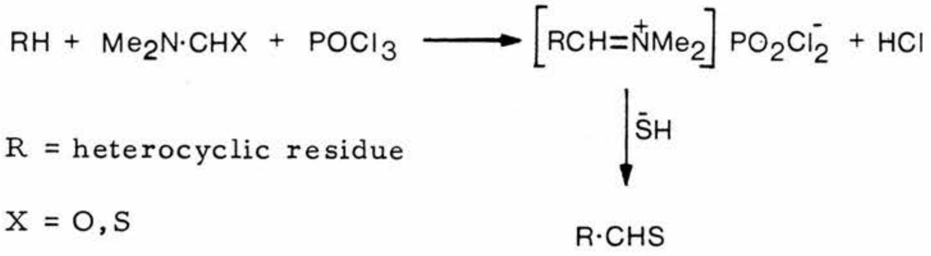


(14)

the Vilsmeier salts giving the carbothialdehydes in high yield (Scheme 2).



$$RH + Me_2N{\cdot}CHX + POCl_3 \longrightarrow [RCH{=}\overset{+}{N}Me_2]\,PO_2Cl_2^- + HCl \xrightarrow{\bar{S}H} R{\cdot}CHS$$

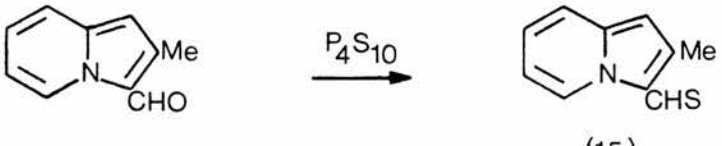
R = heterocyclic residue

X = O, S

Scheme 2

The carbothialdehydes (13) and (14) were also prepared by a variation of this method, dimethylthioformamide being substituted for dimethylformamide (Scheme 2) in the preparation of the Vilsmeier salt. This method was reported[10] to give higher yields of the Vilsmeier salts and hence higher yields of the carbothialdehydes.

Two other routes to indolizine carbothialdehydes were briefly discussed by the same authors[11]. The first involved thionation of an aldehyde with P_4S_{10} (Scheme 3). Yields by this route were

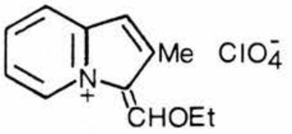


(15)

Scheme 3

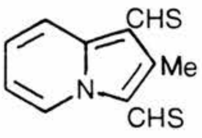
lower and in any case the aldehydes were best prepared from the same Vilsmeier salts as were the carbothialdehydes. For example, compound (15) was obtained in 59% yield, whereas by the Vilsmeier route the same compound was obtained in 86% yield.

The second route involved the solvolysis of 3-ethoxymethylene-3H-indolizinium perchlorate (16) with sodium hydrogen sulphide to



(16)

give (15) in only 33% yield. An attempt to prepare 2-methylindolizine-1,3-dicarbothialdehyde (17) was reported[11] to give only a sparingly soluble orange substance which is probably the trithiane (18).



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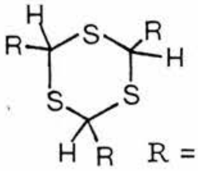
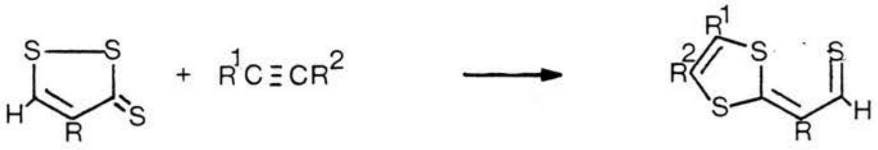


(18)

R = 1-(2-methylindolizinyl-3-carbothialdehyde)

Vialle and Davy[21] have prepared a series of stable heterocyclic carbothialdehydes by the addition of activated alkynes to 1,2-dithiole-3-thiones unsubstituted at position 5 [see (Scheme 4) for examples].



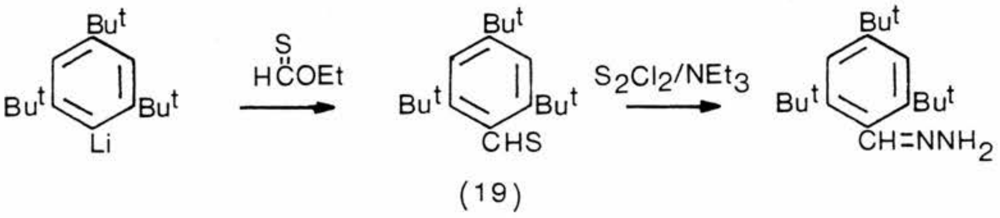
R	R^1	R^2
H	CO_2Me	CO_2Me
C_6H_5	CO_2Me	CO_2Me
H	H	CO_2Me

Scheme 4

In a previous report by other workers[22] the same and similar compounds were obtained as unstable, impure pastes or solids.

b) Carbothialdehydes Stabilised by Steric Effects

The first stable carbothialdehyde (19) not stabilised by conjugation with heteroatoms has recently been prepared by Okazaki and co-workers[13] by the routes shown (Scheme 5). Compound (19) was reported to be a very stable crystalline substance, no appreciable change being observed after storage at room temperature for a period of a year. The stability of this particular thiobenzaldehyde (the first of this class of compound) is probably due to the steric effect of the bulky t-butyl groups preventing any intermolecular reaction and thus oligomerisation and polymerisation.

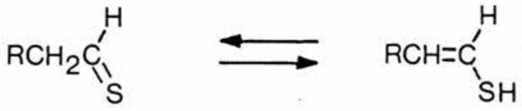


Scheme 5

c) Preparation of Aliphatic Carbothialdehydes

No stable aliphatic carbothialdehydes have been prepared to date, the inductive effect of the alkyl group being insufficient to stabilise the thiocarbonyl function.

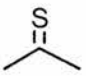
When a hydrogen atom α- to the thiocarbonyl function is available enethiolisation may occur instead of the usual oligomerisation and polymerisation (Scheme 6).



R = H or alkyl

Scheme 6

A number of thioketones are known to exist in equilibrium mixtures of the thioketone and enethiol forms[23] (20)-(22).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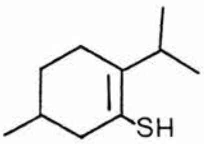
(20)



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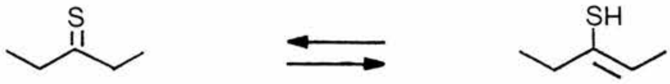
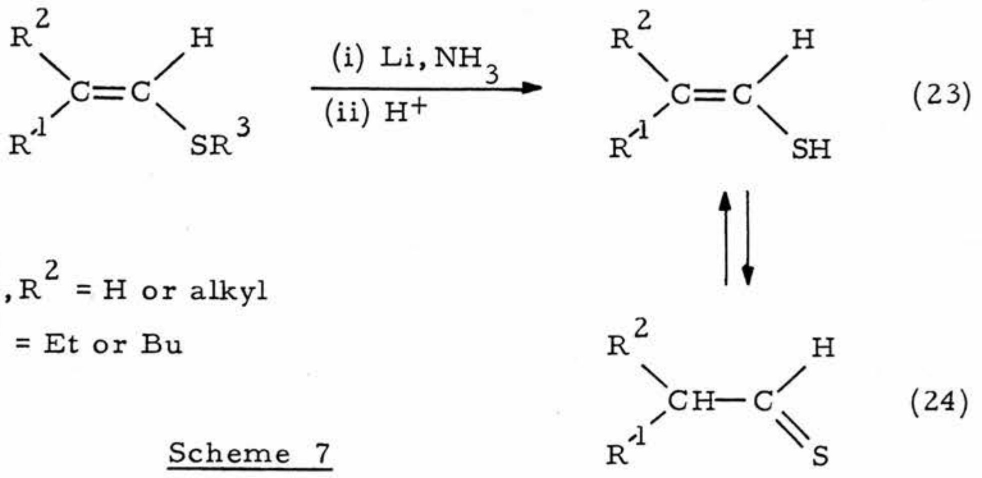


60% (22) 40%

Attempts to prepare simple carbothialdehydes lead not to the expected thial - enethiol equilibrium but to the enethiol form only. Thus Brandsma[24] has cleaved α,β -unsaturated sulphides using lithium in liquid ammonia to give compound (23), the enethiol form of the carbothialdehyde (24) (Scheme 7). Although it was reported that position of the equilibrium lay completely in favour of (23),

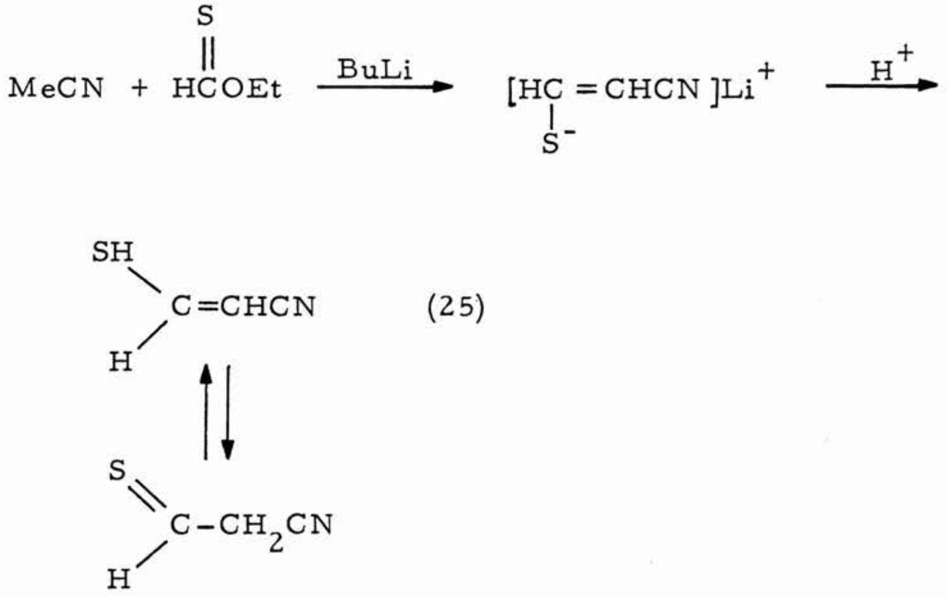


R^1, R^2 = H or alkyl
R^3 = Et or Bu

Scheme 7

no evidence for this was given.

In a similar manner the condensation product of acetonitrile with ethyl thioformate[25] gave, according to infra-red spectral evidence, the enethiol tautomer (25) exclusively (Scheme 8).

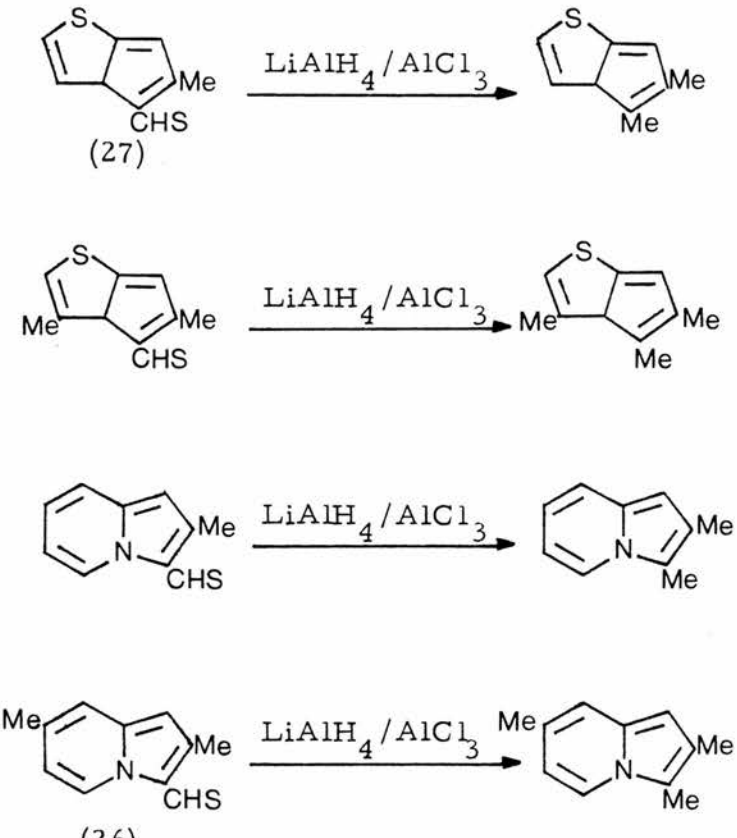


Scheme 8

d) Reactions of Stable Carbothialdehydes

(i) Reactions of Carbothialdehydes Stabilised by Conjugative Effects

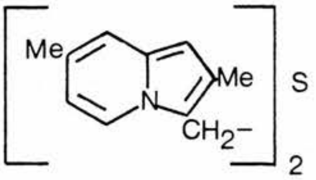
The reactions of indolizine and pyrrolothiazole carbothialdehydes towards oxidising, reducing and Wittig reagents have been investigated by Reid and Webster[26]. They reduced a number of pyrrolothiazole-5-carbothialdehydes and indolizine-3-carbothialdehydes with lithium aluminium hydride-aluminium chloride to the corresponding methyl derivatives (Scheme 9). The same workers reduced the carbothialdehydes (26) and (27) with sodium borohydride in an attempt to prepare the corresponding thiols. Instead of the thiols, however, the



(27)

(26)

sulphides (28) and (29) were obtained.



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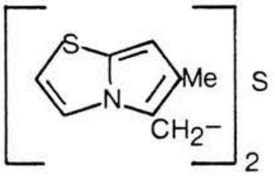
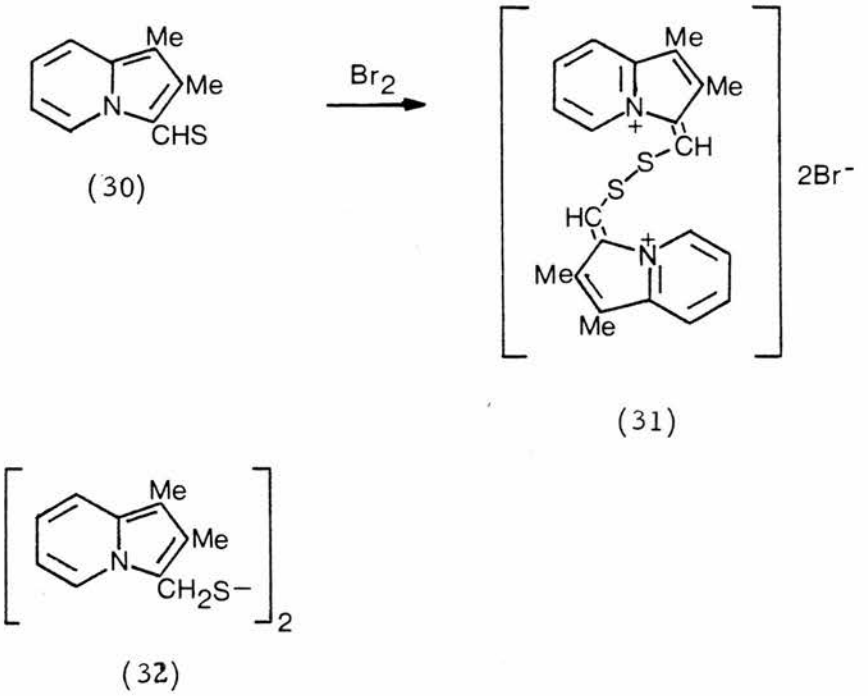


(29)

In an attempt to prepare a disulphide they oxidised the indolizine-3-carbothialdehyde (30) with bromine to obtain (31) as a very hygroscopic light sensitive salt (Scheme 10). However, reduction of this salt with sodium hydrogen sulphide failed to give the neutral disulphide (32). The carbothialdehyde (30) was regenerated in high yield.



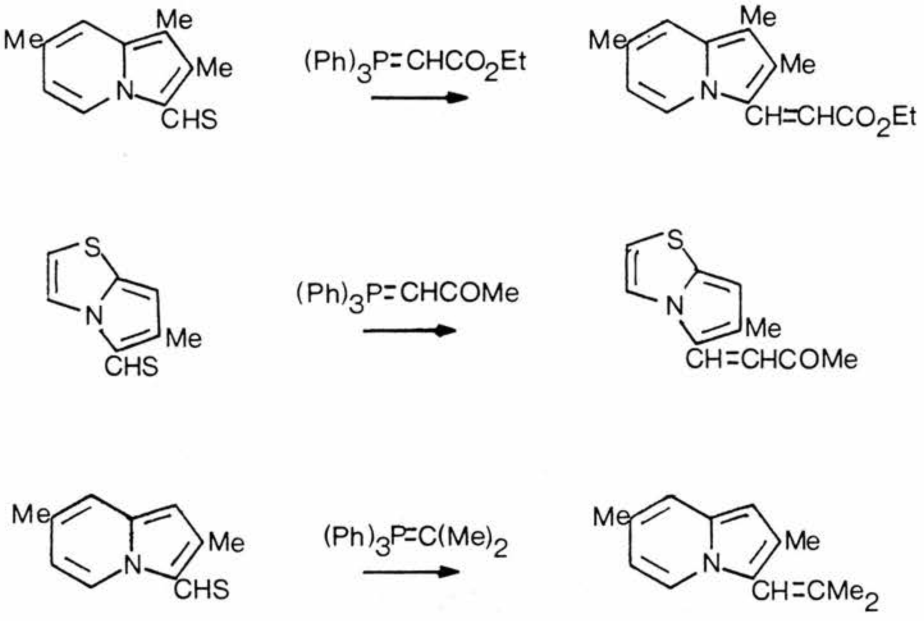
(30)

(31)

(32)

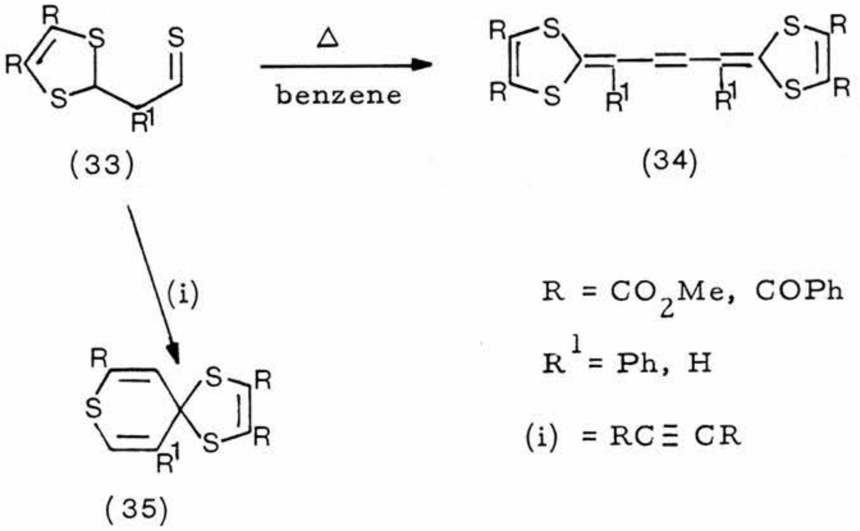
Scheme 10

The reaction of Wittig reagents with carbothialdehydes was also studied. The smooth reaction of stable and reactive Wittig reagents with various indolizine and pyrrolothiazole carbothialdehydes gave the corresponding vinyl products in high yield (80-90%) [see (Scheme 11) for examples].



Scheme 11

The reactions of the carbothialdehydes (33) have been described by McKinnon and Buchshriber[22] (Scheme 12). In all cases heating the carbothialdehyde in solution produced compounds (34). Spiro compounds (35) were produced in the cases where R^1 = Ph.



R = CO_2Me, COPh

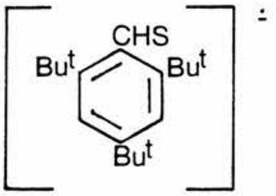
R^1 = Ph, H

(i) = RC≡CR

Scheme 12

(ii) The Reactions of Carbothialdehydes Stabilised by Steric Effects

Okazaki and his co-workers have recently reported[27] the reactions of the thiobenzaldehyde (19) with organometallic compounds (Scheme 13). A mechanism involving single electron transfer was proposed to account for the formation of the products. The formation of dimers (36)-(37) was taken as evidence for the involvement of the thioketyl radical anion (38).



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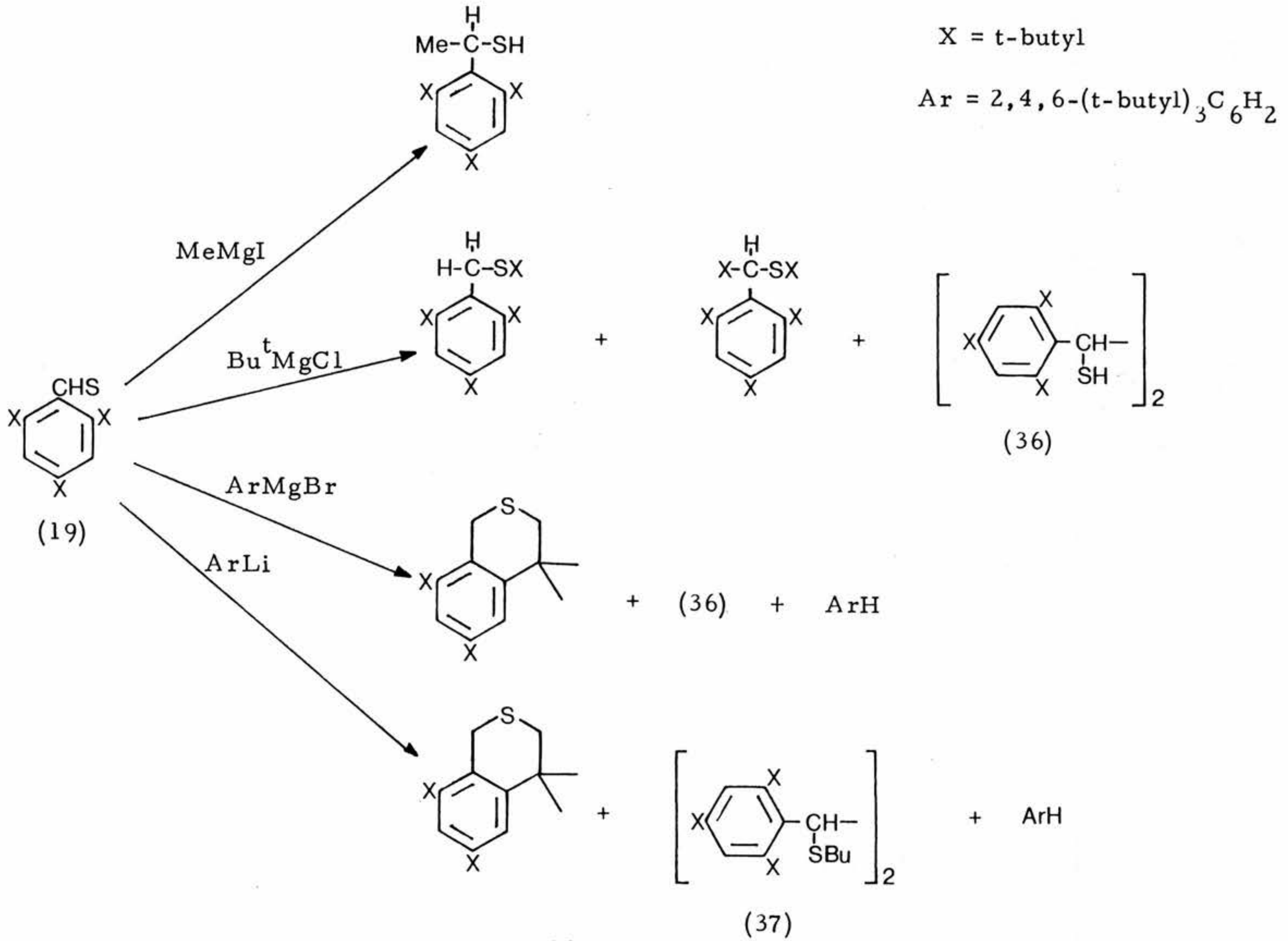


X = t-butyl

Ar = 2,4,6-(t-butyl)$_3$C$_6$H$_2$

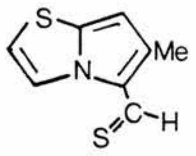
Scheme 13

(iii) Physical Properties of Stable Carbothialdehydes

Stable carbothialdehydes are highly coloured, almost odourless, crystalline compounds, ranging in colour from yellow [e.g. compound (39)] through orange [e.g. compound (12)] to red [compound (9)] to purple in the case of compound (19).

X-Ray Crystallography

Only one class of carbothialdehyde, that of the pyrrolo[2,1-b]-thiazole-5-carbothialdehydes, has been subjected to X-ray analysis[28]. The derivatives (26),(39),(40) were found to adopt the configurations shown (26),(39),(40). The observed structures of (26) and (39) were in



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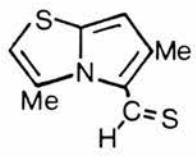
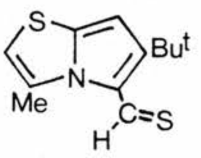


anti

(39)



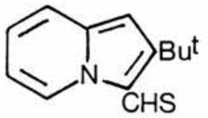
anti

(40)

agreement with the structures deduced from a ^{1}H NMR study of these compounds by Reid and his co-workers[12], but compound (40) was deduced by this ^{1}H NMR study to have the syn configuration in solution.

NMR Spectroscopy

Reid and his co-workers[11,12] have thoroughly studied the ^{1}H NMR spectra of a number of indolizine and pyrrolothiazole carbothialdehydes. They found that the chemical shift of the thioformyl proton in these compounds is quite characteristic and occurs at low field. A typical range is δ 10.4-10.7 for indolizine-3-carbothialdehydes. The anomalous value (δ 10.95) of the thioformyl proton in the derivative (41) was attributed to Van der Waals deshielding of the CHS proton by the t-butyl group. A similar range was found for the pyrrolothiazole carbothialdehydes. The 5-syn CHS proton resonated in the range δ 10.2-10.4, the 5-anti CHS proton between δ 11.0 and δ 11.1 and the 7-syn CHS proton between δ 10.5 and δ 10.8 . The exceptionally high values, δ 10.87 for (42) and δ 11.11 for (43), are again attributed to Van der Waals deshielding by the t-butyl group.



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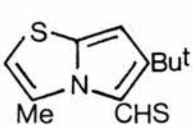
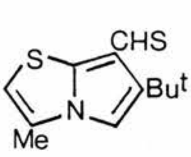


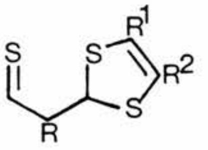
(42)



(43)

The lower field values for the thioformyl proton in the 5-anti compounds compared with the corresponding proton in the 5-syn compounds was said to be due to a combination of deshielding by the 3-Me substituent and the increased ring current deshielding of the thiazole ring.

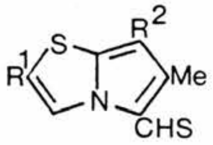
A similar range of values δ 10.68-11.12 for the thioformyl proton in the carbothialdehydes (44) has been reported by Davy and Vialle[21].



R = H, Me, Ph
R^1 = CO_2Me, CO_2Et, CO_2Ph, H
R^2 = CO_2Me, CO_2Et, CO_2Ph, CO_2H

(44)

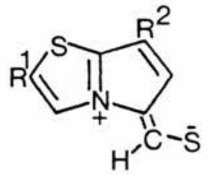
Restricted rotation about the ring-to-CHS bond in a number of carbothialdehydes (45) has been reported[12]. This may be taken



R^1 = H, R^2 = Me
R^1,R^2 = Me

(45)

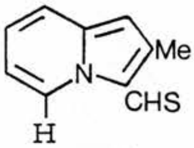
as evidence of an increased contribution of the polarised form (46) to the ground state of the molecules in question.



R^1 = H, R^2 = Me
R^1,R^2 = Me

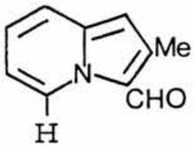
(46)

Evidence for the greater diamagnetic anisotropy of the C=S group compared with the C=O group has been reported[11]. A comparison of the chemical shift of the 5-H proton in the pair of compounds (15) and (47) and that of the 8-H protons in the pair of compounds (48) and (49) indicated that the thioformyl group exerted a greater diamagnetic anisotropic effect than that of the formyl group.



(15)

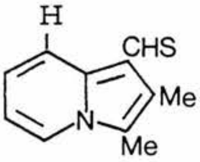
δ11.25



(47)

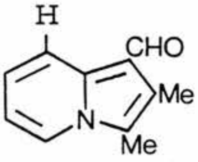
δ9.66

δ 8.94



(48)

δ 8.14



(49)

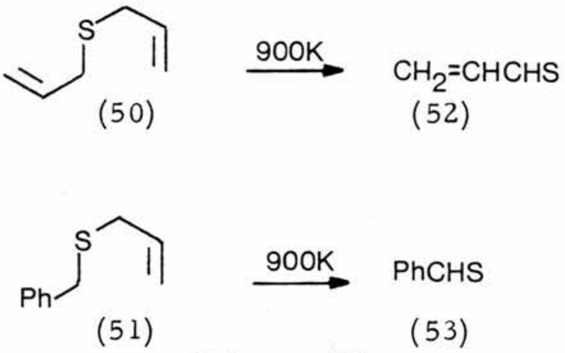
2. Unstable Carbothialdehydes

Reports of carbothialdehydes as possible reaction intermediates are fairly common[64 - 85]. Recently, research workers have begun to look systematically at the generation, trapping, and reactivity of such intermediates, and it is this work which will be discussed here.

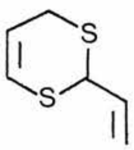
a) Isolation of Unstable Carbothialdehydes

A number of unstable carbothialdehydes have been prepared under conditions that have allowed them to survive long enough to be characterised spectroscopically.

The allyl sulphides (50) and (51) undergo pyrolitic elimination[33, 34] to give the carbothialdehydes (52) and (53). These were then identified by ultraviolet and infrared spectroscopy after cooling to 77 K (Scheme 14). Thioacrolein has also been detected, in the gas phase in a similar reaction, using photoelectron spectroscopy[35]. A mixture of the dimers (54) and (55) (formed from the thioacrolein initially produced) trapped at liquid nitrogen temperatures, was reheated to give the pure thioacrolein.



Scheme 14



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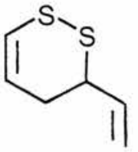
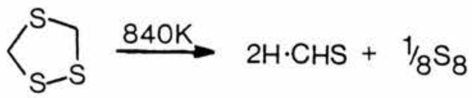


(55)

Thioformaldehyde[36] has been generated in the gas phase by the decomposition of MeSCl to give H·CHS and HCl, the HCl being removed by the controlled addition of ammonia gas. The thermolysis of 1,2,4-trithiolan has been reported[37] to give thioformaldehyde (Scheme 15). Thioformaldehyde has also been detected in

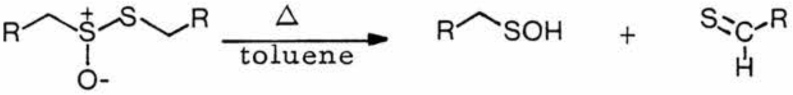


Scheme 15

interstellar space[38]. The relatively large distances between molecules and the low probability of collisions between them are some of the factors explaining the persistence of this highly reactive molecule in space.

b) Preparation of Unstable Carbothialdehydes

The thiosulphinates (56) undergo sigmatropic elimination when heated in toluene[14] to give the carbothialdehydes (57) and sulphenic acids (Scheme 16). In the absence of a trap the thiosulphinate (56) R=Ph produced a blue solution in toluene with a uv spectra similar



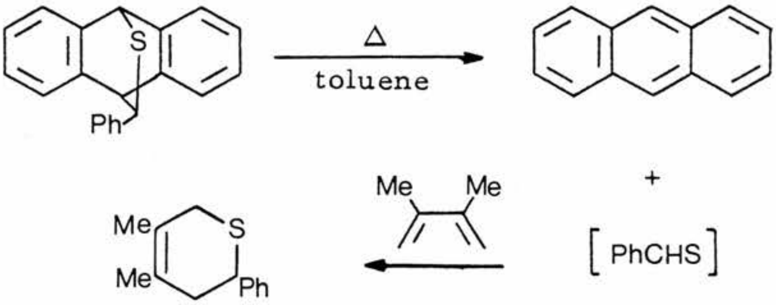
(56)

(57)

R = Ph, Me,

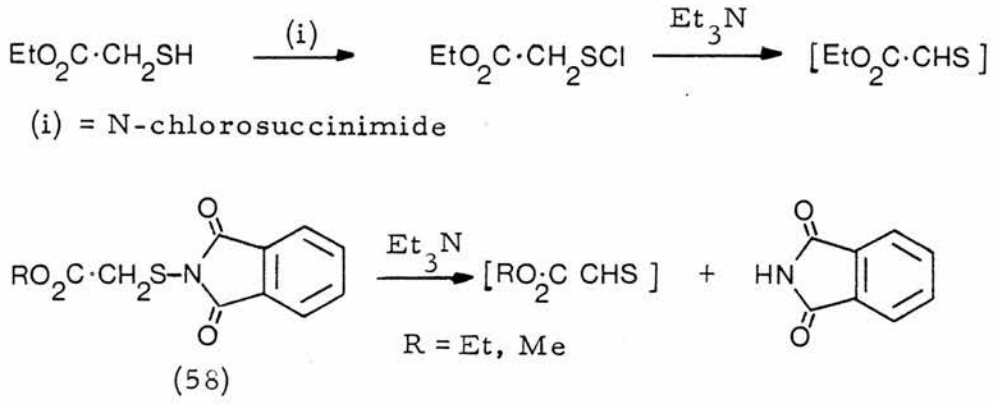
Scheme 16

to that of a uv of thiobenzaldehyde generated by the pyrolysis of allyl benzyl sulphide[34]. The adduct formed from thiobenzaldehyde and anthracene was shown by the same workers to regenerate anthracene and thiobenzaldehyde when heated in toluene in the presence of 2,3-dimethylbutadiene (Scheme 17). This reversible



Scheme 17

reaction has the advantage of being free from potentially reactive sulphenic acids and water which are produced when thiosulphinates are thermolysed (Scheme 16). Alkyl thioxoacetates have been generated at room temperature in a 1,2-elimination reaction by the routes shown[15,19] (Scheme 18). The latter route was devised



Scheme 18

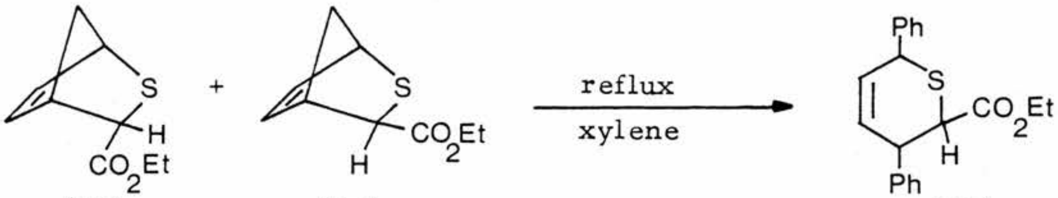
because the sulphenyl chloride required in the former route competes with the carbothialdehyde for the diene used for trapping. Further work by the same workers[29] has led to the generation of carbothialdehydes from the treatment of sodium thiosulphate S-esters with triethylamine (Scheme 19). They have also used the

$$ZCH_2SX + Et_3N \longrightarrow [ZCHS] + Et_3\overset{+}{N}H + \bar{X}$$

$X = SO_3Na$ Z = electron-withdrawing group

Scheme 19

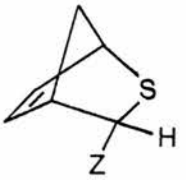
mixture of adducts (59) and (60), obtained from the treatment of (58) R = Et with triethylamine in the presence of cyclopentadiene, as a source of carbothialdehyde[15]. Heating the mixture of adducts (59) and (60) in the presence of trans, trans-1,4-diphenylbuta-1,3-diene gave the major isomer (61) in 48% yield (Scheme 20). In contrast,



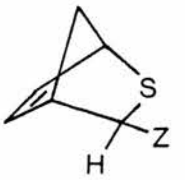
(59) (60) (61)

Scheme 20

treatment of trans, trans-1,4-diphenylbuta-1,3-diene with (58) R = Et and triethylamine gave a mixture of isomers of (61) in 9% yield. The cyclopentadiene adducts (62) and (63) were also shown to be useful sources of carbothialdehydes[29].



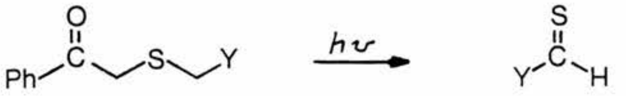
(62)



(63)

Z = EtO_2C, PhNHCO, PhCO, NC, 4-$NO_2C_6H_4$

Vedejs and his co-workers[16, 39] have reported the generation among others, of the carbothialdehydes (64) using a photolysis method (Scheme 21).



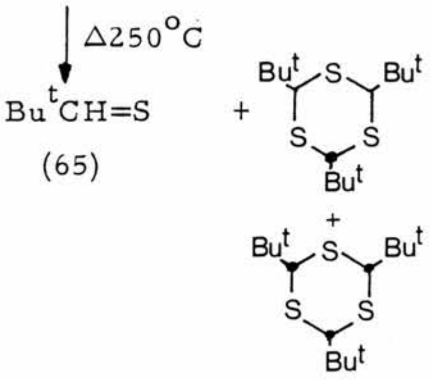
(64)

$Y = C(Me)_3$, CH_2CH_2Ph, COPh, COMe

Scheme 21

The first aliphatic carbothialdehyde known to survive in solution has recently been prepared by Vedejs and Perry[17] (Scheme 22).

$$PhCOCH_2SCH_2Bu^t \xrightarrow{h\nu} [Bu^tCH{=}S]_n + PhCOMe$$



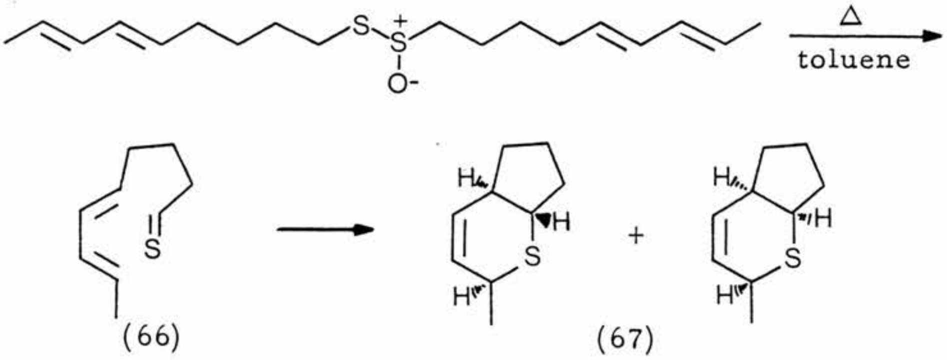
Scheme 22

The pink colour of (65) is reported to persist in solution in various solvents for up to 16 hours at 20°C. The solutions are not air sensitive and can be manipulated without special precautions.

c) Reactions of Unstable Carbothialdehydes

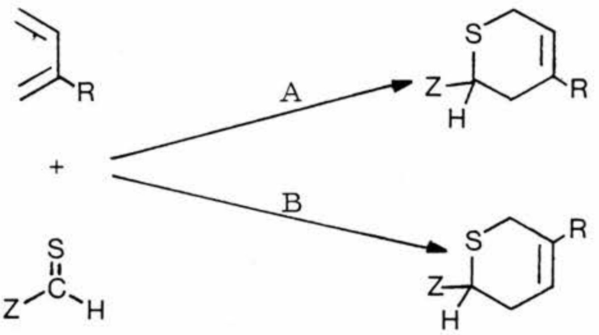
Almost all the reported reactions of unstable carbothialdehydes are those involving 1,3-dienes, the diene being present when the carbothialdehyde is generated.

Anthracene, 9,10-dimethylanthracene and 2,3-dimethylbutadiene have been used to prepare the corresponding adducts with thiobenzaldehyde and thioacetaldehyde[14]. The same workers have reported a successful intramolecular Diels-Alder-type cycloaddition reaction with (66) to give the thiabicyclononenes (67) (Scheme 23).



Scheme 23

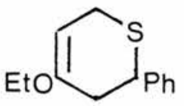
Vedejs and his co-workers[16, 39] have studied the regiochemistry of the reaction of a number of carbothialdehydes with dienes. They conclude that the regiochemistry of cycloaddition with dienes is reversed for carbothialdehydes containing only alkyl or aryl groups, compared with carbothialdehydes containing acyl or CN groups, e.g. in (Scheme 24). When Z = CN the yield of product was 4 % from route A and 70% from route B. When Z = H the yield by route A was 68% and by route B, 6%.



$R = OSiMe_2Bu^t$

Scheme 24

An interesting comparison of the photochemical versus thermolysis methods for the generation of unstable carbothialdehydes is provided by the reaction of thiobenzaldehyde with 2-ethoxybutadiene to give (68) and (69). In the cases of the thermolysis reaction (68) and (69) were produced and hydrolysed to the corresponding thianones (70) and (71). The yields of the thianones (70) and (71) were 31% and 13% respectively[14]. However with the photochemical method[16] (68) and (69) were not isolated, owing presumably to their rapid decomposition by irradiation.



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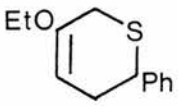
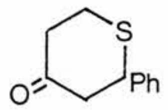
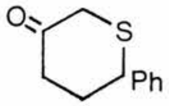


(69)



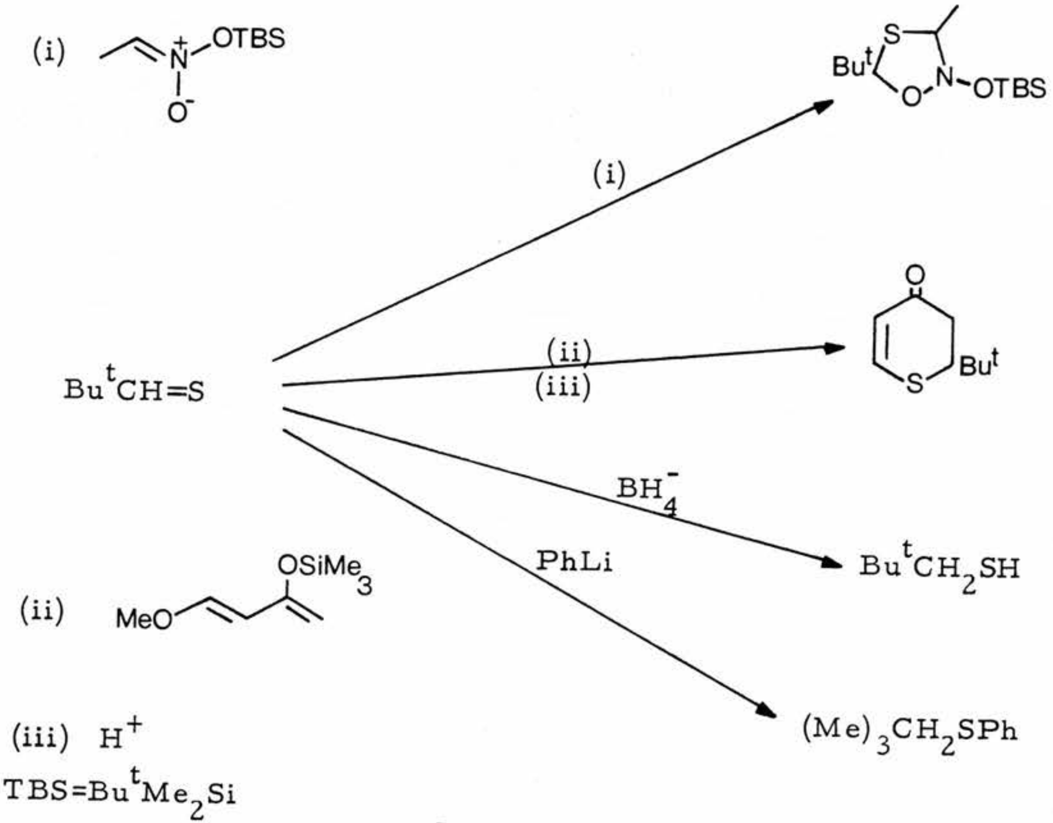
(70)



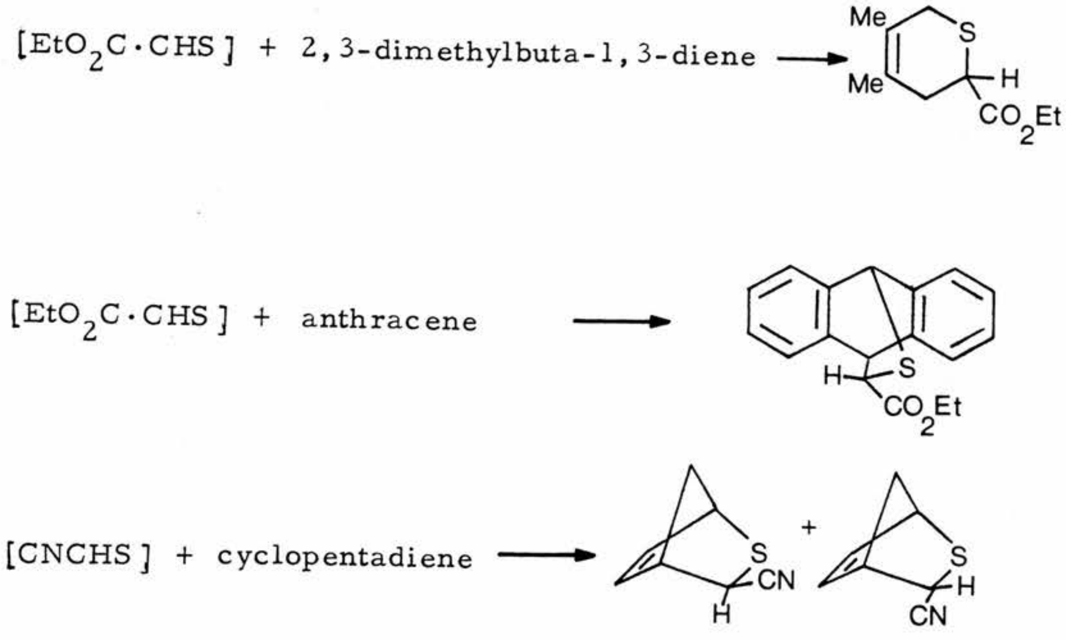
(71)

2,2-Dimethylpropane carbothialdehyde (65) was shown[17] to behave as a typical thiocarbonyl compound towards a variety of reagents; these reactions are summarised in (Scheme 25).

Kirby and co-workers[15, 19, 29] have generated carbothialdehydes in the presence of a variety of conjugated dienes. Some typical examples are shown (Scheme 26).

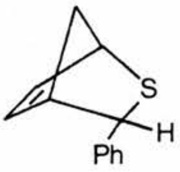


Scheme 25

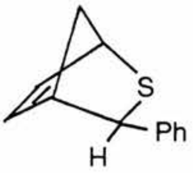


Scheme 26

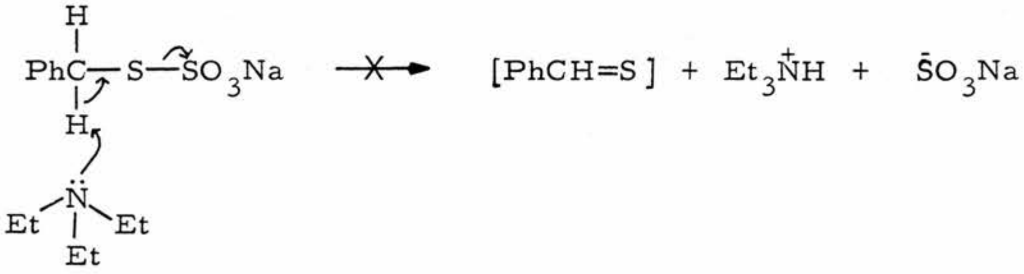
Attempts by these workers to generate PhCHS from $PhCH_2SSO_3Na$ and Et_3N in the presence of cyclopentadiene were unsuccessful[29]. No detectable amounts of the expected adducts (72) and (73) were obtained. The methylene protons are not sufficiently acidic, due to the poor electron-withdrawing properties of the benzene ring, to allow the elimination with Et_3N to take place (Scheme 27).



(72)



(73)

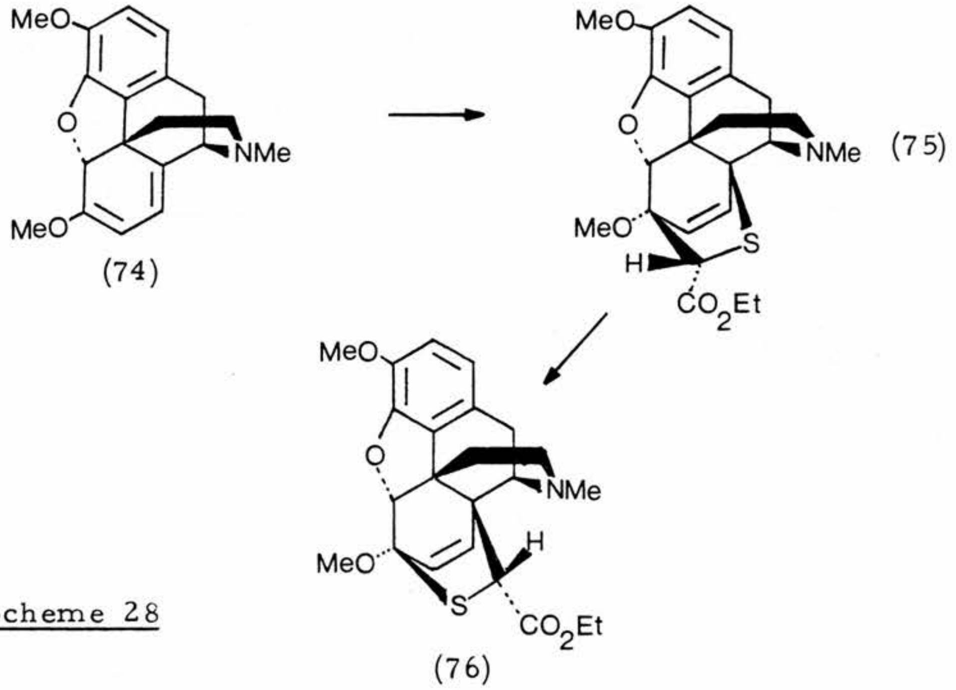


$$\mathrm{PhCH_2S{-}SO_3Na} \; \xrightarrow{\quad} \!\!\!\!\!\!\!\!\times\;\;\; [\mathrm{PhCH{=}S}] + \mathrm{Et_3\overset{+}{N}H} + \mathrm{\bar{S}O_3Na}$$

Scheme 27

The treatment of thebaine (74) with [$EtO_2C\cdot CHS$] was reported[19] to give the cycloadduct (75) free from any appreciable amounts of isomeric product. Heating compound (75) at reflux in toluene for 8 hours gave the isomer (76). This indicated that the addition of [$Et_2O_2C\cdot CHS$] to compound (74) to give compound

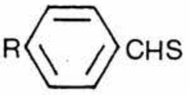
(75) had occurred under kinetic control (Scheme 28).



Scheme 28

d) Metal Complexes of Unstable Carbothialdehydes

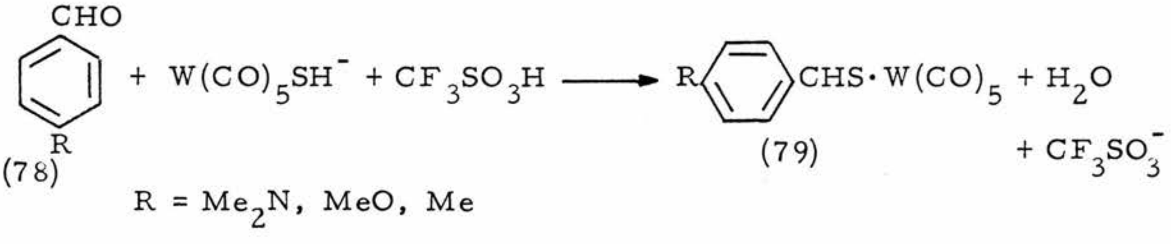
Metal complexes (79) of the previously unknown thiobenzaldehydes (77) have been prepared by Angelici and Gingerich[18] from the



(77)

R = Me$_2$N, MeO, Me

corresponding aldehydes (78) (Scheme 29). Attempts to prepare

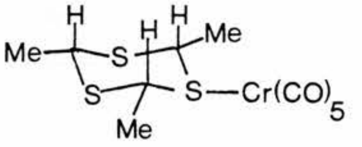


$$\text{RC}_6\text{H}_4\text{CHO} + W(CO)_5SH^- + CF_3SO_3H \longrightarrow \text{RC}_6\text{H}_4\text{CHS}\cdot W(CO)_5 + H_2O + CF_3SO_3^-$$

R = Me$_2$N, MeO, Me

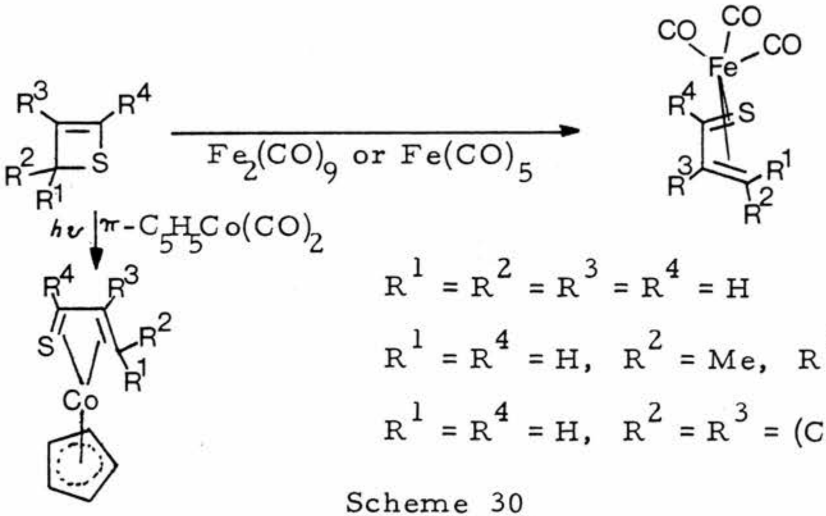
Scheme 29

similar complexes from a variety of alkyl aldehydes were unsuccessful. An earlier attempt by the same workers[40] to prepare the pentacarbonyl chromium (0) complex of thioacetaldehyde gave only the trithiane complex (80).



(80)

Several cobalt and iron complexes of thioacreolins have been prepared[41] by photolysis of the corresponding thiet in the presence of a metal carbonyl (Scheme 30).



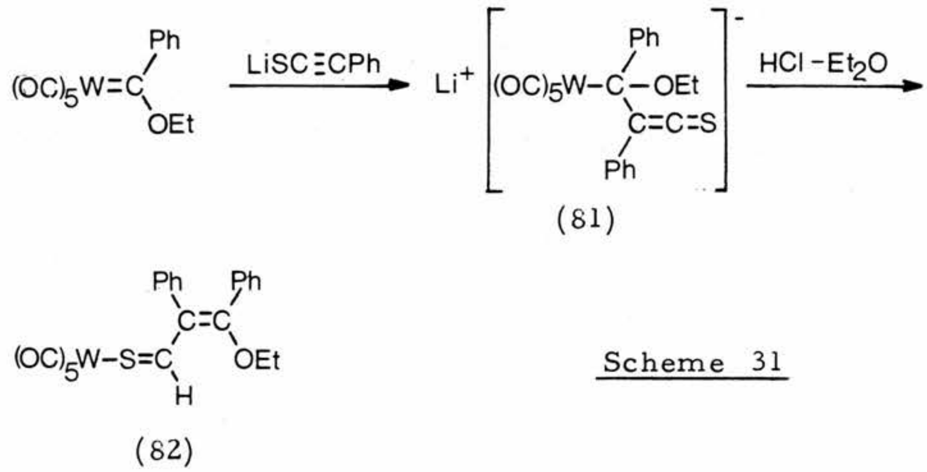
$R^1 = R^2 = R^3 = R^4 = H$

$R^1 = R^4 = H, \ R^2 = Me, \ R^3 = Et$

$R^1 = R^4 = H, \ R^2 = R^3 = (CH_2)_5$

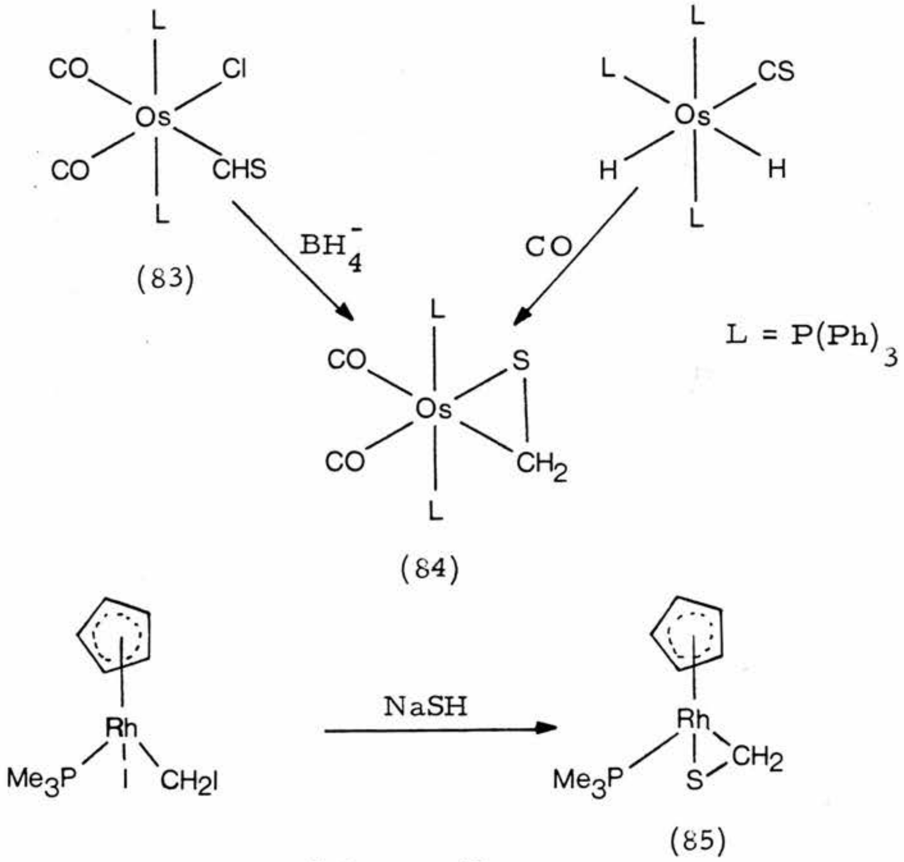
Scheme 30

The formation of an unusual adduct (81) from pentacarbonyl-α-ethoxybenzylidenetungsten and lithium phenylethynethiolate has been reported recently[30]. This adduct is nucleophilic and reacts under mild conditions with a variety of reagents to give thiocarbonyl tungsten complexes. One of these reactions for the formation of the carbothialdehyde tungsten complex (82) is shown (Scheme 31).



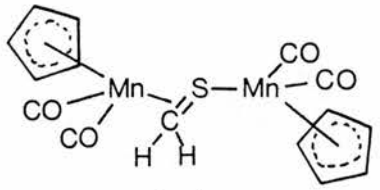
Scheme 31

Stable mononuclear complexes of thioformaldehyde have been prepared. The osmium complex (84)[42] and the rhodium compound (85)[31] were prepared by the routes shown (Scheme 32).



Scheme 32

A dinuclear thioformaldehyde complex (86)[32] and a trinuclear thioformaldehyde complex (87)[62] have also been prepared.

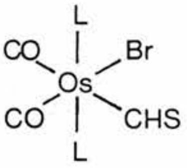


(86)

$Os_3(CO)n(PMe_2Ph)S(CH_2S)$ n = 8,9

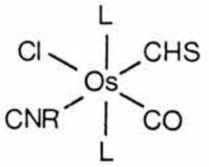
(87)

The osmium complex (83) (Scheme 32) is the first example of a stable organometallic carbothialdehyde. Further work[63] has led to the preparation of the stable organometallic carbothialdehydes (88) and (89). The chemistry of these compounds has not been



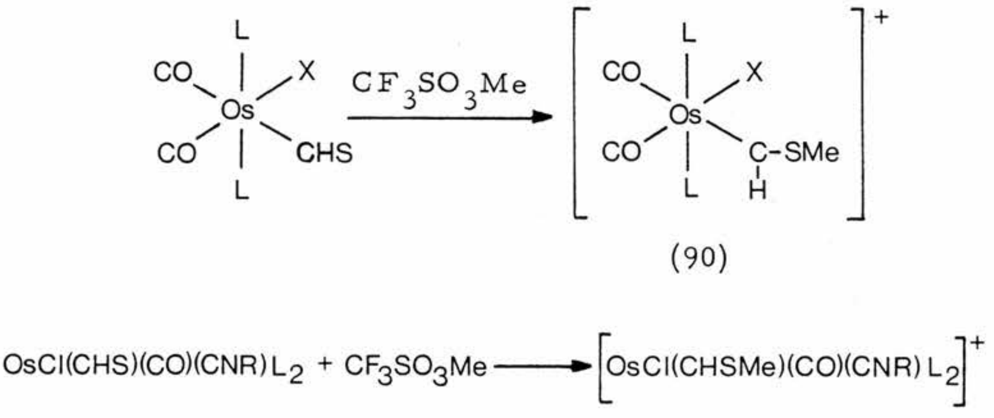
(88)

L = P(Ph)$_3$



(89)

systematically investigated. Reduction (Scheme 32) and methylation with CF_3SO_3Me to give the cations (90) and (91) are the only reported reactions of compounds (83), (88) and (89) (Scheme 33). The



(90)

$$OsCl(CHS)(CO)(CNR)L_2 + CF_3SO_3Me \longrightarrow \left[OsCl(CHSMe)(CO)(CNR)L_2\right]^+$$

(91)

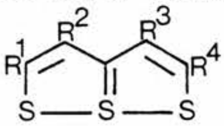
<ins>Scheme 33</ins>

thioformyl proton signal in the organometallic carbothialdehydes (83), (88) and (89) occurs at very low field and is in the range δ 16.9 - δ 17.5 . In contrast the thioformyl proton signal of 2,4,6-tri-t-butylthiobenzaldehyde occurs at δ 13.02[13].

C. 1,6,6aλ^4-TRITHIAPENTALENES AS POTENTIAL THIOCARBONYL COMPOUNDS

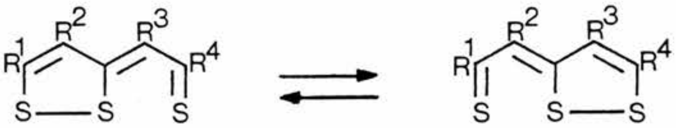
1. Introduction

1,6,6aλ^4-Trithiapentalenes are bicyclic compounds[43-48] (92) employing four-electron three-centre bonding[49] in the S–S–S sequence.



(92)

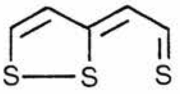
An alternative system of rapidly interconverting thiocarbonyl valence isomers (Scheme 34) has been proposed by Leaver[50], but attempts to detect these isomers using variable temperature ^{1}H nmr spectroscopy[51-53] have been unsuccessful.



Scheme 34

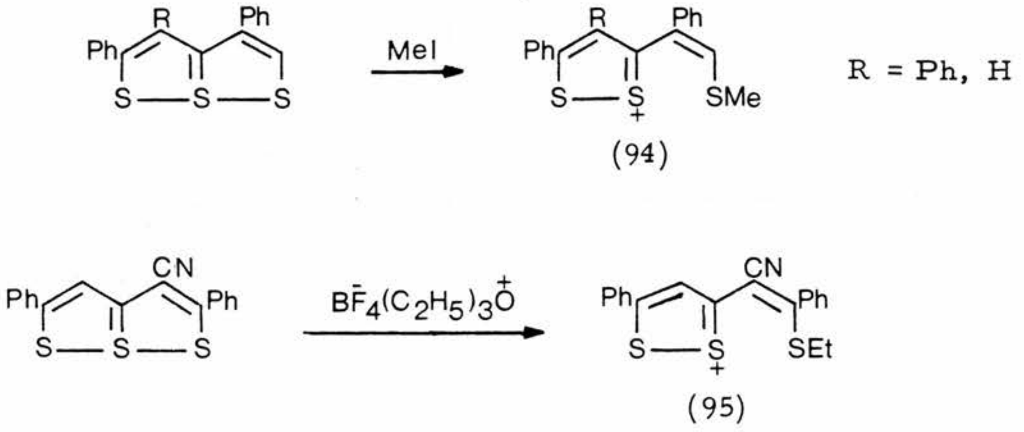
2. Thiocarbonyl Reactions

Although trithiapentalenes are bicyclic they may be regarded as 'masked' carbothialdehydes or thioketones and react as though they possess the thiocarbonyl structure (93). For example,



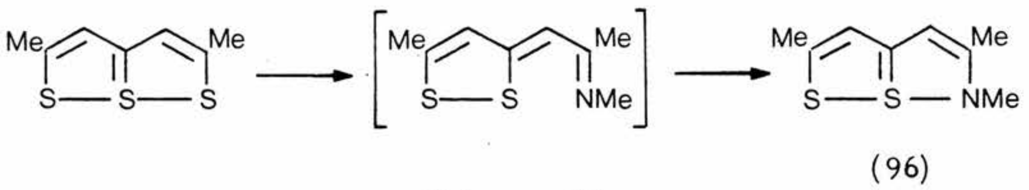
(93)

trithiapentalenes are alkylated at sulphur by methyl iodide[54,55] or triethyloxonium fluoroborate[52] to give the 1,2-dithiolylium salts (**94**) or (95) (Scheme 35). Treatment of trithiapentalenes with methylamine



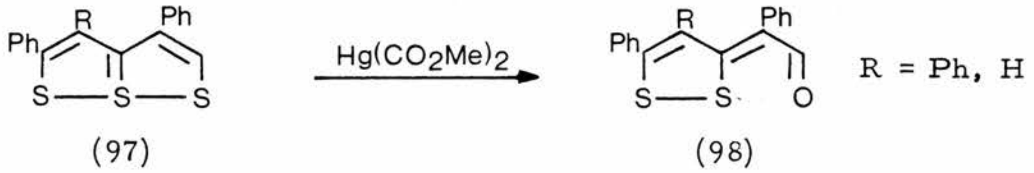
Scheme 35

gives products which are best formulated as bicyclic structures (96)[56] (Scheme 36). Mercury (II) salts partially desulphurise the



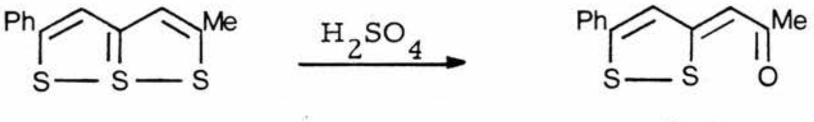
Scheme 36

trithiapentalenes (97) to give the corresponding dithiolylidene aldehydes[57] (98) (Scheme 37). Treatment of trithiapentalenes[58] with



Scheme 37

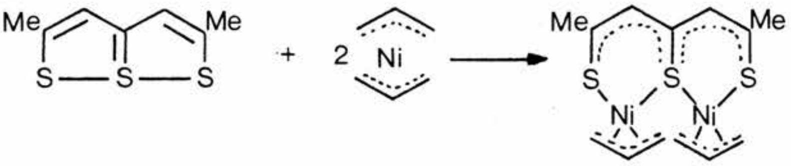
strong acid gives the corresponding dithiolylidene ketones, e.g. (99) (Scheme 38).



(99)

3. Metal Complexes of 1, 6, 6aλ^4-Trithiapentalenes

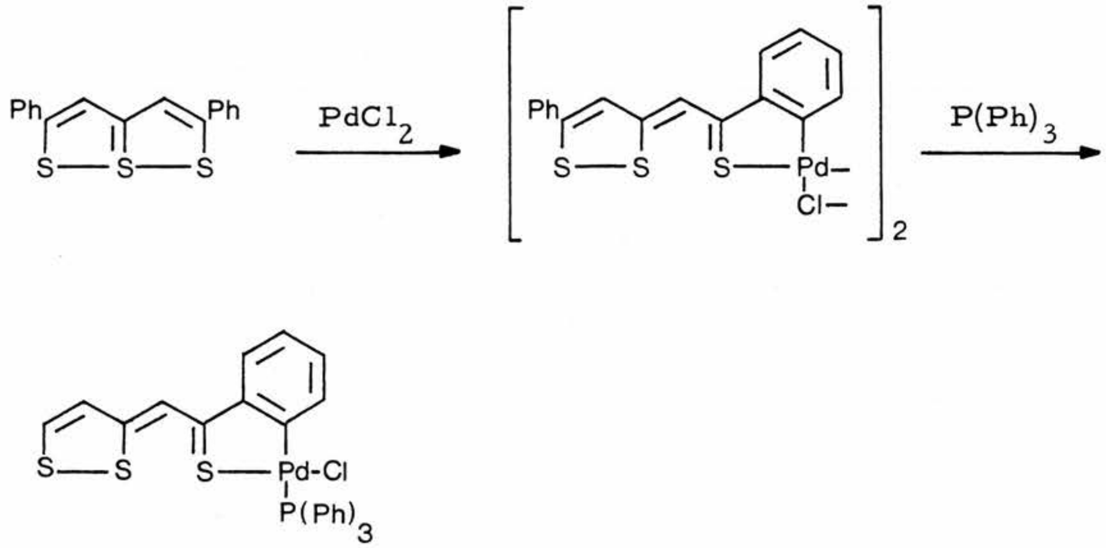
At the beginning of the work described in this thesis only two metal complexes derived from trithiapentalenes had been reported. Bogdonovic and his co-workers[59] prepared a nickel trithioketone complex from 2, 5-dimethyl-1, 6, 6aλ^4-trithiapentalene and bis(η^3-allyl)nickel as violet crystals in 70% yield (Scheme 39).



Scheme 39

An alternative route using η^3-allyl nickel chloride gave the same complex but in lower yield (48%).

The same authors[60] have also reported the formation of a complex of palladium derived from 2, 5-diphenyl-1, 6, 6a λ^4-trithiapentalene as violet crystals in 97% yield (Scheme 40).

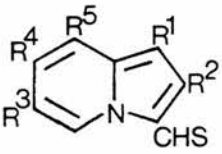


Scheme 40

DISCUSSION

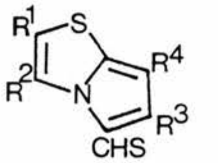
A. PYRROLE CARBOTHIALDEHYDES

Workers in this laboratory have previously prepared a series of stable heterocyclic carbothialdehydes e.g. (1), (2) and (3) using a novel variation of the Vilsmeier reaction[9-12].



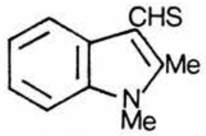
(1)

$R^1, R^2, R^3, R^4, R^5 = H$
$R^1, R^3, R^4, R^5 = H,\ R^2 = Bu^t$
$R^1, R^3, R^4 = H,\ R^2, R^5 = Me$



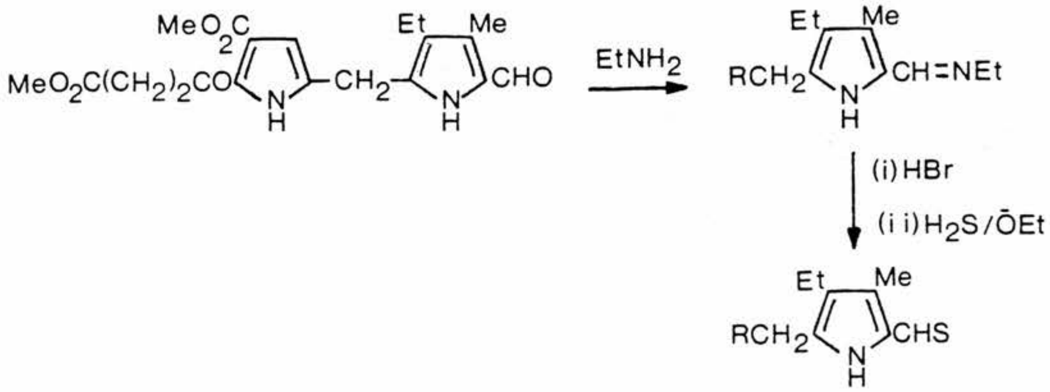
(2)

R^1	R^2	R^3	R^4
H	H	Me	H
Me	H	Me	H
H	H	Me	Me
H	Me	Bu^t	H
H	Me	Me	H
Me	Me	Me	H



(3)

One of the aims of the work described in this thesis was to extend this work on heterocyclic carbothialdehydes by preparing a series of alkylpyrrole carbothialdehydes. The only member of this class of compound hitherto reported is compound (4)[8] prepared by the route shown (Scheme 1).

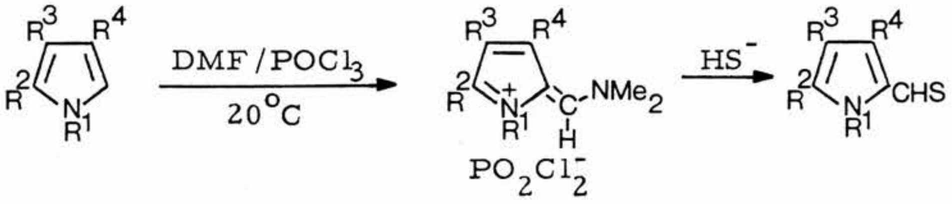


(4)

Scheme 1

The position of electrophilic substitution in pyrroles is well-documented[86]. Formylation occurs exclusively at position 2, or at position 3 if the 2 position is already substituted. Substitution does not take place so readily at position 3 and forcing conditions are usually required.

In order to prepare pyrrole carbothialdehydes, solutions of the pyrroles (5) in dimethylformamide were added to a solution of phosphorus oxychloride in dimethylformamide to give the Vilsmeier salts (6). In situ solvolysis of these salts with aqueous sodium hydrogen sulphide (Scheme 2) yielded the carbothialdehydes (7c)-(7h) as stable crystalline solids and compound (7b) as a cherry red glass.



(5) (6) (7)

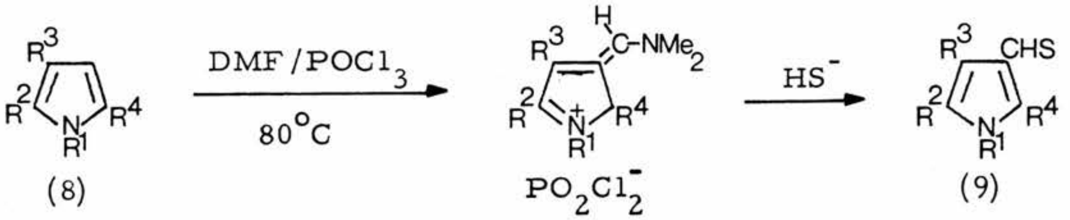
a) $R^1, R^2, R^3, R^4 = H$
b) $R^1, R^3, R^4 = H,\ R^2 = Me$
c) $R^1, R^4 = H,\ R^2, R^3 = Me$
d) $R^1, R^3 = H,\ R^2, R^4 = Me$
e) $R^1, R^2 = H,\ R^3, R^4 = Me$
f) $R^1 = H,\ R^4, R^2 = Me,\ R^3 = Et$
g) $R^1, R^2, R^3 = Me,\ R^4 = H$
h) $R^1, R^2, R^4 = Me,\ R^3 = H$

Scheme 2

Pyrrole-2-carbothialdehyde (7a) was not isolated. Treatment of the pyrrole (5a) as shown (Scheme 2) gave the Vilsmeier salt. In situ solvolysis of this salt with aqueous sodium hydrogen sulphide and extraction of the resulting mixture with ether gave a reasonably stable (ca. ½ hr at RT) solution of compound (7a). Evaporation of this ether solution gave only polymeric material.

Thioformylation of the pyrroles (8a) and (8b) required higher temperatures and longer reaction times (Scheme 3). The resulting carbothialdehydes (9a) and (9b) were isolated as stable crystalline solids.

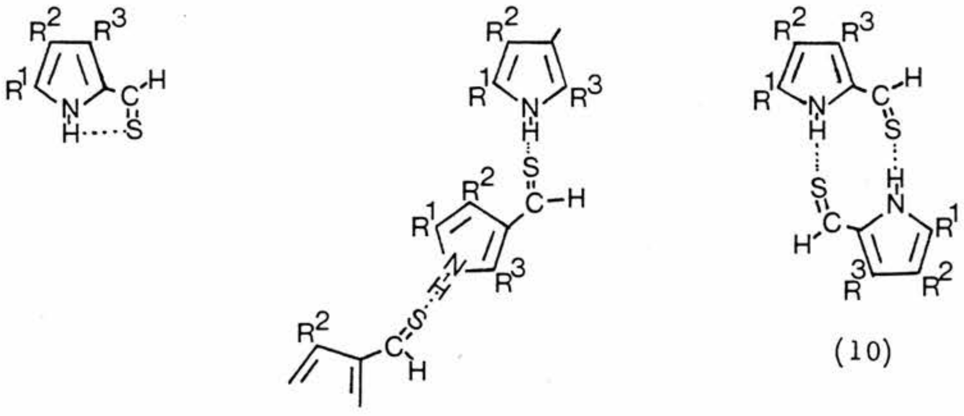
Pyrrole-3-carbothialdehydes are less stable than pyrrole-2-carbothialdehydes and readily decompose to give insoluble polymeric material. The thioformyl proton signals of the pyrrole-3-carbothialdehydes (9a) and (9b) occur at lower field than those of the



a) R^1, R^2, R^4 = Me, R^3 = H b) R^1, R^3 = H, R^2, R^4 = Me

Scheme 3

pyrrole-2-carbothialdehydes (7b)-(7h) (Table 2, Appendix A). This indicates that the thioformyl group in compounds (9a) and (9b) is less polarised than the thioformyl group in compounds (7b)-(7h). Consequently the pyrrole-3-carbothialdehydes will in general tend to polymerise more readily than the pyrrole-2-carbothialdehydes and this may be a factor affecting their stability. Another feature of the stability of the pyrrole carbothialdehydes is the lower stability of compounds with an N-Me group (7g), (7h) and (9a). These compounds decompose readily to give insoluble polymeric material. A possible explanation may be the existence of hydrogen bonds involving the thiocarbonyl sulphur atom and the N-H group in compounds (7b)-(7f) and (9b) (Scheme 4).

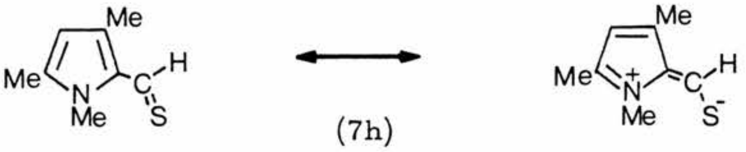


Scheme 4

Formation of association dimers (10) is only possible for compounds (7b)-(7f). The existence of association dimers has been established[87] for the pyrrole carboxaldehydes corresponding to the carbothialdehydes (7d) and (7f). The absence of N—H···S hydrogen bonds in compounds (7g), (7h) and (9a) may be a factor affecting their stability.

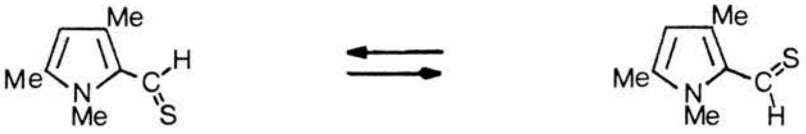
The ^{1}H nmr and ^{13}C nmr spectra of the pyrrole-2-carbothialdehydes and pyrrole-3-carbothialdehydes are consistent with the products as formulated. A characteristic feature in the ^{1}H nmr spectra of pyrrole carbothialdehydes is the chemical shift of the thioformyl proton. The normal range for the 2-thioformyl proton signal in compounds (7b)-(7h) is δ 10.3-10.8, whereas the 3-thioformyl proton signal is δ 11.01 for (9a) and δ 11.03 for (9b). These values are similar to those found in the ^{1}H nmr spectra of indolizine and pyrrolothiazole carbothialdehydes.

Restricted rotation about the ring-thioformyl bond was detected in compound (7h), and probably arises from the contribution of the dipolar form. At ambient temperature the ^{1}H nmr spectrum of compound (7h) in chloroform-d solution showed line broadening of the signals at δ 10.64, δ 5.94 and δ 3.94 (see Table 2, Appendix A for assignments). Cooling the solution to -20°C caused each of



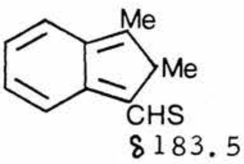
(7h)

these signals to split and give two signals in the ratio 4:1. On raising the temperature to 0°C each of these pairs of signals coalesced. Further heating to 50°C caused each of these coalesced signals to become progressively sharper. The line widths of the signals at δ 2.27 and δ 2.20 remained unchanged throughout this experiment. One possible explanation of this behaviour is that compound (7h) can exist at low temperatures as the isomers (7h) and (7h'). Consideration of the deshielding effect of the thiocarbonyl group suggests that the N-Me proton signal for isomer (7h) should occur at lower field than the N-Me proton signal for isomer (7h'). Therefore the N-Me signal at δ 4.05 is assigned to the N-Me group in isomer (7h). This isomer was shown by integration of its ^{1}H nmr spectrum to be the major isomer.

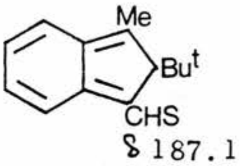


(7h) (7h')

In the ^{13}C nmr spectrum of the pyrrole-2-carbothialdehydes the most notable feature was the thioformyl carbon signal. The chemical shift of the thioformyl carbon in compounds (7b)-(7f) occurs in the range δ 191-198. These values are comparable with those found for the thioformyl carbon signal in compounds (11) and (12)[88].



(11)



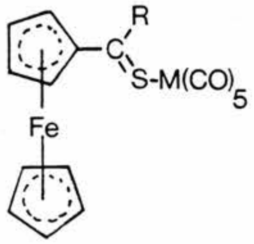
(12)

^{13}C Nmr spectra of the compounds (9a), (9b), (7g) and (7h) were not obtained since solutions of these compounds in chloroform-d decomposed during the nmr experiment.

In conclusion it has been shown that simple alkylpyrrole carbothialdehydes can be readily prepared by a variation of the Vilsmeier reaction and that they are comparable in stabilities to compounds such as indolizine and pyrrolothiazole carbothialdehydes. The failure to isolate pyrrole-2-carbothialdehyde indicated that at least one C-methyl group must be present in the ring to confer stability on the carbothialdehydes under the experimental conditions used here. The presence of an N-Me group in compounds (7g) and (7f) made them less stable in solution than compounds (7c) and (7d).

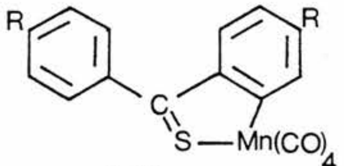
B. CARBOTHIALDEHYDE METAL COMPLEXES

Thiocarbonyl compounds behave as two-electron donors and can form a variety of metal complexes with suitable metal compounds. Some examples are shown [(13), (14), (15)]$^{89-91}$.



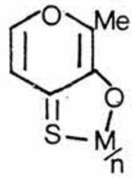
(13)

R = Ph, M = Cr, Mo, W
R = Me, M = W



(14)

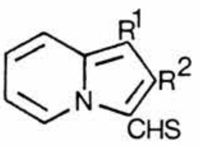
R = N(Me)$_2$, N(Et)$_2$



(15)

M = Fe, Co   n = 3
M = Ni, Zn, Cd, Hg   n = 2

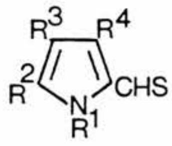
Metal complexes of carbothialdehydes are rare. The only known examples were prepared from unstable carbothialdehydes (see Introduction, page 29). The aim of the work described in this section was to investigate the formation of metal complexes from the carbothialdehydes (16), (7) and (9).



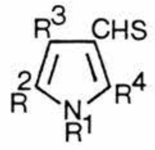
(16)

a) R^1 = H, R^2 = Me

b) R^1, R^2 = Me



(7)



(9)

a) R^1, R^2, R^4 =Me, R^3=H

b) R^1, R^3=H, R^2, R^4 =Me

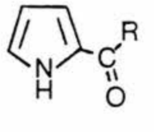
(7)b) R^1, R^3, R^4=H, R^2=Me
c) R^1, R^4=H, R^2, R^3=Me
d) R^1, R^3=H, R^2, R^4=Me
e) R^1, R^2=H, R^3, R^4=Me

(7) f) R^1=H, R^4, R^2=Me, R^3=Et
g) R^1, R^2, R^3=Me, R^3=H
h) R^1, R^2, R^4 =Me, R^3=H

Compounds (16), (7) and (9), as carbothialdehydes, are potential two-electron donors and their reaction to form pentacarbonyl tungsten (0) complexes will be discussed later (page 56). For compounds (7b)-(7f) the formation of bidentate chelate complexes with suitable metal compounds is possible and the formation of such complexes will now be discussed.

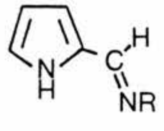
1. Chelate Complexes from Pyrrole-2-Carbothialdehydes

Compounds such as (17) and (18) behave as mononegative bidentate ligands and form a number of chelate complexes with suitable metal compounds[92, 93]. The pyrrole-2-carbothialdehydes (7b)-(7f)



(17)

R = Me, H



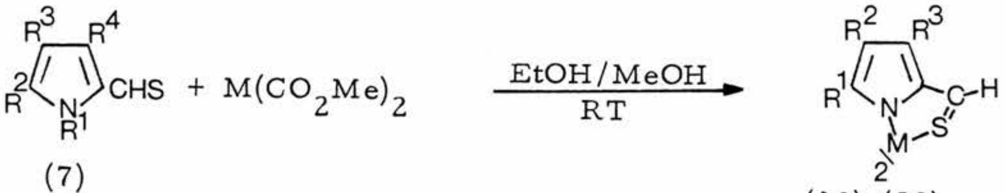
(18)

R = alkyl

would be expected to behave in an analogous manner. Preliminary experiments in which metal acetates were allowed to react with the pyrrole-2-carbothialdehydes (7b)-(7f) gave tris chelate complexes when cobalt acetate was used and bis chelate complexes when the acetates of copper, nickel, cadmium, zinc and palladium were used.

a) Bis Chelate Complexes

Reaction of the pyrrole-2-carbothialdehydes (7b)-(7f) with copper (II), cadmium (II), zinc (II), nickel (II), and palladium (II) acetates gave bis chelates as shown (Scheme 5). After work-up and purification the complexes (19)-(23) were obtained as stable crystalline solids.



(7)

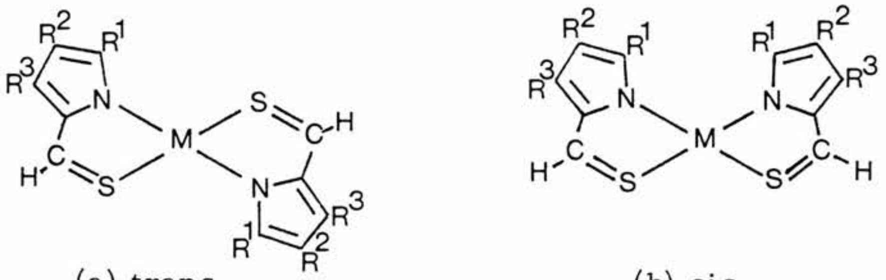
(19)-(23)

Compound	M
(19)	Pd
(20)	Ni
(21)	Cu
(22)	Zn
(23)	Cd

a) R^1=Me; R^2, R^3=H
b) R^1, R^2=Me; R^3=H
c) R^1, R^3=Me; R^2=H
d) R^1=H; R^2, R^3=Me
e) R^1, R^3=Me; R^2=Et

Scheme 5

The ^{1}H nmr spectra of the bis complexes indicate that the pyrrole-2-carbothialdehyde chelate rings are magnetically equivalent and this is consistent with the complexes having either a square planar structure (24) which may be cis or trans, or a tetrahedral structure.



(a) trans (24) (b) cis

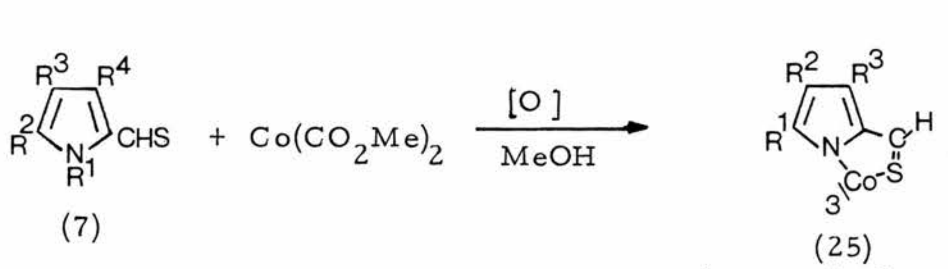
No paramagnetic line broadening was observed in the ^1H nmr spectra of the nickel and palladium complexes, indicating that in solution these complexes are diamagnetic and probably have square planar as opposed to tetrahedral structures. For steric reasons the nickel and palladium complexes probably have the trans structure (24a). In contrast no signals were observed in the ^1H nmr spectra of the copper complexes, indicating that in solution the complexes are paramagnetic. For the copper, zinc and cadmium complexes, insufficient evidence is available to decide between square planar or tetrahedral structures.

A feature of the ^1H nmr spectra of the bis complexes is the chemical shift of the thioformyl proton (Tables 3-6, Appendix A). The thioformyl proton signal of compounds (19), (20), (22) and (23) occurs at higher field than the thioformyl proton signal of the corresponding carbothialdehyde ligands. This large shift is probably due to the shielding effect of the metal atom and to a reduction in the diamagnetic anisotropy of the thiocarbonyl group through bonding with the metal. The palladium and nickel complexes experience larger upfield shifts than do the zinc and cadmium complexes. Whether this is due to more efficient shielding by the palladium and nickel atoms or to a large decrease in the diamagnetic anisotropy of the thiocarbonyl function is not known.

In conclusion it has been shown that pyrrole-2-carbothialdehydes react readily with copper (II), zinc (II), cadmium (II), nickel (II) and palladium (II) acetates to form bis chelate complexes. From the ^1H nmr evidence the nickel and palladium complexes probably have square planar trans structures. For the other complexes further evidence e.g. x-ray analysis, is required to establish their structures.

b) Tris Chelate Complexes

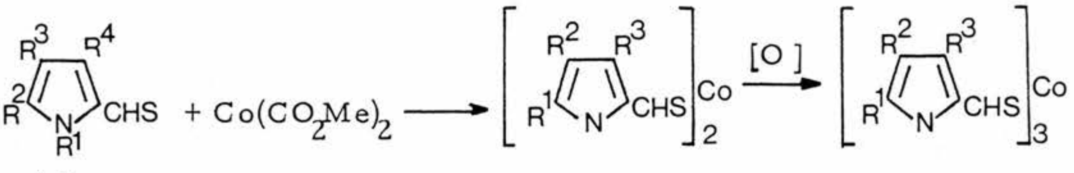
The tris chelate complexes (25a)-(25e) were isolated as stable crystalline solids when cobalt (II) acetate was allowed to react in the presence of air with the carbothialdehydes (7b)-(7f) in methanol (Scheme 6).



a) R^1=Me; R^2, R^3=H
b) R^1, R^2=Me; R^3=H
c) R^1, R^3=Me; R^2=H
d) R^1=H; R^2, R^3=Me
e) R^1, R^3=Me; R^2=Et

Scheme 6

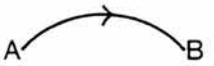
Bis chelates were not observed or isolated. They may be formed initially, then react further to give the tris chelates (Scheme 7).



(7)

Scheme 7

Tris chelate complexes containing bidentate ligands of type (26)



A ≠ B

(26)

can exist in two geometric forms, mer and fac (Fig. 1).

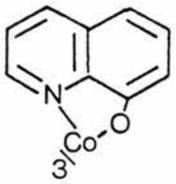
fac

mer

Fig. 1

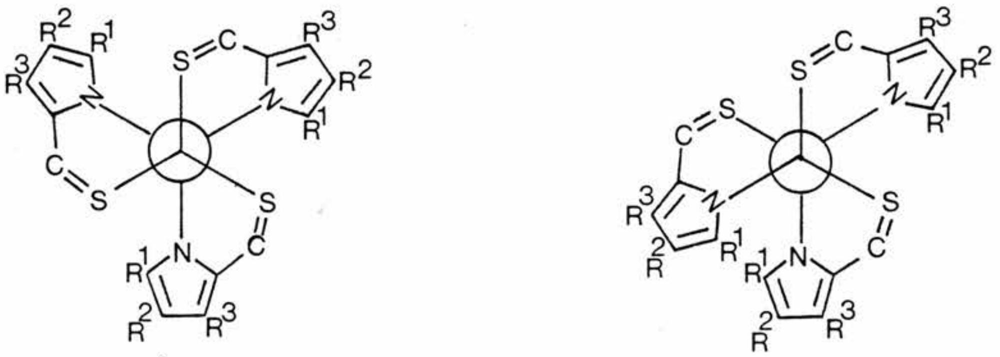
Tlc of each reaction mixture (Scheme 6) showed two spots, a major fast-moving component and a minor slower-moving component. For each reaction mixture the major component was isolated by chromatography and shown by ^{1}H nmr spectroscopy to be the mer isomer. Attempts to isolate the minor component in each reaction mixture were frustrated by the very small quantity of material available and by decomposition of the product when chromatographed. In only one reaction, when (7b) was used as ligand, was any of the minor component isolated, and this was shown by ^{1}H nmr spectroscopy to be the fac isomer. The ratio of fac isomer to mer isomer in this case was 1:26.

In a recent paper[94] on transition metal oxinates, including the cobalt oxinate (27), two main reasons for the preponderance of mer isomer over fac isomer for these compounds were suggested. One argument was based on statistical grounds and a fac isomer to mer isomer ratio of 1:3 would be expected, all other factors being equal. The other argument invoked steric factors and suggested that the fac isomer is more sterically hindered than the mer isomer.



(27)

If one looks at Fig. 2 it can be seen that in the fac isomer a substituent in position 5 of the pyrrole ring can interact with the neighbouring pyrrole ring. As each ligand in this isomer is identical three such interactions are possible. In the mer isomer however only one such interaction is possible. Inspection of molecular models of these

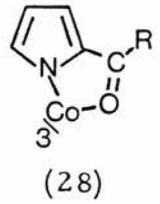


fac

mer

Fig. 2

mer and fac isomers clearly show that such interactions are possible. This suggests that for the fac isomers at least, complexes prepared from pyrrole-2-carbothialdehydes unsubstituted at position 5 should be less sterically hindered and more readily formed than complexes prepared from pyrrole-2-carbothialdehydes substituted at position 5. This and the fact that the only fac isomer isolated (25b') is substituted in position 5 suggests that instability to chromatography during work-up is the overriding factor behind the failure to isolate the fac isomers. It is interesting to note that chromatography of a mixture of the fac and mer isomers of cobalt oxinate (27) resulted in extensive decomposition (an estimated 80%) of the fac isomer[94]. That other factors affect the relative amounts of fac and mer isomers formed is shown by the report that (28) is isolated exclusively as the fac isomer[92].



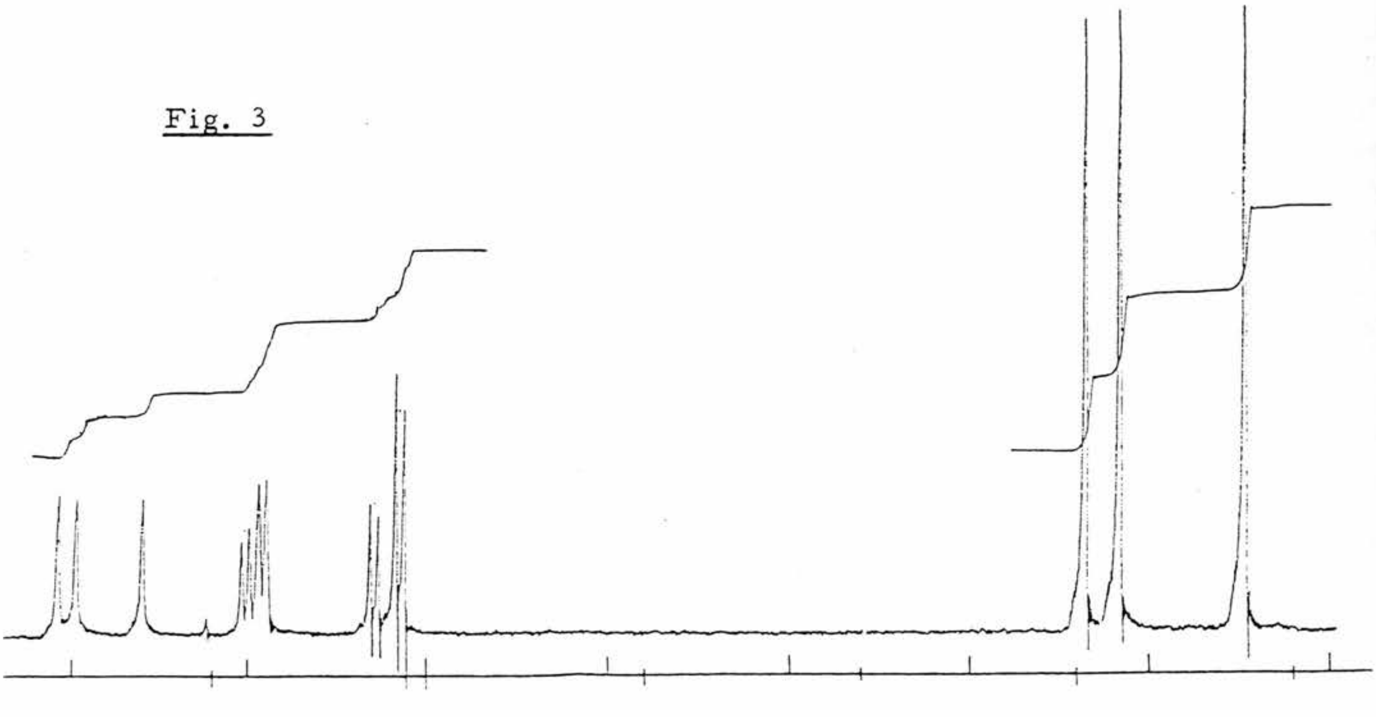
R = Me, H

(28)

Isomerisation of mer and fac isomers by heating in inert solvents is well known[95]. When the mer isomer (25b) was heated at reflux in toluene for 3 hours a mixture of fac and mer isomers was obtained. After separation of the isomers by chromatography and evaporation of the solvent the yield of fac isomer was (0.201g, 43%) and that of the mer isomer (0.248g, 52%). The ratio of fac isomer to mer isomer was 1:1.2. This experiment was then repeated, the mer isomer (25b) being heated at reflux for 6 hours instead of 3 hours. After separation of the isomers the yield of fac isomer was (0.193g, 41%) and that of the mer isomer (0.239g, 51%). The ratio of fac isomer to mer isomer was found to be 1:1.2. This unchanged fac to mer isomer ratio indicates that the isomerisation was at equilibrium.

Fac isomers have a three-fold symmetry axis whereas mer isomers have no axis of symmetry. Therefore, in principle, a given substituent in each chelating ligand in the mer isomer should give a separate nmr signal, whereas the same substituent in each chelating ligand in the fac isomer should give only one nmr signal. ^{1}H Nmr spectra of the major products (25a)-(25e) in each case show that the ligands are magnetically non-equivalent. This is clearly shown by the presence of three distinct methyl resonances in the spectrum of (25a) (Fig. 3). This demonstrates that the major isomers are

Fig. 3



the mer isomers. The chemical shifts of the thioformyl protons and the ring protons in the complexes (25d) and (38a) could not be assigned with any certainty due to the extensive overlap of the relevant peaks.

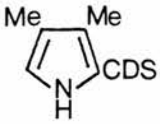
The ^{1}H nmr spectrum of the fac isomer (25b') shows the expected magnetic equivalence of the chelate rings. However, the signal assigned to the Me group adjacent to the nitrogen atom is broadened somewhat. The signal due to the thioformyl proton appears as a very broad hump (ca. δ 7.3 - 7.9). Similar spectra have been reported for the complexes (28)[92].

In the ^{1}H nmr spectrum of the fac isomer (25b') the 5-Me signal at δ 1.50 occurs at higher field than that of the uncomplexed carbothialdehyde ligand ($\Delta\ \delta$ 0.7). This large shift is probably caused by the close proximity of the 5-Me to a pyrrole ring on an adjacent ligand, as shown in Fig. 2. In the corresponding mer isomer (25b) three separate 5-Me signals are observed in the ^{1}H nmr spectrum. The 5-Me signal at δ 1.37 occurs at higher field than the 5-Me signal in the uncomplexed ligand ($\Delta\ \delta$ 0.8), whereas the 5-Me signals at δ 2.09 and δ 2.30 are little changed, $\Delta\,\delta$ 0.1 and $\Delta\ \delta$ 0.1 respectively, compared with the 5-Me signal in the uncomplexed ligand. This large upfield shift indicates that this particular 5-Me is in close contact with a pyrrole ring on an adjacent ligand, as shown in Fig. 2. Similar conclusions can be drawn from the ^{1}H nmr spectra of the *mer* isomers (25a) and (25c). Similar ^{1}H nmr behaviour has been reported for some transition metal oxinates [94].

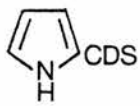
In conclusion it can be said that pyrrole-2-carbothialdehydes form tris as opposed to bis chelate complexes with cobalt (II) acetate and that the tris complexes are predominantly the *mer* isomers, the *fac* isomer being isolated in only one case.

The isomerisation of (25b) to give reasonable quantities of the *fac* isomer could, if shown to be of general application, be a useful preparative route to the other *fac* isomers in this series.

The problem of fully assigning the peaks in the ^{1}H nmr spectra of (25d) and (38a) can only be resolved by preparing the deuterated complexes (29) and (30) and work is at present being done in these laboratories towards this end.



(29)



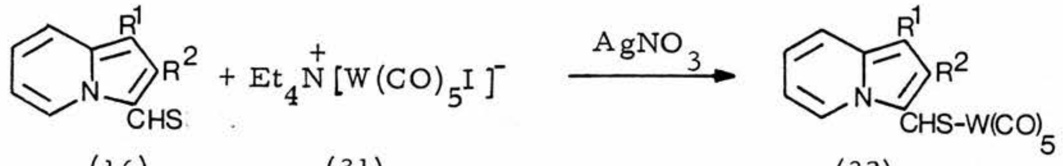
(30)

2. Pentacarbonyl Group $\overline{\text{VI}}$ Metal Complexes of Pyrrole Carbothialdehydes and Indolizine Carbothialdehydes

As mentioned previously (page 46) carbothialdehydes are potential two-electron donors and can in theory form compounds $RCHSM(CO)_5$. The aim of the work described in this section was to explore this potential for complex formation by studying the reactions of the compounds (16a), (16b), (7c), (7d), (9a) and (9b) with the tungstate (31).

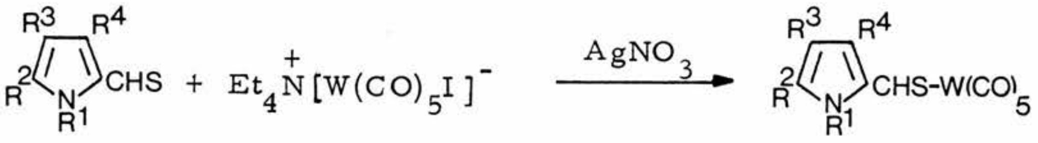
It has been shown[96] that a variety of two-electron ligands (L) react with tetra-alkylammonium pentacarbonylhalogenometallate (0) salts $R_4\overset{+}{N}[M(CO)_5X]$ (M = W, Cr, Mo; X = Cl, Br, I) in the presence of a Lewis acid to form compounds $LM(CO)_5$. Accordingly, solutions of the compounds (16a), (16b), (7c), (7d), (9a) and (9b) and the tungstate (31) in dichloromethane were allowed to react with aqueous silver nitrate (Scheme 7). Subsequent work-up and recrystallisation gave the complexes (32a), (32b), (33a), (33b), (34a) and (34b) as air-stable crystalline compounds.

Tlc of each carbothialdehyde-tungstate solution prepared for use in the above reaction, ie. before the addition of $AgNO_3$, revealed the presence of a trace of the desired product. A possible explanation for the formation of these products is that the tungstate (31) is attacked by the carbothialdehydes (16a), (16b), (7c), (7d), (9a) and (9b) in a nucleophilic displacement reaction. One possible mechanism for



(16) (31) (32)

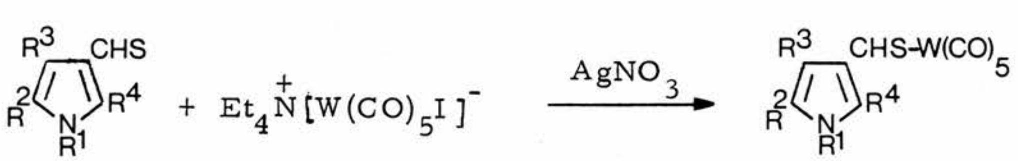
a) R^1 = H, R^2 = Me b) R^1, R^2 = Me



(7) (33)

(7) c) R^1, R^4=H, R^2, R^3=Me
d) R^1, R^3=H, R^2, R^4=Me

(33) a) R^1, R^4=H, R^2, R^3=Me
b) R^1, R^3=H, R^2, R^4=Me

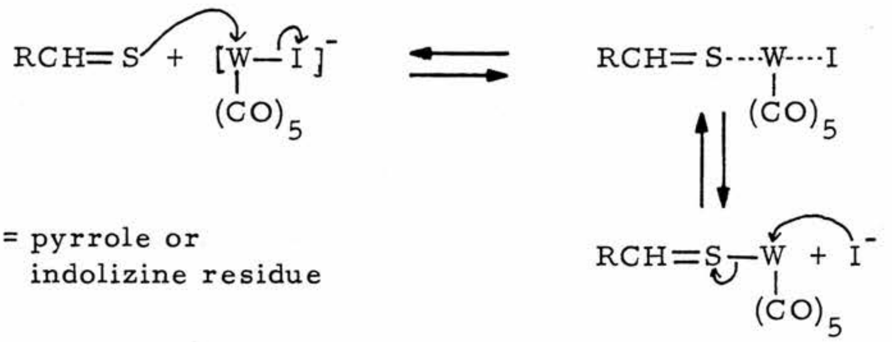


(9) (34)

a) R^1, R^2, R^4=Me, R^3=H b) R^1, R^3=H, R^2, R^4=Me

Scheme 7

such a reaction is shown (Scheme 8).



R = pyrrole or
indolizine residue

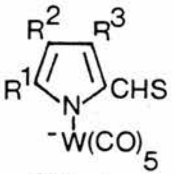
Scheme 8

In the ^{1}H nmr spectra of the complexes (32a), (32b), (33a), (33b), (34a) and (34b) the thioformyl proton signal occurs at higher field than the thioformyl proton signal in the corresponding uncomplexed ligand (Table 1). Shielding by the metal atom and a reduction in the diamagnetic anisotropy of the thiocarbonyl group are the most likely reasons for this upfield shift of the thioformyl proton signals of the

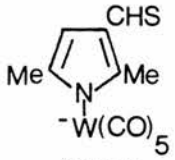
Table 1

	(33a)	(33b)	(34a)	(34b)	(32a)	(32b)
Chemical shift of the thioformyl proton in the metal complexes.	9.77	9.82	10.56	10.58	9.93	9.80
Chemical shift of the thioformyl proton in the corresponding uncomplexed ligand.	10.27	10.34	11.03	11.01	10.55	10.40
$\Delta\delta$	0.50	0.52	0.47	0.43	0.62	0.60

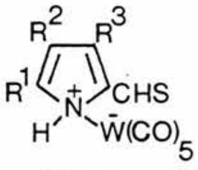
complexes. Such a large shift indicates that the carbothialdehyde ligand in the complexes (32a), (32b), (33a), (33b), (34a) and (34b) is bonded to the metal through the sulphur atom. The complexes (33a), (33b) and (34b) show N-H stretching bands in their infrared spectra (Table 2, Appendix B) and signals corresponding to N-H protons in their ^{1}H nmr spectra (Table 2, Appendix A). These observations rule out the possibility of alternative structures such as (35a) and (35b) for these complexes. Other alternative structures such as (36a) and (36b) for the complexes (33a), (33b), (34a) and (34b) and (37) for the complexes (32a) and (32b) are unlikely as the formation of a nitrogen to tungsten bond in these cases would destroy the aromaticity of the heterocyclic rings.



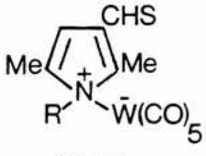
(35a)



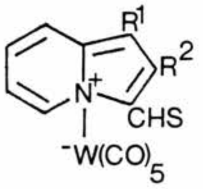
(35b)



(36a)

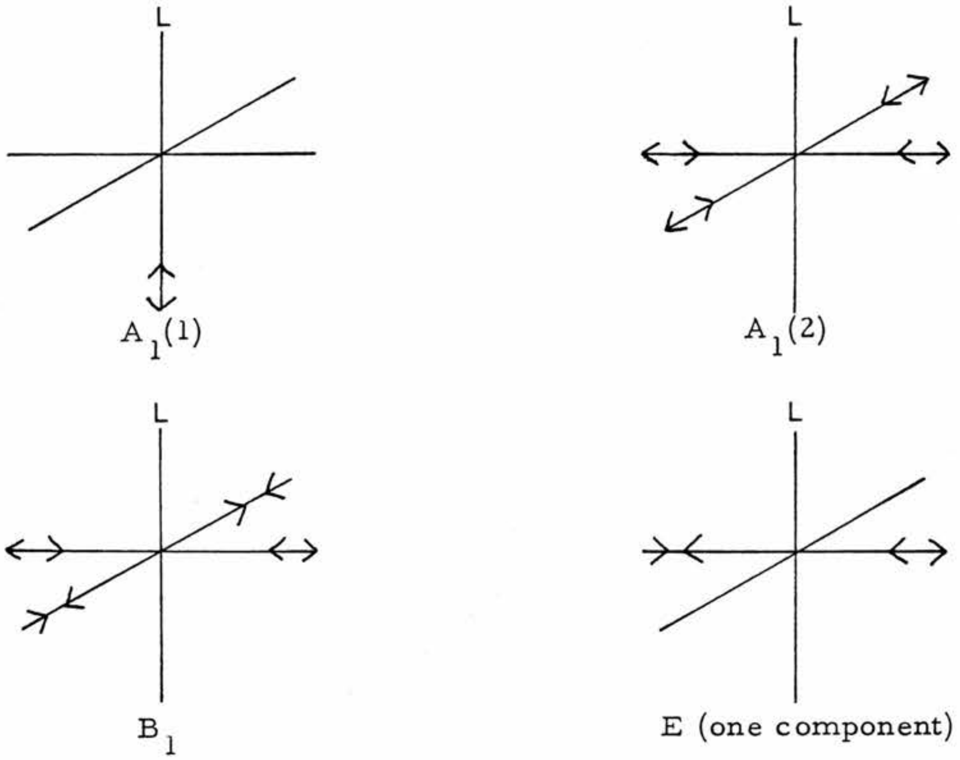


(36b)



(37)

Compounds of general formula $M(CO)_5L$ have idealised symmetry C_{4v} and can have three carbonyl stretching vibrations in their infrared spectra, two of symmetry A_1 and one of symmetry E. There is also an infrared inactive mode of symmetry B_1[97] (Scheme 9). The general pattern of the carbonyl vibrations in the infrared spectra of these compounds is always an $A_1(2)$ band at high frequency[97]. This band may be anything from medium to extremely weak in intensity and is followed by an intense E band with one or two weaker side bands. One of these side bands is due to the $A_1(1)$ mode and is usually present as a band or shoulder of weak to medium intensity. If the other band is present it is usually extremely weak and is due to the formally inactive infrared B_1 mode.



Scheme 9

It has been pointed out[98] that in addition to the expected carbonyl frequencies observed in the infrared spectra of compounds $M(CO)_5L$, splitting of the E band, and the appearance of a B_1 band of low intensity, may be observed if the ligand (L) lacks axial symmetry. Infrared spectra confirming this deduction have since been made[99].

These theoretical conclusions about the number, intensity and position of the carbonyl stretching vibrations in compounds $M(CO)_5L$ are in close agreement with the observed spectra of the complexes (32a), (32b), (33a), (33b), (34a) and (34b). Tentative assignments based on these conclusions have been made (Tables 1 and 3, Appendix B). The splitting of the E band in the infrared spectra of the complexes (32a), (32b), (33b), (34a) and (34b) is not unexpected as the carbothialdehyde ligands in these complexes lack axial symmetry. The expected B_1 band is probably too weak to be observed.

In conclusion it can be said that the carbothialdehydes (16a), (16b), (7c), (7d), (9a) and (9b) react readily with the tungstate (31) to give the expected monosubstituted pentacarbonyl complexes. The structure of the complexes (32a), (32b), (33a), (33b), (34a) and (34b) as formulated (Scheme 7) is in good agreement with their infrared and ^1H nmr data.

C. THE STABILISATION OF PYRROLE-2-CARBOTHIALDEHYDE BY METAL COMPLEX FORMATION

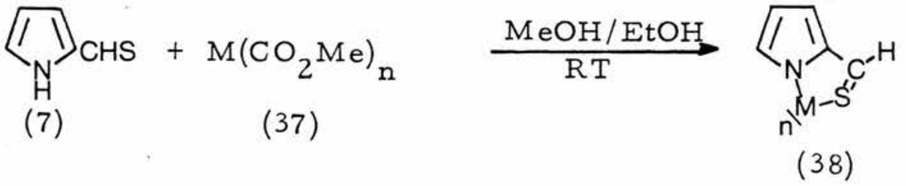
Pyrrole-2-carbothialdehyde (7a) is unstable and, as mentioned previously (page 40), can only be obtained as a solution in ether. The aims of the work described in this section of the thesis were:

(a) to stabilise the carbothialdehyde by complex formation;

(b) to test the effectiveness of the metal acetates [(37) M = Co, Ni, Pd, Cu, Cd, Zn] and the tungstate (31) as trapping reagents for the carbothialdehyde (7a).

Reaction of Pyrrole-2-carbothialdehyde with Metal Acetates

A solution of compound (7a) in ether was obtained when pyrrole was thioformylated in the usual way (Scheme 2, page 40). This ether solution was immediately treated with a solution of the appropriate metal acetate [(37), M=Co, Ni, Pd, Cu, Cd, Zn] in methanol or ethanol (Scheme 10).



(7) (37) (38)

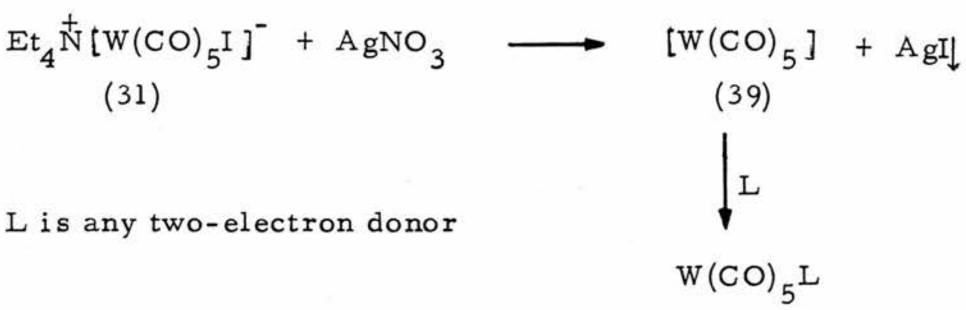
	M	n
a)	Co	3
b)	Ni	2
c)	Pd	2
d)	Cu	2
e)	Cd	2
f)	Zn	2

Scheme 10

After work-up and recrystallisation the complexes (38a), (38b), (38c) and (38d) were isolated as air-stable crystalline compounds in moderate yield. The zinc and cadmium complexes (38e) and (38f) decompose rapidly in solution and were therefore not isolated. Mixing the reagents in the usual way produced the expected bright yellow colour of the bis chelate complex but this faded rapidly (1-2 min) leaving a dark, almost black, solution containing, as shown by tlc, neither starting material nor product. Why this should happen is not clear. However, acetic acid is a by-product of these reactions and it may be that these complexes are particularly acid sensitive.

Reaction of Pyrrole-2-carbothialdehyde with Tetraethylammonium Pentacarbonyliodotungstate (0)

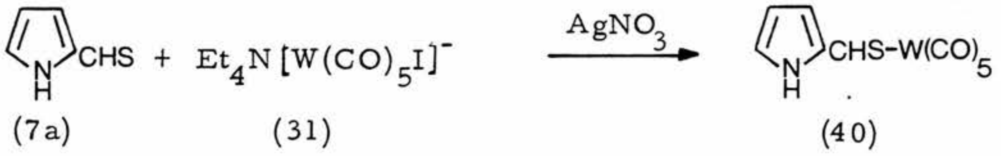
For the reaction of the carbothialdehyde (7a) with the tungstate (31) it was thought that a solution of the carbothialdehyde (7a) in benzene rather than in ether would give better results. The reason for this change was the possibility of diethyl ether interfering in the reaction of the tungstate (31) with compound (7a). From the mechanism of the reaction[96] (Scheme 11), it can be seen that diethyl ether, a potential 2-electron donor, may react with the reactive intermediate (39). Therefore, compound (7a) was prepared in the usual manner (Scheme 2, page 40) except that benzene instead of ether was used for the extraction. This benzene solution was immediately treated with a solution of the tungstate (31) in



L is any two-electron donor

Scheme 11

dimethylformamide.and then with aqueous silver nitrate (Scheme 12). Subsequent work-up followed by recrystallisation gave the air-stable



Scheme 12

crystalline complex (40). The yields of the various pyrrole-2-carbothialdehyde complexes are shown in Table 2. The yields given in Table 2 clearly show that the most useful reagents for trapping compound (7a) were nickel (II) acetate, cobalt (II) acetate, and copper (II) acetate. The tungstate (31) was not a very effective

Table 2

Complex	% Yield
(38a)	43
(38b)	46
(38c)	22
(38d)	46
(40)	11

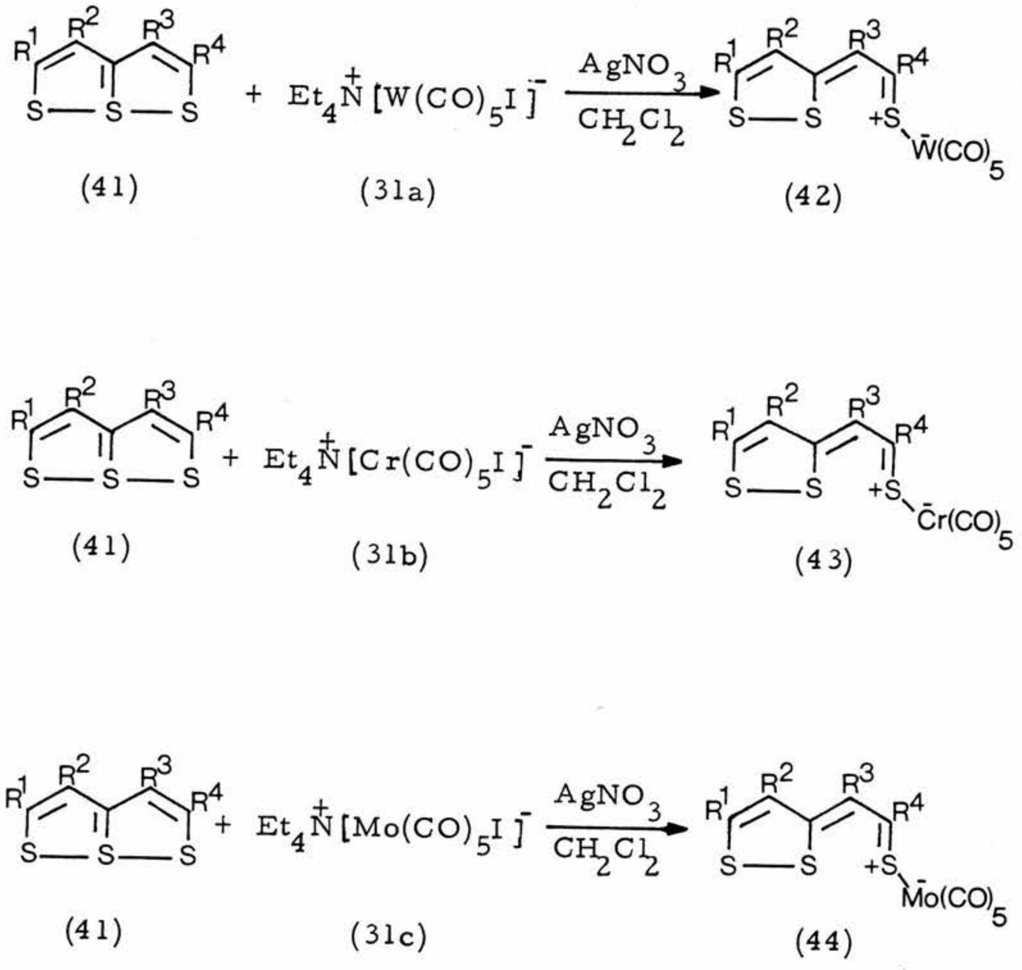
trapping reagent for compound (7a) as judged by the yield of complex (40). It is however a potentially more useful trapping reagent than the metal acetates [(37), M = Co, Ni, Pd, Cu] as it can, in principle, be used to trap any carbothialdehydes that are stable in solution. In contrast, the application of the metal acetates [(37), M=Co, Ni, Pd, Cu] as trapping reagents is probably limited to the trapping of other pyrrole-2-carbothialdehydes or to carbothialdehydes that are potential bidentate ligands.

D. GROUP $\underline{VI}$ METAL PENTACARBONYL COMPLEXES OF SOME TRITHIAPENTALENE VALENCE ISOMERS

The carbothialdehydes (16a), (16b), (7c), (7d), (9a) and (9b) behave as two-electron donors, reacting rapidly with tungstate (31a) in the presence of silver nitrate to give the complexes (32), (33) and (34) (see section B, page 56). Trithiapentalenes are potential two-electron donors as they have a non-bonding electron pair on each terminal sulphur atom, and could conceivably react with the metallates (31a), (31b) and (31c) in a similar manner to the carbothialdehydes mentioned above.

Therefore solutions of the 1, 6, 6a λ^4-trithiapentalenes (41a), (41b), (41c) and (41d) and the metallate (31) in dichloromethane were allowed to react under argon with aqueous silver nitrate (Scheme 13). After work-up and subsequent purification the complexes (42a), (42b), (42c), (42d), (43a), (43b), (43c), (43d), (44a) and (44d) were isolated as air-stable crystalline solids. The molybdenum complexes (44b) and (44c) could not be isolated free from the starting 1, 6, 6a λ^4-trithiapentalene. In solution, the complexes were sensitive to light and heat, the molybdenum complexes especially so.

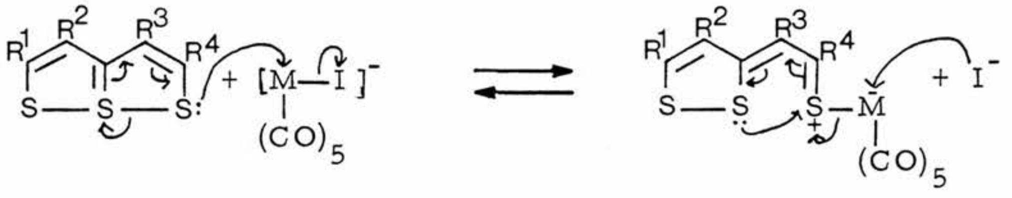
Tlc of each 1, 6, 6a λ^4-trithiapentalene-metallate solution prepared for use in the above reaction, ie. before the addition of silver nitrate (Scheme 13), showed a trace of the desired product. This formation of the products indicates the possibility of a



	R^1	R^2	R^3	R^4
a)	H	$-(CH_2)_3-$		H
b)	H	$-(CH_2)_4-$		H
c)	Me	H	H	Me
d)	Bu^t	H	H	H

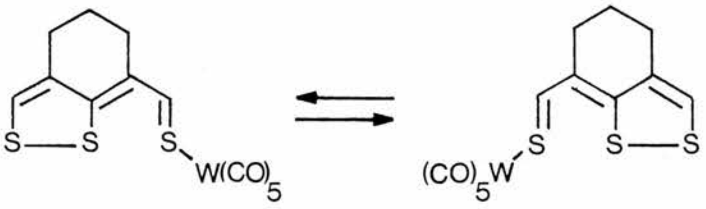
Scheme 13

nucleophilic attack by sulphur on the metallate (31). A possible mechanism for this nucleophilic reaction is shown (Scheme 14).



Scheme 14

The ^{1}H nmr spectra of the complexes (42a),(42b),(42c),(43a),(43b),(43c), and (44a) show extensive line broadening at ambient temperature. This is indicative of a dynamic process and in order to investigate further this process the complexes (42a),(42b),(42c),(43a),(43b),(43c) and (44a) were studied by variable temperature ^{1}H nmr spectroscopy^{100}. The behaviour of the complex (42a) was typical and will be discussed in detail here. As the position of the cycloalkyl proton signals in this complex vary little over the temperature range studied they will not be discussed further. At -10°C the ^{1}H nmr spectrum of complex (42a) in chloroform-d solution shows two sharp singlets at δ 8.18 (3-H) and δ 9.46 (1'-H). Reasons for these assignments are given on page 72. Warming the solution causes these signals to broaden until at 34°C they coalesce to a broad singlet at δ 8.79. Further heating to 60°C causes this singlet to become progressively sharper. This behaviour is reversed when the solution is cooled to -10°C. These observations indicate that compound (42a) is fluxional in solution. This fluxional process in which the $W(CO)_5$ group oscillates between the end sulphur atoms in compound (42a) is shown (Scheme 15)



Scheme 15

Repeating the variable-temperature ^1H nmr experiment using different concentrations of complex (42a) showed that the coalescence temperature (T_c) was independent of the concentration of (42a) (Table 3). Solutions of the complex (42a) containing added ligand (41a) were

Table 3

T_c °C	Concentration of (42a) in $CDCl_3$
34	0.4 M
34	0.2 M
35	0.1 M
34	0.075 M

also studied by variable temperature ^1H nmr and showed (Table 4) that the coalescence temperature (T_c) is independent of added ligand. This behaviour indicates that the fluxional process shown (Scheme 15) is intramolecular. It should be noted however that because of

Table 4

T_c °C	Concentration of added ligand in $CDCl_3$
34	0.2 M
34	0.4 M

Complex (42a) was 0.2 M in $CDCl_3$

solubility difficulties the range of concentrations studied was not very wide. Therefore the possibility that the fluxional process is intermolecular cannot be ruled out.

$\Delta G^\ddagger$ Values were calculated for each fluxional process (Table 5). For the complexes (42a), (43a) and (44a) the

Table 5. $\Delta G^\ddagger$ Values

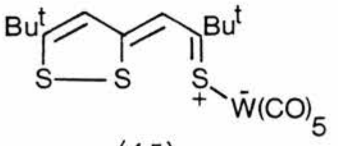
Compound	$\Delta G^\ddagger$ (Kcal mol^{-1}) *
(42a)	14.69
(43a)	15.30
(44a)	12.16
(42b)	14.37
(43b)	14.88
(44b)	compound not isolated
(42c)	14.45 (Me) 14.04 (H)
(43c)	14.38 (Me) 14.10 (H)
(44c)	compound not isolated

* Values calculated using the formula[116],

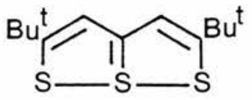
$$\frac{\Delta G^\ddagger}{RT_c} = \text{Log e}\left[\frac{\sqrt{2R}}{\pi Nh}\right] + \text{Log e}\left[\frac{T_c}{\delta \nu}\right]$$

activation energies for the fluxional process in the tungsten and chromium complexes are of comparable value and are much higher than the activation energy for the fluxional process in the molybdenum complex. This is in accord with the relative stabilities of solutions of the complexes to heat and light. The molybdenum complexes were observed to be less stable in this respect than the tungsten and chromium complexes.

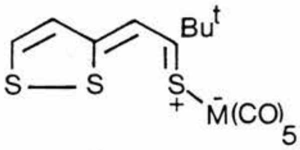
The ^{1}H nmr spectra of the complexes (42d), (43d) and (44d) were temperature invariant over the range -70 - +50°C. The $M(CO)_5$ group in these compounds is probably attached to the least hindered end of the molecule as shown (Scheme 13). An attempt to prepare (45) by the usual method (Scheme 13) failed. Work-up of the reaction mixture gave back the ligand (46) in high yield (84%). This suggests that a structure such as (47) for complexes (42d), (43d) and (44d) is unlikely.



(45)



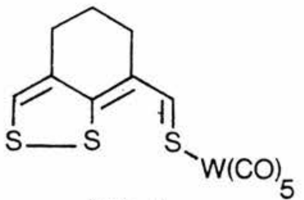
(46)



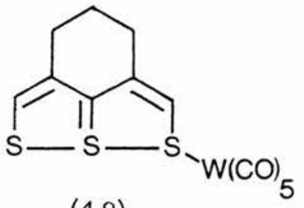
(47)

The ^1H nmr spectrum of complex (42d) (Table 11, Appendix A) shows three one-proton signals, a singlet at δ 7.54 and two doublets, which are coupled together, at δ 7.56 and δ 9.65. There is also a nine-proton signal at δ 1.51. The signal at δ 1.51 is assigned to the t-butyl group. The singlet at δ 7.54 is assigned to the proton adjacent to the t-butyl group and the doublet at δ 7.56 to 2-H. The corresponding proton signals in complex (42c) (Table 12, Appendix A) occur at δ 7.45 and δ 7.66. The remaining doublet at δ 9.65 is assigned to 1-H. In the low temperature (-10°C) ^1H nmr spectrum of complex (42a) (Table 13, Appendix A) the low field singlet at δ 9.46 is assigned to 1'-H on the basis of a comparison with the similarly situated 1-H proton in the ^1H nmr spectrum of complex (42d). The singlet at δ 8.18 is assigned to 3-H.

An X-ray single crystal structure determination[101] has established that the complex (42a) has the structure (42a) rather



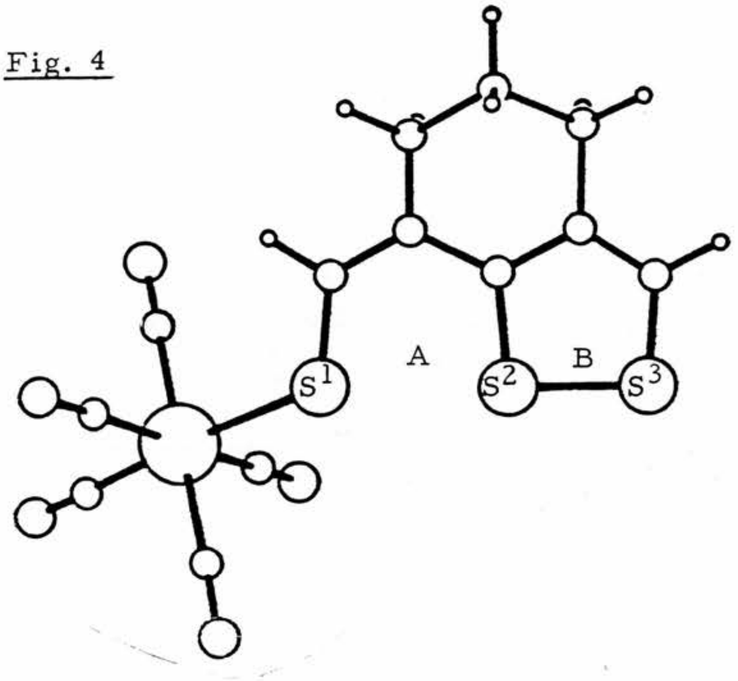
(42a)



(48)

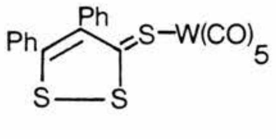
than structure (48). Some bond lengths are shown (Fig. 4). The S_2-S_3 bond length is 2.08 Å and is similar to the S-S bond length (2.06 Å) found in compound (49)[30] and to the S-S bond length

Fig. 4

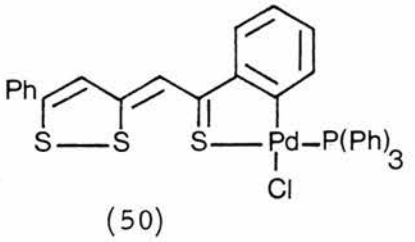


A = 2.75 Å
B = 2.08 Å

(2.07 Å) found in compound (50)[60]. The S_1-S_2 distance is 2.75 Å and lies well outside the range of the S-S bond lengths in the free



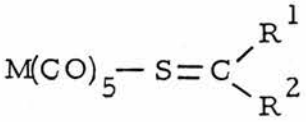
(49)



(50)

ligand[102] (the bond lengths are 2.30 Å and 2.39 Å and 2.28 Å and 2.41 Å, respectively, for two crystallographically independent molecules) and is similar to the non-bonding S-----S distance of 2.80 Å in compound (50)[60].

Infrared spectral data for the complexes is consistent with the pentacarbonyl structure established by x-ray analysis (Table 4, Appendix B). It can be seen that the observed spectra are in good agreement with the predicted spectra [97] and are very similar to those published for the complexes (51)[40].

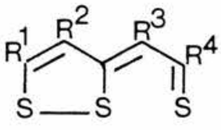


$$\mathrm{M(CO)_5{-}S{=}C\begin{matrix}\diagup R^1\\ \diagdown R^2\end{matrix}}$$

(51)

R^1	R^2	M
Me	Me	Cr
Me	Me	W
Me	Et	W
Me	Ph	W
Ph	Ph	W

In conclusion it has been established that the reaction of tetraethylammonium pentacarbonyliodometallate (0) salts $\mathrm{Et_4\overset{+}{N}[M(CO)_5I]^-}$; M = W, Cr, Mo with 1, 6, 6a λ^4-trithiapentalenes in the presence of silver nitrate gives pentacarbonyl group VI metal (0) complexes of the previously unknown 1, 6, 6a λ^4-trithiapentalene valence isomers (52).



(52)

The symmetrical complexes (42a), (42b), (42c), (43a), (43b), (43c), and (44a) are fluxional in solution and it was established that this fluxional process is probably intramolecular.

EXPERIMENTAL

INTRODUCTORY NOTES

Melting points were determined on a Kofler hot-stage apparatus.

Yields refer to recrystallised tlc pure material.

Ultraviolet and visible spectra were measured using a Unicam SP800 spectrophotometer, solutions were in cyclohexane unless stated otherwise.

Infra-red spectra were recorded using a Perkin-Elmer 1330 spectrophotometer, solutions were 2×10^{-3} in cyclohexane unless stated otherwise.

^{13}C NMR spectra were recorded at ca. 38°C using a Varian CFT-20 spectrometer operating at 20 MHz. Solutions in chloroform-d were 0.5M.

^{1}H NMR spectra were recorded at ca. 33°C unless stated otherwise using a Varian HA100 spectrometer operation at 100 MHz. For variable temperature ^{1}H NMR spectroscopy coalescence temperatures were measured using a Wilmad probe thermometer accurate to $\pm 1^{\circ}C$. Solutions in chloroform-d, dimethyl sulphoxide-d_6 and pyridine-d_5 were 0.4M unless stated otherwise. Chemical shifts (δ) are given in ppm downfield from tetramethylsilane as internal reference, J values are in Hz. Unless stated otherwise (d=doublet, t=triplet, q=quartet, quin=quintet, dd=double doublet, dq=double quartet, m=multiplet, b=broad). Chemical shift values refer to singlet absorptions.

Carbon, hydrogen and nitrogen elementary microanalyses were carried out by Mrs. Sylvia Smith and Mr. J. Bews, Department of Chemistry, University of St. Andrews.

PROCEDURES

Criteria used in the identification of products included melting points, tlc behaviour, nmr, and ir.

Thin layer chromatography (tlc) was carried out with silica (MN - KIESELGEL-G) and alumina (MN ALUMINIUM OXIDE-G) coated plates (ca. 0.25 mm thick).

Alumina (CAMAG 100-250 mesh, activity II, pH 9.3-9.7) and silica (SORBSIL M60) were used for column chromatography.

Solutions were dried over anhydrous sodium sulphate and solvents were evaporated at reduced pressure using a rotary film evaporator.

Solids were dried in vacuo over phosphoric anhydride.

MATERIALS

'Petroleum' refers to petroleum ether of boiling range 40-60°C and 'ether' refers to diethyl ether. Acetic acid, acetone, cyclohexane, ethanol, methanol, n-hexane and petroleum were all redistilled commercial solvents. Ether, benzene and xylene were boiled over sodium wire for 1 hour then distilled to give the dry solvents. These solvents were stored over sodium wire. The crude ether was pre-dried over calcium chloride for ca. 3 days before the sodium wire was added.

Benzene for chromatography was dried by azeotropic distillation, the first 25% of the distillate being used for extractions. Ether for chromatography was dried over calcium chloride for ca. 3 days, decanted and distilled.

Methylene chloride was boiled over calcium hydride (2g per litre) for 1 hour and then distilled.

Acetonitrile was boiled over sodium hydride (50% dispersion in oil, 2g per litre) for 30 minutes, distilled, boiled over phosphoric anhydride for 1 hour, distilled and redistilled.

Dimethylformamide was dried for ca. 1 week over powdered calcium hydride then distilled at 15 mm Hg.

Tetrahydrofuran was boiled over lithium alumimium hydride (2g per litre) for 1 hour and then distilled. The dry tetrahydrofuran thus obtained was stored over sodium wire.

n-Butanol, bromoacetone, diethylene glycol, dimethyl acetylenedicarboxylate, ethyl acetoacetate, 3-ethylpyridine, methyl chloroformate, methyl iodide, 2-methylpyridine, phosphoryl chloride and vinyl acetate were all redistilled commercial reagents.

Aqueous 2M-sodium hydrogen sulphide solutions were prepared by saturating aqueous 1M-sodium sulphide solutions with hydrogen sulphide gas.

Solvents used for ultraviolet, visible and infra-red spectroscopy were of spectroscopic grade.

A. PREPARATION OF ALKYLPYRROLES

Pyrrole, 2,5-dimethylpyrrole, and 3-ethyl-2,4-dimethylpyrrole (kryptopyrrole), purchased from the Aldrich Chemical Co. Ltd., were redistilled before use.

The following pyrroles were prepared by the methods cited: 2-methylpyrrole[103,104], 2,3-dimethylpyrrole[105], 3,4-dimethylpyrrole[106], and 2,4-dimethylpyrrole[107].

Preparation of N-Methylpyrroles

1,2,3-Trimethylpyrrole, 1,2,4-trimethylpyrrole and 1,2,5-trimethylpyrrole were prepared by the following method, which is essentially that of Potts and Saxton[108].

Sodium (1.7 g, 75 mmol) in small pieces was added to liquid ammonia (150 ml) containing a catalytic amount of ferric nitrate nonahydrate (10 mg). The blue colour was allowed to discharge between each addition. A solution of the pyrrole (50 mmol) in dry ether (12.5 ml) was added dropwise over 5 minutes, and the mixture was stirred for 10 minutes. A solution of methyl iodide (6.5 ml, 100 mmol) in dry ether (12.5 ml) was then added dropwise over 5 minutes and the mixture stirred for a further 15 minutes.

The ammonia was allowed to evaporate and the residue, dissolved in water (100 ml), was extracted with ether. The extracts were washed with water (2 x 100 ml), dried and evaporated, and the residue was distilled. The following N-methylpyrroles were prepared.

2,5-Dimethylpyrrole (4.76 g) gave 1,2,5-trimethylpyrrole (73%), b.p. 61-62°C at 14 mm.

2,4-Dimethylpyrrole (4.76g) gave 1,2,4-trimethylpyrrole (71%), b.p. 63-66°C at 17 mm.

2,3-Dimethylpyrrole (4.76g) gave 1,2,3-trimethylpyrrole (68%), b.p. 64-66°C at 21 mm.

B. PREPARATION OF PYRROLE CARBOTHIALDEHYDES

The pyrroles were prepared by the methods given on page 78.

1. Preparation of Pyrrole-2-carbothialdehydes

A solution of the pyrrole (10 mmol) in dimethylformamide (10 ml) was added dropwise over a period of 10 minutes to a stirred solution of phosphorus oxychloride (1 ml, 11 mmol) in dimethylformamide (10 ml). The resulting solution was stirred at room temperature for 30 minutes, then poured into aqueous 2M-sodium hydrogen sulphide (50 ml). The mixture was diluted with water (200 ml) before being extracted with ether (3 x 100 ml). The extracts were washed with water (6 x 100 ml), dried, and evaporated. The residue, dissolved in a minimum volume of benzene, was chromatographed on alumina (20 x 2.5 cm) with benzene as eluant. The red eluates were collected and evaporated, and the residue was recrystallised. The following pyrrole-2-carbothialdehydes were prepared.

5-Methylpyrrole-2-carbothialdehyde (7b)

2-Methylpyrrole (0.811 g) gave the carbothialdehyde (7b) (0.908 g, 73%), a cherry red glass unstable to air and heat, b.p. 110°C/0.1 mm.

Found:	C, 57.5%;	H, 5.7%;	N, 10.9%.
C_6H_7NS requires:	C, 57.6%;	H, 5.6%;	N, 11.2%.

^{1}H NMR - see Appendix A, Table 2.

^{13}C NMR - see Appendix A, Table 1.

3,5-Dimethylpyrrole-2-carbothialdehyde (7d)

2,4-Dimethylpyrrole (0.951 g) gave the carbothialdehyde (7d) (0.971 g, 70%), orange prisms from methanol, m.p. 133-135°C.

Found: C, 60.3%; H, 6.7%; N, 10.0%.

C_7H_9NS requires: C, 60.4%; H, 6.5%; N, 10.1%.

^1H NMR - see Appendix A, Table 2.

^{13}C NMR - see Appendix A, Table 1.

3,4-Dimethylpyrrole-2-carbothialdehyde (7e)

3,4-Dimethylpyrrole (0.951 g) gave the carbothialdehyde (7e) (0.932 g, 67%), brown needles with a violet cast from cyclohexane, m.p. 107-109°C.

Found: C, 60.4%; H, 6.7%; N, 10.0%.

C_7H_9NS requires: C, 60.4%; H, 6.5%; N, 10.1%.

^1H NMR - see Appendix A, Table 2.

^{13}C NMR - see Appendix A, Table 1.

4,5-Dimethylpyrrole-2-carbothialdehyde (7c)

2,3-Dimethylpyrrole (0.951 g) gave the carbothialdehyde (7c) (0.914 g, 66%), orange sheets with a violet cast from cyclohexane, m.p. 80-82°C.

Found: C, 60.1%; H, 6.6%; N, 10.0%.

C_7H_9NS requires: C, 60.4%; H, 6.5%; N, 10.1%.

^1H NMR - see Appendix A, Table 2.

^{13}C NMR - see Appendix A, Table 1.

3,5-Dimethyl-4-ethylpyrrole-2-carbothialdehyde (7f)

2,4-Dimethyl-3-ethylpyrrole (1.232 g) gave the carbothialdehyde (7f) (1.122 g, 67%), orange prisms from acetonitrile, m.p. 135-137°C.

Found: C, 64.7%; H, 7.9%; N, 8.3%.

$C_9H_{13}NS$ requires: C, 64.6%; H, 7.8%; N, 8.4%.

^1H NMR - see Appendix A, Table 2.

^{13}C NMR - see Appendix A, Table 1.

1,3,5-Trimethylpyrrole-2-carbothialdehyde (7h)

1,2,4-Trimethylpyrrole (1.092 g) gave the carbothialdehyde (7h) (0.399 g, 26%), red plates from methanol, m.p. 85-89°C.

Found: C, 62.5%; H, 7.1%; N, 8.8%.

$C_8H_{11}NS$ requires: C, 62.7%; H, 7.2%; N, 9.1%.

^1H NMR - see Appendix A, Table 2.

^{13}C NMR - see Appendix A, Table 1.

1,4,5-Trimethylpyrrole-2-carbothialdehyde (7g)

1,2,3-Trimethylpyrrole (1.092 g) gave the carbothialdehyde (7g) (0.477 g, 31%), red prisms from n-hexane, m.p. 85-88°C.

Found: C, 62.4%; H, 7.1%; N, 9.1%.

$C_8H_{11}NS$ requires: C, 62.7%; H, 7.2%; N, 9.1%.

^1H NMR - see Appendix A, Table 2.

^{13}C NMR - see Appendix A, Table 1.

2. Attempted Preparation of Pyrrole-2-carbothialdehyde (7a)

A solution of pyrrole (0.671 g, 10 mmol) in dimethylformamide (10 ml) was added dropwise over a period of 10 minutes to a stirred solution of phosphorus oxychloride (1 ml, 11 mmol) in dimethylformamide (10 ml). The resulting solution was stirred at room temperature for 30 minutes, then poured into aqueous 2M-sodium hydrogen sulphide (50 ml). The mixture was diluted with water (200 ml) before being extracted with ether (3 x 100 ml). The extracts were washed with water (6 x 100 ml) then dried. These extracts were evaporated and yielded an insoluble polymeric material. The experiment was abandoned at this stage.

3. Preparation of Pyrrole-3-carbothialdehydes

The procedure was identical with that for the preparation of pyrrole-2-carbothialdehydes, except that the mixture was heated for 2 hours at 80°C instead of $\frac{1}{2}$ hour at room temperature. The following pyrrole-3-carbothialdehydes were prepared.

1,2,5-Dimethylpyrrole-3-carbothialdehyde (9a)

1,2,5-Trimethylpyrrole (1.092 g) gave a carbothialdehyde which was thermally labile, therefore the following method was adopted for purification. The residue was dissolved in cold acetone (25 ml), then cold cyclohexane (100 ml) was added and the solution filtered. The acetone was evaporated at room temperature until crystals appeared. Filtration gave the carbothialdehyde (9a) (1.005 g, 66%), orange microneedles, m.p. 123-125°C.

Found: C, 62.8%; H, 7.3%; N, 9.0%.

$C_8H_{11}NS$ requires: C, 62.7%; H, 7.2%; N, 9.1%.

^1H NMR - see Appendix A, Table 2.

^{13}C NMR - see Appendix A, Table 1.

2,5-Dimethylpyrrole-3-carbothialdehyde (9b)

2,5-Dimethylpyrrole (0.951 g) gave a carbothialdehyde which was insoluble in ether, therefore the following method was adopted for the work-up and subsequent purification. The sodium hydrogen sulphide mixture was filtered and the resulting brown solid was washed with water (4 x 50 ml) and dried before being extracted with hot benzene (5 x 50 ml). The extracts were evaporated and the resulting yellow solid recrystallised to give the carbothialdehyde (9b) (0.574 g, 41%), yellow needles from carbon tetrachloride, m.p. 144-145°C.

Found: C, 60.6%; H, 6.7%; N, 10.1%.

C_7H_9NS requires: C, 60.4%; H, 6.5%; N, 10.1%.

^1H NMR - see Appendix A, Table 2.

^{13}C NMR - see Appendix A, Table 1.

C. PREPARATION OF METAL COMPLEXES OF PYRROLE-2-CARBOTHIALDEHYDES (METAL = Co, Ni, Cu, Zn, Pd, Cd)

Different methods were employed depending on the metal used. For the preparation of metal complexes of pyrrole-2-carbothialdehyde see page 80.

The pyrrole-2-carbothialdehydes were prepared by the method given on page 96.

1. Preparation of Nickel, Zinc and Cadmium Complexes of Pyrrole-2-carbothialdehydes

General Method

A filtered solution of the metal acetate (5 mmol; nickel (II) acetate, 1.24 g; zinc (II) acetate, 1.098 g; cadmium (II) acetate, 1.333 g) in methanol (10 ml) was added to a stirred solution of the pyrrole-2-carbothialdehyde (5 mmol)* in methanol (10 ml). The resulting mixture was stirred for 2 minutes, then filtered, and the resulting crystals were washed with methanol (2 ml), dried and recrystallised.

The following nickel complexes were prepared.

bis(5-Methylpyrrole-2-carbothialdehydato)Ni(II), (20a) (0.348 g, 45%), black sheets from n-hexane, m.p. 160-161°C.

Found: C, 46.9%; H, 4.2%; N, 9.2%.

$C_{12}H_{12}N_2S_2Ni$ requires: C, 46.9%; H, 3.9%; N, 9.1%.

^{1}H NMR - see Appendix A, Table 3.

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[*] Footnote: 5-methylpyrrole-2-carbothialdehyde, 0.626 g;
3,5-dimethylpyrrole-2-carbothialdehyde, 0.696 g;
4,5-dimethylpyrrole-2-carbothialdehyde, 0.696 g;
3,5-dimethyl-4-ethylpyrrole-2-carbothialdehyde, 0.836 g;
3,4-dimethylpyrrole-2-carbothialdehyde, 0.696 g.

bis(4,5-Dimethylpyrrole-2-carbothialdehydato)Ni(II), (20b) (0.481 g, 57%), brown prisms with a metallic lustre from n-hexane, m.p. 167-169°C.

Found: C, 50.0%; H, 4.7%; N, 8.3%.

$C_{14}H_{16}N_2S_2Ni$ requires: C, 50.2%; H, 4.8%; N, 8.4%.

^1H NMR - see Appendix A, Table 3.

bis(3,5-Dimethylpyrrole-2-carbothialdehydato)Ni(II), (20c) (0.457 g, 55%), black needles with a metallic lustre from n-hexane, m.p. 170-171°C.

Found: C, 49.9%; H, 5.0%; N, 8.2%.

$C_{14}H_{16}N_2S_2NI$ requires: C, 50.2%; H, 4.8%; N, 8.4%.

^1H NMR - see Appendix A, Table 3.

bis(3,4-Dimethylpyrrole-2-carbothialdehydato)Ni(II), (20d) (0.413 g, 49%), lustrous green prisms from benzene, m.p. 225°C (grad.decomp.).

Found: C, 50.0%; H, 4.8%; N, 8.2%.

$C_{14}H_{16}N_2S_2Ni$ requires: C, 50.2%; H, 4.8%; N, 8.4%.

^1H NMR - see Appendix A, Table 3.

bis(3,5-Dimethyl-4-ethylpyrrole-2-carbothialdehydato)Ni(II), (20e) (0.637 g, 64%), black prisms with a green cast from n-hexane, m.p. 196-198°C.

Found: C, 55.4%; H, 6.3%; N, 7.2%.

$C_{18}H_{24}N_2S_2Ni$ requires: C, 55.3%; H, 6.2%; N, 7.2%.

^1H NMR - see Appendix A, Table 3.

The following cadmium complexes were prepared.

bis(5-Methylpyrrole-2-carbothialdehydato)Cd(II), (23a) (0.532 g, 59%), yellow needles from cyclohexane, m.p. 165°C (grad. decomp.).

Found: C, 39.9%; H, 3.1%; N, 7.6%.

$C_{12}H_{12}N_2S_2Cd$ requires: C, 39.9%; H, 3.3%; N, 7.8%.

^1H NMR - see Appendix A, Table 5.

bis(4,5-Dimethylpyrrole-2-carbothialdehydato)Cd(II), (23b) (0.716 g, 74%), yellow needles from benzene, m.p. 136°C (grad. decomp.).

Found: C, 43.0%; H, 4.2%; N, 7.0%.

$C_{14}H_{16}N_2S_2Cd$ requires: C, 43.2%; H, 4.1%; N, 7.2%.

^1H NMR - see Appendix A, Table 5.

bis(3,5-Dimethylpyrrole-2-carbothialdehydato)Cd(II), (23c) (0.722 g, 77%), yellow needles from benzene, m.p. 171°C (grad. decomp.).

Found: C, 43.0%; H, 4.1%; N, 7.0%.

$C_{14}H_{16}N_2S_2Cd$ requires: C, 43.2%; H, 4.1%; N, 7.2%.

^1H NMR - see Appendix A, Table 5.

bis(3,4-Dimethylpyrrole-2-carbothialdehydato)Cd(II), (23d) (0.457 g, 47%), yellow needles from carbon tetrachloride, m.p. 156°C (decomp.).

Found: C, 42.9%; H, 4.2%; N, 7.3%.

$C_{14}H_{16}N_2S_2Cd$ requires: C, 43.2%; H, 4.1%; N, 7.2%.

^1H NMR - see Appendix A, Table 5.

bis(3,5-Dimethyl-4-ethylpyrrole-2-carbothialdehydato)Cd(II), (23e) (0.714 g, 64%), golden yellow needles from cyclohexane, m.p. 155°C (grad. decomp.).

Found: C, 48.6%; H, 5.4%; N, 6.3%.

$C_{18}H_{24}N_2S_2Cd$ requires: C, 48.9%; H, 5.5%; N, 6.3%.

^{1}H NMR - see Appendix A, Table 5.

The following zinc complexes were prepared.

bis(5-Methylpyrrole-2-carbothialdehydato)Zn(II), (22a) (0.347 g, 44%), yellow prisms from n-hexane, m.p. 159-160°C.

Found: C, 46.2%; H, 3.8%; N, 9.0%.

$C_{12}H_{12}N_2S_2Zn$ requires: C, 45.9%; H, 3.9%; N, 8.9%.

^{1}H NMR - see Appendix A, Table 6.

bis(4,5-Dimethylpyrrole-2-carbothialdehydato)Zn(II), (22b) (0.623 g, 73%), bright yellow prisms from cyclohexane, m.p. 148-149°C (decomp.).

Found: C, 49.3%; H, 4.9%; N, 8.3%.

$C_{14}H_{16}N_2S_2Zn$ requires: C, 49.2%; H, 4.7%; N, 8.2%.

^{1}H NMR - see Appendix A, Table 6.

bis(3,5-Dimethylpyrrole-2-carbothialdehydato)Zn(II), (22c) (0.298 g, 35%), yellow prisms from cyclohexane, m.p. 174-175°C.

Found: C, 49.0%; H, 4.7%; N, 8.0%.

$C_{14}H_{16}N_2S_2Zn$ requires: C, 49.2%; H, 4.7%; N, 8.2%.

^{1}H NMR - see Appendix A, Table 6.

bis(3,4-Dimethylpyrrole-2-carbothialdehydato)Zn(II), (22d) (0.647 g, 76%), yellow prisms from cyclohexane, m.p. 124°C (grad. decomp.).

Found: C, 49.0%; H, 4.7%; N, 8.0%.

$C_{14}H_{16}N_2S_2Zn$ requires: C, 49.2%; H, 4.7%; N, 8.2%.

^{1}H NMR - see Appendix A, Table 6.

bis(3,5-Dimethyl-4-ethylpyrrole-2-carbothialdehydato)Zn(II), (22e) (0.437 g, 44%), yellow prisms from cyclohexane, m.p. 183-184°C.

Found: C, 54.1%; H, 6.1%; N, 6.9%.

$C_{18}H_{24}N_2S_2Zn$ requires: C, 54.3%; H, 6.1%; N, 7.0%.

^1H NMR - see Appendix A, Table 6.

2) Preparation of Copper Complexes of Pyrrole-2-carbothialdehydes

General Method

A filtered solution of the copper(II) acetate (5 mmol, 0.998 g) in ethanol (30 ml) was added to a stirred solution of the pyrrole-2-carbothialdehyde (5 mmol, see footnote, page 85) in ethanol (20 ml). The resulting mixture was stirred for 5 minutes then evaporated to dryness. The residue, dissolved in a minimum volume of benzene, was chromatographed on alumina (5 x 3 cm) with benzene as eluant. The brown eluates were collected and evaporated and the residue was recrystallised.

The following copper complexes were prepared.

bis(5-Methylpyrrole-2-carbothialdehydato)Cu(II), (21a) (0.405 g, 52%), black prisms from cyclohexane, m.p. 137-139°C .

Found: C, 46.3%; H, 3.7%; N, 8.8%.

$C_{12}H_{12}N_2S_2Cu$ requires: C, 46.2%; H, 3.9%; N, 9.0%.

bis(4,5-Dimethylpyrrole-2-carbothialdehydato)Cu(II), (21b) (0.427 g, 50%), black prisms with a metallic reflex from n-hexane, m.p. 130-132°C.

Found: C, 49.4%; H, 4.9%; N, 8.2%.

$C_{14}H_{16}N_2S_2Cu$ requires: C, 49.5%; H, 4.7%; N, 8.2%.

bis(3,5-Dimethylpyrrole-2-carbothialdehydato)Cu(II), (21c) (0.493 g, 58%), dark blue needles from n-hexane, m.p. 140-141°C.

Found: C, 49.2%; H, 4.9%; N, 8.1%.

$C_{14}H_{16}N_2S_2Cu$ requires: C, 49.5%; H, 4.8%; N, 8.2%.

bis(3,4-Dimethylpyrrole-2-carbothialdehydato)Cu(II), (21d) (0.703 g, 83%), black prisms from benzene, m.p. 156-158°C.

Found: C, 49.4%; H, 4.7%; N, 8.2%.

$C_{14}H_{16}N_2S_2Cu$ requires: C, 49.5%; H, 4.7%; N, 8.2%.

bis(3,4-Dimethyl-4-ethylpyrrole-2-carbothialdehydato)Cu(II), (21e) (0.457 g, 46%), navy blue needles from n-hexane, m.p. 136-138°C.

Found: C, 54.7%; H, 5.8%; N, 7.2%; S, 16.1%.

$C_{18}H_{24}N_2S_2Cu$ requires: C, 54.6%; H, 6.1%; N, 7.1%; S, 16.2%.

3) Preparation of Palladium Complexes of Pyrrole-2-carbothialdehydes

General Method

A filtered solution of palladium (II) acetate (5 mmol, 1.222 g) in methanol (20 ml) was added to a stirred solution of the pyrrole-2-carbothialdehyde (5 mmol, see footnote, page 85) in methanol (10 ml). The resulting mixture was stirred for 5 minutes then evaporated to dryness. The residue, dissolved in a minimum volume of benzene, was chromatographed on alumina (15 x 3 cm), with benzene as eluant. The orange eluates were collected and evaporated, and the residue was recrystallised.

The following palladium complexes were prepared.

bis(5-Methylpyrrole-2-carbothialdehydato)Pd(II), (19a) (0.502 g, 57%), orange needles from cyclohexane, m.p. 145-146°C.

Found: C, 40.9%; H, 3.5%; N, 7.7%.

$C_{12}H_{12}N_2S_2Pd$ requires: C, 40.6%; H, 3.4%; N, 7.9%.

^{1}H NMR - see Appendix A, Table 4.

bis(4,5-Dimethylpyrrole-2-carbothialdehydato)Pd(II), (19b) (0.704 g, 74%), orange plates from benzene, m.p. 199-201°C.

Found: C, 44.2%; H, 4.1%; N, 7.2%.

$C_{14}H_{16}N_2S_2Pd$ requires: C, 43.9%; H, 4.2%; N, 7.3%.

^{1}H NMR - see Appendix A, Table 4.

bis(3,5-Dimethylpyrrole-2-carbothialdehydato)Pd(II), (19c) (0.631 g, 66%), orange prisms from benzene, m.p. 230°C (grad. decomp.)

Found: C, 43.8%; H, 4.3%; N, 7.3%; S, 16.8%.

$C_{14}H_{16}N_2S_2Pd$ requires: C, 43.9%; H, 4.2%; N, 7.3%; S, 16.5%.

^{1}H NMR - see Appendix A, Table 4.

bis(3,4-Dimethylpyrrole-3-carbothialdehydato)Pd(II), (19d) (0.518 g, 54%), orange prisms from benzene, m.p. 260°C (decomp.).

Found: C, 44.1%; H, 4.3%; N, 7.1%.

$C_{14}H_{16}N_2S_2Pd$ requires: C, 43.9%; H, 4.2%; N, 7.3%.

^{1}H NMR - see Appendix A, Table 4.

bis(3,5-Dimethyl-4-ethylpyrrole-2-carbothialdehydato)Pd(II), (19e) (0.655 g, 60%), orange prisms from cyclohexane, m.p. 221-222.5°C.

Found: C, 49.3%; H, 5.3%; N, 6.1%.

$C_{18}H_{24}N_2S_2Pd$ requires: C, 49.3%; H, 5.5%; N, 6.4%.

^{1}H NMR - see Appendix A, Table 4.

4. Preparation of Cobalt Complexes of Pyrrole-2-carbothialdehydes

General Method

A filtered solution of cobalt(II) acetate (5 mmol, 1.245 g) in methanol (10 ml) was added to a stirred solution of the pyrrole-2-carbothialdehyde (5 mmol, see footnote, page 85) in methanol (10 ml). The resulting mixture was stirred for 10 minutes then evaporated. Tlc of the reaction mixture before evaporation showed the presence of two products. The residue, dissolved in a minimum volume of benzene, was chromatographed on alumina (details for each reaction are given in the text).

The following cobalt complexes were prepared.

mer-tris(5-Methylpyrrole-2-carbothialdehydato)Co(III) (25a)

The residue was chromatographed on alumina (30 x 2.6 cm). Elution with petrol:benzene (1:1) gave brown eluates which afforded the complex (25a), (0.396 g, 55%), black prisms with a metallic lustre from n-hexane, m.p. 165-167°C.

Found: C, 50.2%; H, 4.2%; N, 9.9%.

$C_{18}H_{18}N_3S_3Co$ requires: C, 50.0%; H, 4.2%; N, 9.7%.

^{1}H NMR - see Appendix A, Table 7.

Further elution of the column with benzene then ether gave no useful material.

mer-tris(3, 5-Dimethylpyrrole-2-carbothialdehydato)Co(III) (25c)

The residue was chromatographed on alumina (40 x 2.6 cm). Elution with benzene:petrol (1:1) gave brown eluates which afforded the complex (25c), (0.542 g, 69%), black lustrous prisms from n-hexane, m.p. 230°C (grad. decomp.).

Found: C, 53.0%; H, 4.9%; N, 8.9%; S, 20.1%.

$C_{21}H_{24}N_3S_3Co$ requires: C, 53.3%; H, 5.1%; N, 8.9%; S, 20.3%.

^1H NMR - see Appendix A, Table 7.

Further elution of the column with benzene then ether gave no useful material.

mer-tris(3, 4-Dimethylpyrrole-2-carbothialdehydato)Co(III) (25d)

The residue was chromatographed on alumina (30 x 2.6 cm). Elution with benzene gave brown eluates which afforded the complex (25d), (0.513 g, 65%), black lustrous prisms from cyclohexane, m.p. 231°C (grad. decomp.).

Found: C, 53.4%; H, 5.2%; N, 8.7%.

$C_{21}H_{24}N_3S_3Co$ requires: C, 53.3%; H, 5.1%; N, 8.9%.

^1H NMR - see Appendix A, Table 7.

Further elution of the column with benzene then ether gave no useful material.

mer-tris(3, 5-Dimethyl-4-ethylpyrrole-2-carbothialdehydato)Co(III) (25e)

The residue was chromatographed on alumina (45 x 2.6 cm). Elution with petrol:benzene (2:1) gave brown eluates which afforded the complex (25e), (0.629 g, 68%), black prisms with a metallic lustre from n-hexane, m.p. 208°C (decomp.).

Found: C, 58.0%; H, 6.7%; N, 7.5%.

$C_{27}H_{36}N_3S_3Co$ requires: C, 58.2%; H, 6.5%; N, 7.5%.

^{1}H NMR - see Appendix A, Table 7.

Further elution of the column with benzene then ether gave no useful material.

mer-tris(4,5-Dimethylpyrrole-2-carbothialdehydato)Co(III) (25b) and fac-tris(4,5-Dimethylpyrrole-2-carbothialdehydato)Co(III) (25b')

The residue was chromatographed on alumina (40 x 2.6 cm). Elution with petrol:benzene (1:1) gave brown eluates which afforded the complex (25b), (0.618 g, 78%), clusters of black prisms with a metallic lustre from n-hexane, m.p. 166-168°C.

Found: C, 53.2%; H, 5.3%; N, 9.0%.

$C_{21}H_{24}N_3S_3Co$ requires: C, 53.3%; H, 5.1%; N, 8.9%.

^{1}H NMR - see Appendix A, Table 7.

Further elution with benzene:petrol (3:2) gave brown eluates which afforded the complex (25b'), (0.024 g, 3%), dark blue spars from cyclohexane, m.p. 243-245°C.

Found: C, 53.5%; H, 5.2%; N, 8.9%

$C_{21}H_{24}N_3S_3Co$ requires: C, 53.3%; H, 5.1%; N, 8.9%.

^{1}H NMR - see Appendix A, Table 7.

5. Isomerisation of mer-tris(4,5-dimethylpyrrole-2-carbothialdehydato)Co(III) (25b)

A solution of mer-tris(4,5-dimethylpyrrole-2-carbothialdehydato)Co(III) (1 mmol, 0.474 g) in toluene (50 ml) was heated at reflux for 3 hours. Tlc of the reaction mixture after this time showed two spots. The toluene was evaporated and the resulting residue chromatographed on alumina (40 x 2.6 cm). Elution with benzene:petrol (1:1) gave brown eluates which afforded the starting material (25b), (0.248 g, 52%). This was shown by tlc and ^{1}H nmr to be identical with an authentic sample of complex (25b) previously prepared. Further elution with benzene:petrol (3:2) gave brown eluates which afforded fac-tris(4,5-dimethylpyrrole-2-carbothialdehydato)Co(III) (25b'), (0.201 g, 43%). This was shown by tlc and ^{1}H nmr to be identical with an authentic sample of complex (25b') previously prepared. The ratio by weight of the fac isomer to mer isomer was 1:1.2 .

The experiment was repeated with another sample of complex (25b), (1 mmol, 0.474 g) in toluene (50 ml). Except in this case the solution was heated at reflux for 6 hours instead of 3 hours. Tlc of the mixture after this time again showed two spots. The toluene was evaporated and the resulting residue chromatographed on alumina (40 x 2.6 cm). Elution with benzene:petrol (1:1) gave brown eluates which afforded the starting material (25b), (0.239 g, 51%). Further elution with benzene:petrol (3:2) gave brown eluates which afforded fac-tris(4,5-dimethylpyrrole-2-carbothialdehydato)Co(III) (25b'), (0.193 g, 41%). The ratio by weight of the fac isomer to mer isomer in this case was 1:1.2 .

6. Preparation of the Metal Complexes of Pyrrole-2-carbothialdehyde

M = Co, Ni, Cu, Zn, Pd, Cd

General Method

A solution of pyrrole (0.336 g, 5 mmol) in dimethylformamide (5 ml) was added dropwise over a period of 10 minutes to a stirred solution of phosphorus oxychloride (0.5 ml, 5.5 mmol) in dimethylformamide (5 ml). The resulting solution was stirred at room temperature for 30 minutes, then poured into aqueous 2M-sodium hydrogen sulphide (25 ml). The mixture was diluted with water (100 ml) before being extracted with ether (2 x 50 ml). The extracts were washed with water (6 x 100 ml). To these extracts was added a solution of the metal acetate [5 mmol, nickel (II) acetate, 1.24 g; zinc (II) acetate, 1.098 g; cadmium (II) acetate, 1.333 g; cobalt (II) acetate, 1.245 g; in methanol (50 ml), 5 mmol, copper (II) acetate, 0.998 g in ethanol (50 ml)]. The resulting mixture was stirred for 2 minutes then evaporated. The residue was then chromatographed on alumina, details are given for each reaction.

bis(Pyrrole-2-carbothialdehydato)Ni(II) (38b)

The residue was chromatographed on alumina (20 x 2.2 cm). Elution with benzene gave purple eluates which afforded the complex (38b), (0.321 g, 46%), brown prisms with a metallic lustre from cyclohexane, m.p. 196-198°C.

Found: C, 43.2%; H, 3.0%; N, 10.3%.

$C_{10}H_8N_2S_2Ni$ requires: C, 43.1%; H, 2.9%; N, 10.1%.

^1H NMR - see Appendix A, Table 3.

bis(Pyrrole-2-carbothialdehydato)Pd(II) (38c)

The residue was chromatographed on alumina (10 x 2.2 cm). Elution with benzene gave orange eluates which afforded the complex (38c), (0.181 g, 22%), dark orange needles from cyclohexane, m.p. 165°C (grad.decomp.).

Found: C, 36.9%; H, 2.5%; N, 8.3%.

$C_{10}H_8N_2S_2Pd$ requires: C, 36.8%; H, 2.5%; N, 8.6%.

^{1}H NMR - see Appendix A, Table 4.

mer-tris(Pyrrole-2-carbothialdehydato)Co(III) (38a)

The residue was chromatographed on alumina (30 x 2.2 cm). Elution with petrol:benzene (2:1) gave brown eluates which afforded the complex (38a), (0.276 g, 43%), deep red needles with a blue metallic lustre from n-hexane, m.p. 242-245°C.

Found: C, 46.4%; H, 3.0%; N, 10.7%.

$C_{15}H_{12}N_3S_3Co$ requires: C, 46.3%; H, 3.1%; N, 10.8%.

^{1}H NMR - see Appendix A, Table 7.

bis(Pyrrole-2-carbothialdehydato)Cu(II) (38d)

The residue was chromatographed on alumina (5 x 2.2 cm). Elution with benzene gave brown eluates which afforded the complex (38d), (0.329 g, 46%), brown needles from cyclohexane, m.p. 120°C (grad. decomp.).

Found: C, 42.5%; H, 2.9%; N, 9.8%.

$C_{10}H_{18}N_2S_2Cu$ requires: C, 42.3%; H, 2.8%; N, 9.9%.

Attempted Preparation of bis(pyrrole-2-carbothialdehydato)Zn(II) (38f)

Pyrrole-2-carbothialdehyde was prepared by the general method (page 96). Zinc (II) acetate (5 mmol, 1.098 g) in methanol (50 ml) was added to the ether extracts of pyrrole-2-carbothialdehyde. The initial yellow colour produced faded rapidly (1-2 mins) leaving a dark, almost black, solution. Tlc of the reaction mixture after this time showed neither starting material nor product. The experiment was abandoned at this stage.

Attempted Preparation of bis(pyrrole-2-carbothialdehydato)Cd(II) (38e)

Pyrrole-2-carbothialdehyde was prepared by the general method (page 96). Cadmium (II) acetate (5 mmol, 1.333 g) in methanol (50 ml) was added to the ether extracts of pyrrole-2-carbothialdehyde. The initial yellow colour produced faded rapidly (1-2 mins) leaving a dark, almost black, solution. Tlc of the reaction mixture after this time showed neither starting material nor product. The experiment was abandoned at this stage.

D. PREPARATION OF TETRAETHYLAMMONIUM PENTACARBONYL-IODOMETALLATES

Tungsten hexacarbonyl, chromium hexacarbonyl and molybdenum hexacarbonyl were purchased from Strem Chemical Co. Ltd. Molybdenum hexacarbonyl obtained from other sources was found to be contaminated with tungsten hexacarbonyl.

The method given below is essentially that of Abel, Butler and Reid[109].

General Method

Equimolar quantities of the metal hexacarbonyl (20 mmol) and tetraethylammonium iodide (5.143 g, 20 mmol) were heated together in boiling n-butanol (100 ml) under argon for a specified time. Metal hexacarbonyl which sublimed up the condenser was periodically pushed back into the flask using a glass rod. The cooled solution was filtered and the resulting yellow crystals were washed with n-hexane (8 x 50 ml), then dried *in vacuo*. For complete purification, a solution of the crystals in cold acetone was filtered, n-hexane added then cooled in a refrigerator until crystallisation was complete.

Tetraethylammonium Pentacarbonyliodochromate (0), (31b)

Chromium hexacarbonyl (4.401 g, 20 mmol) gave, after 3 hours, the chromate (31b),(6.4 g, 71%), yellow microprisms from acetone (60 ml) and n-hexane (100 ml), m.p. 112-124°C (decomp.).

Found:	C, 34.8%; H, 4.5%; N, 3.1%.
$C_{13}H_{20}CrINO_5$ requires:	C, 34.5%; H, 4.4%; N, 3.0%.

^{1}H NMR - see Appendix A, Table 8.

IR - see Appendix B, Table 5.

Tetraethylammonium Pentacarbonyliodomolybdate (0), (31c)

Molybdenum hexacarbonyl (5.280 g, 20 mmol) gave, after $1\frac{1}{2}$ hours, the molybdate (31c), (8.5 g, 87%), pale yellow microprisms from acetone, (100 ml) and n-hexane (200 ml), m.p. 105-110°C (decomp.).

Found: C, 31.7%; H, 4.1%; N, 2.8%.

$C_{13}H_{20}IMoNO_5$ requires: C, 31.8%; H, 4.2%; N, 2.9%.

^{1}H NMR - see Appendix A, Table 8.

IR - see Appendix B, Table 5.

Tetraethylammonium Pentacarbonyliodotungstate (0), (31a)

Tungsten hexacarbonyl (7.038 g, 20 mmol) gave, after $1\frac{1}{2}$ hours, the tungstate (31a), (10.6 g, 91%), lemon microprisms from acetone (75 ml) and n-hexane (150 ml), m.p. 136-142°C (decomp.)

Found: C, 26.9%; H, 3.5%; N, 2.4%.

$C_{13}H_{20}INO_5W$ requires: C, 26.8%; H, 3.4%; N, 2.3%.

^{1}H NMR - see Appendix A, Table 8.

IR - see Appendix B, Table 5.

E. PREPARATION OF PENTACARBONYL(PYRROLE CARBOTHIALDEHYDE)TUNGSTEN(O) COMPLEXES

The pyrrole carbothialdehydes were prepared by the methods given on page 80.

General Method

Tetraethylammonium pentacarbonyliodotungstate (0) (1.278 g, 2.2 mmol) was added to a solution of the pyrrole carbothialdehyde (2 mmol) in methylene chloride (100 ml), then stirred at room temperature for 5 minutes, by which time the mixture was homogeneous. In each reaction, tlc showed that a trace of the product had formed. 0.1M- Aqueous silver nitrate (25 ml, 2.5 mmol) was added to the vigorously stirred solution and the resulting mixture was stirred for 5 minutes. The mixture was then filtered through Hyflo Super-Cel with the aid of more methylene chloride (2 x 50 ml). The organic layer was separated, washed with water (2 x 100 ml), dried and evaporated. The residue, dissolved in the minimum volume of benzene, was chromatographed on silica and the red or purple eluates collected, evaporated, and the residue recrystallised. The following complexes were prepared.

Pentacarbonyl(4,5-dimethylpyrrole-2-carbothialdehyde-S)tungsten (0),(33a)

4,5-Dimethylpyrrole-2-carbothialdehyde (0.278 g) was used. The residue was chromatographed on silica (20 x 2.6 cm). Elution with benzene gave purple eluates which afforded the complex (33a), (0.703 g, 76%), deep blue prisms with a green lustre from cyclohexane, m.p. 107-110°C (decomp.).

Found: C, 31.0%; H, 1.9%; N, 3.0%.

$C_{12}H_9NO_5SW$ requires: C, 31.1%; H, 2.0%; N, 3.0%.

^{1}H NMR - see Appendix A, Table 9.

IR - see Appendix B, Table 1.

Pentacarbonyl(3,5-dimethylpyrrole-2-carbothialdehyde-S)tungsten (0), (33b)

3,5-Dimethylpyrrole-2-carbothialdehyde (0.278 g) was used. The residue was chromatographed on silica (30 x 2.6 cm). Elution with benzene:petrol (1:1) gave purple eluates which afforded the complex (33b), (0.750 g, 81%), maroon spars with a green lustre from benzene (20 ml) and n-hexane (100 ml), m.p. 131°C (grad.decomp.).

Found: C, 31.1%; H, 1.9%; N, 2.9%.

$C_{12}H_9NO_5SW$ requires: C, 31.1%; H, 2.0%; N, 3.0%.

^{1}H NMR - see Appendix A, Table 9.

IR - see Appendix B, Table 1.

Pentacarbonyl(1,2,5-trimethylpyrrole-3-carbothialdehyde-S)tungsten (0), (34a)

1,2,5-Trimethylpyrrole-3-carbothialdehyde (0.306 g) was used. The residue was chromatographed on silica (30 x 2.6 cm). Elution with benzene gave red eluates which afforded the complex (34a), (0.837 g, 88%), dark red lustrous prisms from methylene chloride (4 ml) and n-hexane (60 ml), m.p. 136-140°C (decomp.).

Found: C, 32.9%; H, 2.3%; N, 2.9%.

$C_{13}H_{11}NO_5SW$ requires: C, 32.7%; H, 2.3%; N, 2.9%.

^{1}H NMR - see Appendix A, Table 9.

IR - see Appendix B, Table 1.

Pentacarbonyl(2,5-dimethylpyrrole-3-carbothialdehyde-S)tungsten (0),(34b)

2,5-Dimethylpyrrole-3-carbothialdehyde (0.278 g) was used. The residue was chromatographed on silica (25 x 2.6 cm). Elution with benzene gave red eluates which afforded the complex (34b), (0.553 g, 60%), red microneedles from methylene chloride (4 ml) and n-hexane (50 ml), m.p. 121-125°C (decomp.).

Found:	C, 31.2%;	H, 1.8%;	N, 2.9%.
$C_{12}H_9NO_5SW$ requires:	C, 31.1%;	H, 2.0%;	N, 3.0%.

^{1}H NMR - see Appendix A, Table 9.

IR - see Appendix B, Table 1.

Pentacarbonyl(pyrrole-2-carbothialdehyde-S)tungsten (0), (40)

As pyrrole-2-carbothialdehyde is unstable the following method was adopted for the preparation of its pentacarbonyl tungsten complex.

A solution of pyrrole (0.336 g, 5 mmol) in dimethylformamide (5 ml) was added dropwise over a period of ten minutes to a stirred solution of phosphorus oxychloride (0.5 ml, 5.5 mmol) in dimethylformamide (5 ml). The resulting solution was stirred at room temperature for 30 minutes, then poured into aqueous 2M-sodium hydrogen sulphide (25 ml). The mixture was diluted with water (100 ml) before being extracted with benzene (2 x 50 ml). The extracts were washed with water (2 x 100 ml). A solution of tetraethylammonium iodopentacarbonyltungstate (0) (3.196 g, 5.5 mmol) in dimethylformamide (10 ml) was added to the benzene extracts followed by 0.1M-aqueous silver nitrate (62.5 ml, 6.25 mmol) and the resulting mixture stirred at room temperature for 5 minutes. The mixture was then filtered through Hyflo Super-Cel with the aid of more benzene (2 x 100 ml). The organic layer was separated, washed with water (6 x 100 ml), dried and evaporated. The residue, dissolved in benzene, was chromatographed on silica (40 x 2.6 cm). Elution with petrol:benzene (4:1) gave purple eluates which afforded the complex (40), (0.234 g, 11%), deep red prisms with a green lustre from benzene (5 ml) and n-hexane (30 ml), m.p. 96-99°C (decomp.).

Found:	C, 27.7%;	H, 1.0%;	N, 3.1%.
$C_{10}H_5NSO_5W$ requires:	C, 27.6%;	H, 1.2%;	N, 3.2%.

^{1}H NMR - see Appendix A, Table 9.

IR - see Appendix B, Table 1.

F. PREPARATION OF PENTACARBONYL(INDOLIZINE CARBOTHIALDEHYDE)TUNGSTEN(O) COMPLEXES

2-Methylindolizine-3-carbothialdehyde and 1,2-dimethylindolizine-3-carbothialdehyde were prepared by the method of McKenzie and Reid[109].

General Method

Tetraethylammonium pentacarbonyliodotungstate (0) (1.278 g, 2.2 mmol) was added to a solution of the indolizine carbothialdehyde (2 mmol) in methylene chloride (100 ml), then stirred at room temperature for 5 minutes, by which time the solution was homogeneous. In each reaction tlc showed that a trace of the product had formed. 0.1M- Aqueous silver nitrate (25 ml, 2.5 mmol) was added to the vigorously stirred solution and the resulting mixture was stirred for 5 minutes. The mixture was then filtered through Hyflo Super-Cel with the aid of more methylene chloride (2 x 50 ml). The organic layer was separated, washed with water (2 x 100 ml), dried and evaporated. The residue, dissolved in the minimum volume of benzene, was chromatographed on silica (25 x 2.6 cm) with benzene as eluant. The purple eluates were collected and evaporated, and the residue was recrystallised.

Pentacarbonyl(1,2-dimethylindolizine-3-carbothialdehyde-S)tungsten(0), (32b)

1,2-Dimethylindolizine-3-carbothialdehyde (0.378 g) gave the complex (32b),(0.828 g, 81%), black needles with a green reflex from cyclohexane, m.p. 150°C (grad. decomp.)

Found: C, 37.6%; H, 2.1%; N, 2.7%.

$C_{16}H_{11}NO_5SW$ requires: C, 37.4%; H, 2.2%; N, 2.7%.

^{1}H NMR - see Appendix A, Table 10.

IR - see Appendix B, Table 3.

Pentacarbonyl(2-methylindolizine-3-carbothialdehyde-S)tungsten (0), (32a)

2-Methylindolizine-3-carbothialdehyde (0.350 g) gave the complex (32a), (0.751 g, 75%), deep red spars with a green reflex from methylene chloride (10 ml) and n-hexane (110 ml), m.p. 147°C (grad. decomp.).

Found: C, 35.8%; H, 1.8%; N, 2.7%; S, 6.5%.

$C_{15}H_9NO_5SW$ requires: C, 36.1%; H, 1.8%; N, 2.8%; S, 6.4%.

^{1}H NMR - see Appendix A, Table 10.

IR - see Appendix B, Table 3.

G. PREPARATION OF PENTACARBONYL GROUP VIA METAL COMPLEXES OF 1,6,6a λ^4-TRITHIAPENTALENES

The following 1,6,6a λ^4-trithiapentalenes were prepared by the methods cited: 2-t-butyl-1,6,6a λ^4-trithiapentalene[111], 2,5-di-t-butyl-1,6,6a λ^4trithiapentalene[112], 2,5-dimethyl-1,6,6a λ^4-trithiapentalene[113], 4,5-dihydro-3H-benzo[c,d]1,6,6a λ^4-trithiapentalene[114] and 3,4,5,6-tetrahydrocyclohepta[c,d]1,6,6a λ^4-trithiapentalene[115].

Different methods were employed depending on the metal used.

General Method

The tetraethylammonium pentacarbonyliodometallate (0) (2.2 mmol) was added to a solution of the 1,6,6a λ^4-trithiapentalene (2 mmol) in methylene chloride (80 ml) under argon, then stirred at room temperature for 5 minutes, by which time the mixture was homogeneous. In each reaction, tlc showed that a trace of the product had formed. 0.25M-Aqueous silver nitrate (8.8 ml, 2.2 mmol) was added to the vigorously stirred solution and the resulting mixture was stirred for a specified time. The mixture was chromatographed directly on silica (20 x 2.6 cm), with benzene as eluant. The blue eluates were collected and evaporated, and the residue was recrystallised.

1. Preparation of Pentacarbonyl(1, 6, 6a λ^4-trithiapentalene)tungsten(0) Complexes

In every case tetraethylammonium pentacarbonyliodotungstate (0) (1.278 g) was used and a reaction time of 15 minutes was employed.

Pentacarbonyl[2-(5-t-butyl-3*H*-1,2-dithiole-3-ylidene)ethanethial-*S*]-tungsten (0), (42d)

2-t-Butyl-1, 6, 6a λ^4-trithiapentalene (0.433 g) gave the complex (42d), (0.882 g, 82%), black prisms with a metallic lustre from benzene (12 ml) and n-hexane (90 ml), m.p. 126°C (grad.decomp.).

Found: C, 31.1%; H, 2.2%

$C_{14}H_{12}O_5S_3W$ requires: C, 31.1%; H, 2.2%

^{1}H NMR - see Appendix A, Table 11.

IR - see Appendix B, Table 4.

uv spectrum - λ_{max}(cyclohexane) 638 (log ε 4.22), 410 sh (3.50), 374(3.74), 329(3.78), and 245 nm (4.88)

Pentacarbonyl[1-(5-methyl-3*H*-1,2-dithiole-3-ylidene)propan-2-thione-*S*]tungsten (0), (42c)

2,5-Dimethyl-1,6,6a λ^4-trithiapentalene (0.377 g) gave the complex (42c), (0.768 g, 75%), dark blue prisms with a bronze reflex from benzene (30 ml) and n-hexane (50 ml), m.p. 139°C (grad. decomp.).

Found: C, 28.0%; H, 1.6%

$C_{12}H_8O_5S_3W$ requires: C, 28.1%; H, 1.6%

^{1}H NMR - see Appendix A, Table 12.

IR - see Appendix B, Table 4.

uv spectrum - λ_{max}(cyclohexane) 602 (log ϵ 4.09), 400 sh (3.74), 366(3.79), 330(3.88), and 244 nm (4.83)

Pentacarbonyl(5,6-dihydro-4H-1,2-benzodithiole-7-carbothialdehyde-$\underline{S}^7$)tungsten (0), (42a)

4,5-Dihydro-3H-benzo[c,d]1,6,6a λ^4-trithiapentalene (0.401 g) gave the complex (42a), (0.882 g, 84%), purple-black spars with a bronze reflex from benzene (15 ml) and n-hexane (90 ml), m.p. 120°C (grad. decomp.).

Found: C, 29.6%; H, 1.5%; S, 18.3%.

$C_{13}H_8O_5S_3W$ requires: C, 29.8%; H, 1.5%; S, 18.4%.

^{1}H NMR - see Appendix A, Table 13.

IR - see Appendix B, Table 4.

uv spectrum - λ_{max} (cyclohexane) 648 (log ϵ 4.16), 424 (3.42), 374(3.65), 330(3.76), 247(4.85), and 220 sh nm (4.62).

Pentacarbonyl(4,5,6,7-tetrahydro-1,2-cycloheptodithiole-8-carbothialdehyde-$\underline{S}^8$)tungsten (0), (42b)

3,4,5,6-Tetrahydrocyclohepta[c,d]1,6,6a λ^4-trithiapentalene (0.429 g) gave the complex (42d), (0.911 g, 85%), blue-black prisms with a bronze reflex from benzene (10 ml) and n-hexane, (100 ml), m.p. 119-122°C (decomp.).

Found: C, 31.4%; H, 1.8%

$C_{14}H_{10}O_5S_3W$ requires: C, 31.2%; H, 1.9%

^{1}H NMR - see Appendix A, Table 14.

IR - see Appendix B, Table 4.

2. Preparation of Pentacarbonyl(1, 6, 6aλ^4-trithiapentalene)-chromium (0) Complexes

In every case tetraethylammonium pentacarbonyliodochromate (0) (0.988 g) was used and a reaction time of 15 minutes was employed.

Pentacarbonyl[2-(5-t-butyl-3*H*-1, 2-dithiole-3-ylidene)ethanethial-*S*]-chromium (0) (43d)

2-t-Butyl-1, 6, 6a λ^4-trithiapentalene (0.433 g) gave the complex (43d), (0.510 g, 62%), black spars with a bronze reflex from benzene (11 ml) and n-hexane (80 ml), m.p. 107°C (grad.decomp.).

Found: C, 40.9%; H, 2.8%

$C_{14}H_{12}O_5S_3Cr$ requires: C, 41.2%; H, 3.0%

^{1}H NMR - see Appendix A, Table 11.

IR - see Appendix B, Table 4.

Pentacarbonyl[1-(5-methyl-3*H*-1, 2-dithiole-3-ylidene)propan-2-thione-*S*]chromium (0), (43c)

2, 5-Dimethyl-1, 6, 6a λ^4-trithiapentalene (0.377 g) gave the complex (43c), (0.423 g, 56%), indigo needles from methylene chloride (30 ml) and n-hexane (50 ml), m.p. 108-110°C (decomp.).

Found: C, 38.0%; H, 2.1%

$C_{12}H_8O_5S_3Cr$ requires: C, 37.9%; H, 2.1%

^{1}H NMR - see Appendix A, Table 12.

IR - see Appendix B, Table 4.

Pentacarbonyl(5,6-dihydro-4*H*-1,2-benzodithiole-7-carbothialdehyde-*S*^{7})chromium (0), (43a)

4,5-Dihydro-3*H*-benzo[c,d]1,6,6a λ^4-trithiapentalene (0.401 g) gave the complex (43a), (0.413 g, 53%), black prisms with a bronze reflex from benzene (8 ml) and n-hexane (100 ml), m.p. 110°C (grad. decomp.).

Found: C, 39.9%; H, 2.0%

$C_{13}H_8O_5S_3Cr$ requires: C, 39.8%; H, 2.0%

^{1}H NMR - see Appendix A, Table 13.

IR - see Appendix B, Table 4.

Pentacarbonyl(4,5,6,7-tetrahydro-1,2-cycloheptodithiole-8-carbothialdehyde-*S*^{8})chromium (0),(43b)

3,4,5,6-Tetrahydrocyclohepta[c,d]1,6,6aλ^4-trithiapentalene (0.429 g) gave the complex (43b), (0.547 g, 67%), blue-black microprisms with a bronze reflex from benzene (10 ml) and n-hexane (100 ml), m.p. 107-110°C (decomp.).

Found: C, 41.5%; H, 2.5%

$C_{14}H_{10}O_5S_3Cr$ requires: C, 41.4%; H, 2.5%

^{1}H NMR - see Appendix A, Table 14.

IR - see Appendix B, Table 4.

3. Preparation of Pentacarbonyl(1, 6, 6a λ^4-trithiapentalene)-molybdenum (0) Complexes

The general method was used except that the residue, obtained by evaporation of the blue eluates, was washed repeatedly with portions of n-hexane (25 ml) until free of the trithiapentalene. In every case, tetraethylammonium pentacarbonyliodomolybdate (0) (1.085 g) was used and a reaction time of 5 minutes was employed.

Pentacarbonyl[2-(5-t-butyl-3H-1,2-dithiole-3-ylidene)ethanethial-S]molybdenum (0), (44d)

2-t-Butyl-1, 6, 6a λ^4-trithiapentalene (0.433 g) gave the complex (44d), (0.518 g, 57%), black prisms with a bronze reflex from benzene (10 ml) and n-hexane (80 ml), m.p. 99-101°C (decomp.).

Found: C, 37.1%; H, 2.7%

$C_{14}H_{12}O_5S_3Mo$ requires: C, 37.2%; H, 2.7%

^{1}H NMR - see Appendix A, Table 11.

Pentacarbonyl(5, 6-dihydro-4H-1, 2-benzodithiole-7-carbothialdehyde-S^7)molybdenum (0), (44a)

4, 5-Dihydro-3H-benzo[c, d]1, 6, 6a λ^4-trithiapentalene (0.401 g) gave the complex (44a), (0.421 g, 48%), black prisms with a bronze reflex from benzene (8 ml) and n-hexane (80 ml), m.p. 100-103°C (decomp.).

Found: C, 35.8%; H, 1.9%

$C_{13}H_8O_5S_3Mo$ requires: C, 35.8%; H, 1.8%

^{1}H NMR - see Appendix A, Table 13.

Attempted Preparation of Pentacarbonyl[1-(5-methyl-3H-1,2-dithiole-3-ylidene)propan-2-thione-S]molybdenum (0), (44c)

A pure product free from 2,5-dimethyl-1,6,6a λ^4-trithiapentalene could not be isolated.

Attempted Preparation of Pentacarbonyl(4,5,6,7-tetrahydro-1,2-cycloheptodithiole-8-carbothialdehyde-S^8)molybdenum (0), (44b)

A pure product free from 3,4,5,6-tetrahydrocyclohepta[c,d]-1,6,6a λ^4-trithiapentalene could not be isolated.

4. Attempted Preparation of Pentacarbonyl[1-(5-t-butyl-3H-1,2-dithiole-3-ylidene)3,3-dimethylbutan-2-thione-S]tungsten(0) (45)

Tetraethylammonium pentacarbonyliodotungstate (0) (2.2 mmol, 1.278 g) was added to a solution of 2,5-di-t-butyl-1,6,6a λ^4-trithiapentalene (2 mmol, 0.545 g) in methylene chloride (80 ml), under argon, then stirred at room temperature for 5 minutes, by which time the mixture was homogeneous. 0.25M-Aqueous silver nitrate (8.8 ml, 2.2 mmol) was added to the vigorously stirred solution and the resulting mixture was stirred for fifteen minutes. There was no blue colour produced after the addition of the silver nitrate. Tlc of the reaction mixture after 15 minutes showed only starting 1,6,6aλ4-trithiapentalene. The mixture was chromatographed directly on silica (20 x 2.6 cm). Elution with benzene gave orange eluates which afforded 2,5-di-t-butyl-1,6,6a λ^4-trithiapentalene, identical (^{1}H nmr, tlc) to an authentic sample (0.437 g, 80%). No other useful material was obtained.

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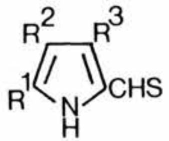
APPENDIX A : NMR DATA

Solutions were 0.4M in chloroform-d for the ^{1}H nmr spectra and 0.5M in chloroform-d for the ^{13}C nmr spectra unless stated otherwise. Signals are singlets unless stated otherwise: b = broad; d = doublet; dd = double double doublet; t = triplet; q = quartet; dq = double quartet, quin = quintuplet; m = multiplet. J values are in Hz, chemical shifts (δ) are in ppm downfield from TMS. Spin decoupling was used as an aid to assignment.

Table 1. ^{13}C Nmr Spectral Data for the Pyrrole-2-carbothialdhydes

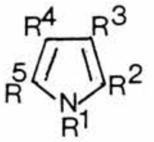


	R^1	R^2	R^3
(7b)	Me	H	H
(7c)	Me	Me	H
(7d)	Me	H	Me
(7e)	H	Me	Me
(7f)	Me	Et	Me

					Ring Carbons			
Compound	CHS	R^1	R^2	R^3	C-2	C-3	C-4	C-5
(7b)	198.4 d $J_{C,H'}$ 167.0	13.8 q $J_{C,H'}$ 128.6	-	-	143.5	122.6 d $J_{C,H'}$ 174.3	113.4 d $J_{C,H'}$ 170.9	143.3
(7c)	196.2 d $J_{C,H'}$ 167.1	12.1 q $J_{C,H'}$ 128.2	10.7 q $J_{C,H'}$ 126.3	-	142.1	122.9 d $J_{C,H'}$ 173.1	122.6	141.6
(7d)	192.8 d $J_{C,H'}$ 165.2	13.8 q $J_{C,H'}$ 128.8	-	11.2 q $J_{C,H'}$ 127.3	143.9	133.5	114.4 d $J_{C,H'}$ 172.8	142.0
(7e)	196.4 d $J_{C,H'}$ 165.8	-	9.2 q $J_{C,H'}$ 126.9	9.6 q $J_{C,H'}$ 126.9	142.2	130.3	123.0	130.3 d $J_{C,H'}$ 183.7
(7f)	190.9 d $J_{C,H'}$ 164.9	14.8 q* $J_{C,H'}$ 125.9	9.28 t* $J_{C,H'}$ 127.1 17.09 q $J_{C,H'}$ 126.7	12.2 q* $J_{C,H'}$ 128.3	142.2	131.0	127.2	141.4

* tentative assignments

Table 2. ^{1}H Nmr Spectral Data for the Pyrrole-2-carbothialdehydes and Pyrrole-3-carbothialdehydes



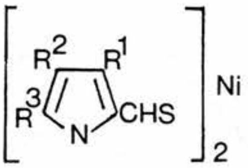
	R^1	R^2	R^3	R^4	R^5
(7b)	H	CHS	H	H	Me
(7c)	H	CHS	H	Me	Me
(7d)	H	CHS	Me	H	Me
(7e)	H	CHS	Me	Me	H
(7f)	H	CHS	Me	Et	Me
(7g)	Me	CHS	H	Me	Me
(7h)	Me	CHS	Me	H	Me
(9a)	Me	Me	CHS	H	Me
(9b)	H	Me	CHS	H	Me

Compound	R^1	R^2	R^3	R^4	R^5
(7b)	9.10 b	10.41	6.71 dd $J_{3,1}$ 3.8 $J_{3,4}$ 3.8	6.18 m	2.31 d $J_{5,4}$ 0.6
(7c)	9.48 vb	10.27	6.56 m	2.02 m	2.20
(7d)	8.30 b	10.34	2.26	5.99 m	2.24
(7e)	9.30 b	10.62	2.19	2.02	7.06 d $J_{5,1}$ 3.0
(7f)	9.52 vb	10.27	2.24	1.06 t 2.38 q	2.18
(7g)	3.90	10.46	6.74 m	2.01 d $J_{4,3}$ 0.7	2.14
(7h) a	3.94	10.64	2.27	5.94	2.19
b	4.05 3.69*	10.55 10.78*	2.25	5.96 6.04*	2.20
c	4.01 vb	10.61 b	2.26	5.94 b	2.20
d	3.95	10.73	2.27	5.91	2.17
(9a)	3.40	2.38	11.03 d $J_{3,4}$ 0.7	6.42 m	2.17 d $J_{5,4}$ 1.1
(9b)	-	2.43	11.01 d $J_{3,4}$ 0.7	6.45 m	2.19 d $J_{5,4}$ 1.1

a. ambient temperature b, -20°C c, 0°C d, 50°C

* Signals due to isomer (7h') ratio of (7h):(7h') = 4:1

Table 3. ^{1}H Nmr Spectral Data for the Bis(pyrrole-2-carbothialdehydato)Ni(II) Complexes

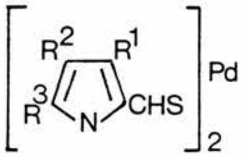


	R^1	R^2	R^3
(38b)	H	H	H
(20a)	H	H	Me
(20b)	H	Me	Me
(20c)	Me	H	Me
(20d)	Me	Me	H
(20e)	Me	Et	Me

Compound	CHS	R^1	R^2	R^3
(38b)*	8.24 d $J_{CHS,5}$ 1.4	6.83 d $J_{3,4}$ 4.8	6.37 d $J_{4,3}$ 4.8	7.51 m
(20a)	7.82	6.64 d $J_{3,4}$ 4.5	6.20 d $J_{4,3}$ 4.5	2.54
(20b)	7.52	6.37 b,m	1.86 d $J_{4,3}$ 1.1	2.46
(20c)	7.65	2.15 m	5.90 q $J_{4,3}$ 1.2	2.46
(20d)	Compound insoluble			
(20e)	7.52	2.06	2.18 q $J_{CH_2,Me}$ 7.9 0.93 t J_{Me,CH_2} 7.9	2.46

* Saturated solution in chloroform-d

Table 4. ^{1}H Nmr Spectral Data for the Bis(pyrrole-2-carbothialdehydato)Pd(II) Complexes



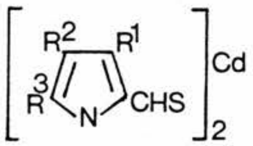
	R^1	R^2	R^3
(38c)	H	H	H
(19a)	H	H	Me
(19b)	H	Me	Me
(19c)	Me	H	Me
(19d)	Me	Me	H
(19e)	Me	Et	Me

Compound	CHS	R^1	R^2	R^3
(38c)*	8.49 d $J_{CHS,5}$ 1.0	6.90 dd $J_{3,4}$ 4.6 $J_{3,5}$ 1.0	6.44 dd $J_{4,3}$ 4.8 $J_{4,5}$ 1.4	7.66 m
(19a)	7.97 m	6.78 dq $J_{3,4}$ 4.6 $J_{3,5}$ 0.6	6.18 d $J_{4,3}$ 4.6	2.57 m
(19b)	7.69 m	6.53 m $J_{3,5}$ 0.6	1.94 d $J_{4,3}$ 1.2	2.48 t $J_{5,CHS}$ 0.5
(19c)+	7.84	2.19 b,d $J_{3,4}$ 0.8	5.91 b	2.49
(19d)	Compound insoluble			
(19e)	7.67	2.10	2.28 q $J_{CH_2,Me}$ 7.8 0.99 t J_{Me,CH_2} 7.8	2.47

* Saturated solution in chloroform-d

+ 0.1 M solution in chloroform-d

Table 5. ^{1}H Nmr Spectra Data for the Bis(pyrrole-2-carbothialdehydato)Cd(II) Complexes



	R^1	R^2	R^3
(38e)	H	H	H
(23a)	H	H	Me
(23b)	H	Me	Me
(23c)	Me	H	Me
(23d)	Me	Me	H
(23e)	Me	Et	Me

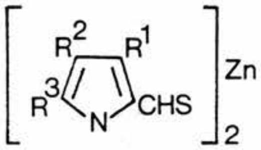
Compound	CHS	R^1	R^2	R^3
(38e)	Compound not isolated			
(23a)*	8.67	6.93 d $J_{3,4}$ 4.3	6.49 d $J_{4,3}$ 4.3	2.23
(23b)+	8.90 b	6.65 m	1.84 d $J_{4,3}$ 1.2	2.27 m
(23c)+	9.08	2.14 d $J_{3,4}$ 0.9	6.18 q $J_{4,3}$ 0.9	2.32
(23d)	Compound insoluble			
(23e)‡	8.37	2.12	2.34 q $J_{CH_2,Me}$ 7.8 1.04 t J_{Me,CH_2} 7.8	2.16

* 0.2M solution in chloroform-d

\+ 0.4M solution in pyridine-d_5

‡ 0.3M solution in chloroform-d

Table 6. ^{1}H Nmr Spectra Data for the Bis(pyrrole-2-carbothialdehydato)Zn(II) Complexes

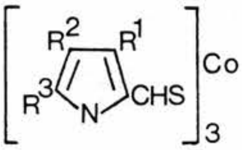


	R^1	R^2	R^3
(38f)	H	H	H
(22a)	H	H	Me
(22b)	H	Me	Me
(22c)	Me	H	Me
(22d)	Me	Me	H
(22e)	Me	Et	Me

Compound	CHS	R^1	R^2	R^3
(38f)	Compound not isolated			
(22a)	8.66 m	6.96 dq $J_{3,4}$ 4.2 $J_{3,5}$ 0.6	6.50 d $J_{4,3}$ 4.2	2.18 m
(22b)	8.38 b	6.67 b, m	2.00 d $J_{4,3}$ 1.1	2.12 t $J_{5,3}$ 0.4 $J_{5,CHS}$ 0.5
(22c)	8.51	2.12	6.20 q $J_{4,5}$ 1.0	2.21 d $J_{5,4}$ 1.0
(22d)*	8.71 b	2.14	1.95 m	7.39 d $J_{5,CHS}$ 1.5
(22e)	8.32	2.10	2.32 q $J_{CH_2,Me}$ 7.9 1.03 t J_{Me,CH_2} 7.9	2.10

* 0.25M solution in chloroform-d

Table 7. ^{1}H Nmr Chemical Shifts for Tris(pyrrole-2-carbothialdehydato)Co(III) Complexes



	R^1	R^2	R^3
(38a)	H	H	H
(25a)	H	H	Me
(25b)	H	Me	Me
(25c)	Me	H	Me
(25d)	Me	Me	H
(25e)	Me	Et	Me
(25b')	H	Me	Me

Compound	CHS	R^1	R^2	R^3
(38a)	8.34, 2H; 8.10, 1H; 7.85, 1H; 7.61, 1H; 7.04 m, 6H; 6.46 m, 6H; 6.03, 1H			
(25a)	8.09 7.99 7.61	7.02 dq 6.92 dq, 2H	6.28 d 6.14 d, 2H	2.35 2.16 1.47
(25b)	7.81 7.73 7.32	6.78 b 6.67 b, 2H	2.00 d 1.91 d 1.89 d	2.30 2.09 1.37
(25c)	7.95 7.82 7.46	2.24 d 2.29 2.21 d	6.00 d 5.86 2H	2.29 2.12 1.44
(25d)	-	2.20 3H 2.13 6H	1.82 6H 1.96 3H	-

The peaks at 8.19 2H; 7.72 2H; 7.47 1H; and 5.93 1H were not assigned.

Compound	CHS	R^1	R^2	R^3
(25e)	7.75 7.64 7.27		0.97 0.92 0.91 Three overlapping triplets	

A peak at 1.38 (3H, Me) and a five peak multiplet, 2.07, 2.11, 2.15, 2.20, 2.26 (21H, 5Me + 3CH$_2$) were not assigned

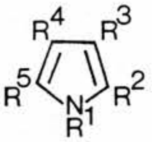
Compound	CHS	R^1	R^2	R^3
(25b')	7.3-7.9 vb	6.86 b	1.99 d $J_{4,3}$ 1.0	1.50 b

Table 8. ^1H Nmr Spectral Data for the Tetraethylammonium Pentacarbonyliodometallates

Solutions were 0.4M in DMSO-d_6

Compound	CH_3	CH_2
$Et_4\overset{+}{N}[W(CO)_5I]^-$ (31a)	1.12, tt J_{Me,CH_2} 7.3 $J_{Me,N}$ 1.8	3.25, q $J_{CH_2,Me}$ 7.3
$Et_4\overset{+}{N}[Cr(CO)_5I]^-$ (31b)	1.40, tt J_{Me,CH_2} 7.2 $J_{Me,N}$ 1.9	3.49, q $J_{CH_2,Me}$ 7.2
$Et_4\overset{+}{N}[Mo(CO)_5I]^-$ (31c)	1.17, tt J_{Me,CH_2} 7.2 $J_{Me,N}$ 1.8	3.22, q $J_{CH_2,Me}$ 7.2

Table 9. ^{1}H Nmr Spectral Data for the Pentacarbonyl(pyrrole-carbothialdehyde-S)tungsten (0) Complexes



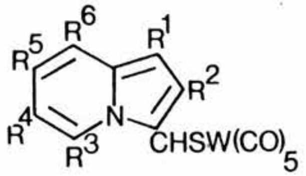
	R^1	R^2	R^3	R^4	R^5
(40)	H	$CHSW(CO)_5$	H	H	H
(33a)	H	$CHSW(CO)_5$	H	Me	Me
(33b)	H	$CHSW(CO)_5$	Me	H	Me
(34a)	Me	Me	$CHSW(CO)_5$	H	Me
(34b)	H	Me	$CHSW(CO)_5$	H	Me

Compound	R^1	R^2	R^3	R^4	R^5
(40)	9.38 vb	10.32	6.96 dd $J_{3,4}$ 4.2 $J_{3,5}$ 0.98	6.52 dd $J_{4,3}$ 4.2 $J_{4,5}$ 2.4	7.47 m
(33a)	9.12 vb	9.77	6.70 m	2.06 d $J_{4,3}$ 0.49	2.27
(33b)	9.08 vb	9.82	2.31	6.10 m	2.23
(34a)	3.44	2.38	10.50	6.46 m	2.21 d $J_{5,4}$ 0.98
(34b)	8.40 vb	2.43	10.58	6.37 m	2.23 d $J_{5,4}$ 1.2

The N-H protons exchanged when D_2O was added

Table 10. ^{1}H Nmr Spectral Data for the Pentacarbonyl(indolizine-3-carbothialdehyde-S)tungsten (0) Complexes

Solutions were 0.2M in $CDCl_3$

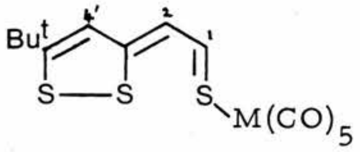


	R^1	R^2	R^3	R^4	R^5	R^6
a)	H	Me	H	H	H	H
b)	Me	Me	H	H	H	H

Compound	R^1	R^2	CHS	R^3	R^4	R^5	R^6
(32a)	6.58 b	2.47 d $J_{2,1}$ 0.98	9.93	10.51 dd $J_{5,6}$ 6.84 $J_{5,7}$ 0.73	7.60 - 7.68 m 6-H + 8-H	7.10 - 7.29 m	7.60 - 7.68 m 6-H + 8-H
(32b)	2.26 or 2.38	2.38 or 2.26	9.80	10.58 d $J_{5,6}$ 6.84	7.62 - 7.71 m 6-H + 8-H	7.21 - 7.31 m	7.62 - 7.71 m 6-H + 8-H

Table 11. ^{1}H Nmr Spectral Data for the Pentacarbonyl[2-(5-t-butyl-3*H*-1,2-dithiole-3-ylidene)ethanethial-*S*] Complexes of W and Cr

Solutions were 0.2M in chloroform-d except where stated otherwise

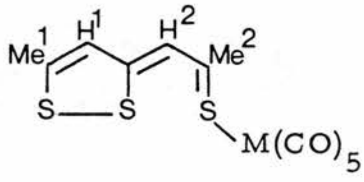


Compound	M	Bu^t	4'-H	2-H	1-H
(42d)	W	1.51	7.54	7.56 d $J_{2,1}$ 7.6	9.65 d $J_{1,2}$ 7.6
		*1.50	7.62	7.58 d $J_{2,1}$ 7.6	9.61 d $J_{1,2}$ 7.6
(43d)	Cr	1.52	7.60	7.73 d $J_{2,1}$ 7.6	9.44 d $J_{1,2}$ 7.6

* 0.2M solution in dichloromethane-d_2

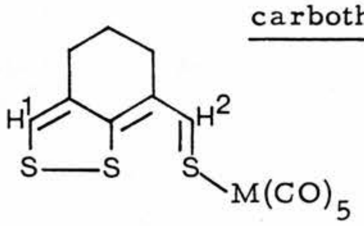
Molybdenum complex (44d) decomposed in solution.

Table 12. Variable Temperature ^{1}H Nmr Spectra Data for the Pentacarbonyl[1-(5-methyl-3H-1,2-dithiole-3-ylidene)propan-2-thione-S] Complexes of W and Cr



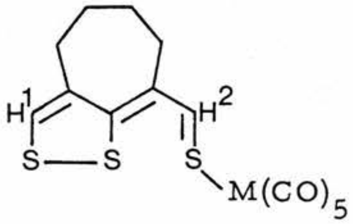
Compound	M	Temp. °C	H^1	H^2	Me^1	Me^2
(42c)	W	-50	7.48	7.69	2.69	2.79
		-4	7.48	7.69	2.66 vb	
		1	7.51 vb		2.66	
		50	7.51		2.66	
(43c)	Cr	-10	7.45	7.67	2.65	2.78
		3	7.53 vb		2.68 vb	
		30	7.53		2.68	

Table 13. Variable Temperature ^{1}H Nmr Spectral Data for the Pentacarbonyl[5,6-dihydro-4$\underline{H}$-1,2-benzodithiole-7-carbothialdehyde-$\underline{S}^7$] Complexes of W, Cr and Mo



Compound	M	Temp °C	H^1	H^2	cycloalkyl protons
(42a)	W	- 10	8.18	9.46	3.04 t, 1.99 quin
		34	8.79 b		3.04 t, 1.99 quin
		60	8.79		3.01 t, 1.99 quin
(43a)	Cr	0	8.10	9.29	3.19 m, 2.08 m
		45.5	8.80 vb		3.14 t, 2.06 quin
		50	8.80		3.10 t, 2.01 quin
(44a)	Mo	- 30	8.20	9.34	3.04 t, 2.03 m
		- 18	8.76 br		3.03 t, 2.03 m
		15	8.76		3.02 t, 2.02 m

Table 14. Variable Temperature ^{1}H Nmr Spectral Data for the Pentacarbonyl[4,5,6,7-tetrahydro-1,2-cyclohepto-dithiole-8-carbothialdehyde-$\underline{S}^8$] Complexes of W and Cr



Compound	M	Temperature °C	H^1	H^2	cycloalkyl protons
(42b)	W	0	8.14	9.39	3.12 m, 2.03 m
		27.5	8.77 vb		3.12 m, 2.02 m
		55	8.77 b		3.15 m, 2.02 m
(43b)	Cr	0	8.07	9.22	3.18 m, 2.03 m
		36.5	8.60 vb		3.18 m, 2.03 m
		50	8.60 br		3.18 m, 2.03 m

APPENDIX B : INFRARED SPECTRAL DATA

Solutions were 2×10^{-3}M in cyclohexane unless otherwise stated. The solution cell windows were KBr and the path length was 1 mm.

w = weak, vw = very weak, s = strong, m = medium, sh = shoulder

Table 1. νCO Values for Pentacarbonyl(pyrrolecarbothialdehyde)-Tungsten (0) Complexes

	νCO Values in cm^{-1}		
Compound	$A_1(2)$	E	$A_1(1)$
(40)	2068 w	1945 s	1930 m
(33a)	2065 w	1939 s	1923 m
(33b)	2062 w	1942 s 1932 s	1921 m
(34b)	2064 w	1942 s 1932 s	1921 m
(34a)	2062 w	1941 s 1934 s	1919 m

Table 2. ν NH Values for Pentacarbonyl(pyrrolecarbothialdehyde)-Tungsten (0) Complexes

Compound	ν NH Values in cm^{-1}
(33a)	3406
(33b)	3408
(34a)	*
(34b)	3418
(40)	3413

* No bands in the region 3000-3800 cm^{-1}

Solutions were 0.1M in CH_2Cl_2

Table 3. νCO Values for Pentacarbonyl(indolizine-3-carbothialdehyde)tungsten (0) Complexes

Compound	$A_1(2)$	E		$A_1(1)$
(32a)	2063 w	1941 s	1931 s	1916 m
(32b)	2067 w	1943 s	1932 s	1917 m

Solutions were saturated 2 x 10^{-3}

Table 4. νCO Values for Pentacarbonyl 1,6,6a ^{4}-Trithiapentalene Group VI Metal Complexes

Compound	$A_1(2)$	B_1	E	$A_1(1)$
	νCO Values in cm^{-1}			
(42d)	2067 w	1978 vw	1940 s	1929 m
(42c)*	2057 w	1974 vw	1939 s	1916 m
(42a)	2065 w	1977 vw	1941 s	1921 m
(42b)	2065 w	1978 vw	1939 s	1917 m
(43d)	2058 vw	1985 w	1946 s	1925 m
(43c)+	2061 vw	1984 w	1946 s	1926 m
(43a)	2058 vw	1984 w	1946 s	1926 m
(43b)	2058 w	1984 w	1945 s	1926 m

* 5×10^{-3}M

\+ saturated solution

Table 5. νCO Values for the Pentacarbonyliodometallate (0) Salts $Et_4\overset{+}{N}[M(CO)_5I]^-$, M = W, Cr, Mo

Compound	$A_1(2)$	B_1	E	$A_1(1)$
	νCO Values in cm^{-1}			
(31a)	2058 w	1960 sh	1917 s	1853 m
(31b)	2049 w	1961 sh	1921 s	1861 m
(31c)	2061 w	1971 sh	1923 s	1856 m

APPENDIX C : PUBLICATIONS

IRON-SULPHUR-CARBONYL AND -NITROSYL COMPLEXES: A LABORATORY EXPERIMENT

by Christopher Glidewell, Andrew R. Hyde,*
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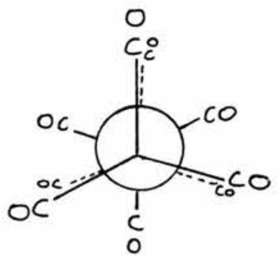
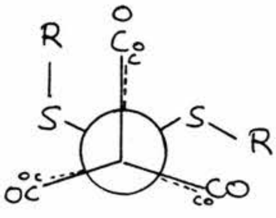
INTRODUCTION

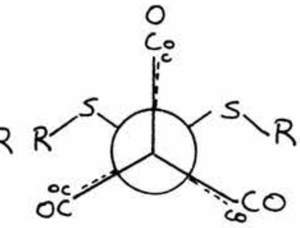
The reaction between $Fe_3(CO)_{12}$ and Me_2S_2 was first shown by King[1] to yield two isomeric forms of $Fe_2(CO)_6(SMe)_2$. Both isomers have structures closely related to that of $Fe_2(CO)_9$ (I): the more abundant *anti* isomer (II,R=CH_3)[2] has two distinct methyl environments, whereas the *syn* isomer (III,R=CH_3) has two identical methyl groups. In the series $Fe_2(CO)_6(SR)_2$ the *anti/syn* ratio increases with the increase in the steric requirements of the group R so that the ratio is *ca.* 4 when R=CH_3, but when R=Me_3C only the *anti* isomer is detectable:[3] on the other hand, when R=H, a third isomer (IV) can be detected in solution.[4] Although the pure *anti* and *syn* isomers can be isolated, they rapidly re-equilibrate in solution,[3] but at a rate sufficiently slow on the n.m.r. timescale for the detection of individual ^1H and ^{13}C resonances at room temperature: on the other hand, the carbonyl groups are rapidly fluxional at room temperature, giving only a single ^{13}C resonance for each isomer.[5,6] The compounds $Fe_2(CO)_6(SR)_2$ can all be readily converted[6] to $Fe_2(NO)_4(SR)_2$, the esters of Roussin's[7,8] red anion $[Fe_2S_2(NO)_4]^{-2}$.



(I)



(II)



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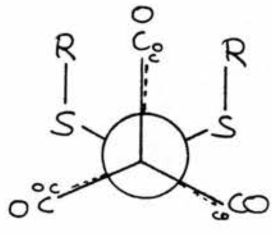


(IV)

We have developed a comprehensive experiment based upon this chemistry, which we have used during the past six years in the third (penultimate) year of our undergraduate course.[9-11] This experiment involves the use of inert atmosphere techniques, and of thin-layer and flexible-column chromatography, and the interpretation of infra-red, ^1H and ^{13}C n.m.r., and mass spectral data. The column chromatography is particularly significant, firstly because the use of silica instead of alumina[1,12] allows the easy separation and isolation of a third product in the $Fe_3(CO)_{12}/Me_2S_2$ reaction, readily identified as the known[13] complex $[MeSFe_2(CO)_6]_2S$, but not previously detected in this reaction, and secondly because the use of a flexible column (*e.g.* of dialysis tubing) instead of a conventional glass column greatly reduces both the time required for the separation and the volume of solvent consumed.

In the experiment, all students prepare $Fe_3(CO)_{12}$ from $Fe(CO)_5$ and react this with Me_2S_2, and then determine the *anti*/*syn* ratio by ^1H n.m.r. Thereafter there are two options. Either the crude mixture is subjected to chromatography, allowing separation and characterisation of three pure components, followed by a study of the *anti* $\rightleftharpoons$ *syn* equilibrium in $Fe_2(CO)_6(SMe)_2$; or the crude mixture is nitrosylated[6] to yield $Fe_2(NO)_4(SMe)_2$. If NO gas is used as the nitrosylating agent, yields of around 90% of the nitrosyl complex are readily obtained; if however an NO cylinder is not available, the nitrosylation can be effected using sodium nitrite instead, but here the yields are typically around 30%.

The preparations of $Fe_3(CO)_{12}$ and $Fe_2(CO)_6(SMe)_2$ are based initially upon those described by King,[12] but they have been the subject of extensive modification and simplification for class use, as described below.

EXPERIMENTAL

Preparation of $Fe_3(CO)_{12}$ (to be performed in a fume-cupboard)

Set up a 3-necked one litre flask with reflux condenser, mechanical stirrer and nitrogen supply: pass N_2 through the flask throughout the preparation. Add to the flask iron pentacarbonyl (21 cm^3) and methanol (85 cm^3): then add a cold solution of 22.5 g NaOH in 45 cm^3 water. Stir the mixture for half an hour.

Meanwhile prepare activated manganese (IV) oxide: add ethanol (150 cm^3) WITH CAUTION to a solution of $KMnO_4$ (33.5 g) in water (150 cm^3) in a one litre beaker covered with a large watch glass. *(N.B.* The beaker should be stood in another container in case of breakage: the reaction may start spontaneously 5-10 minutes after the addition of the ethanol.) When the reaction has subsided, stir the mixture thoroughly until no purple colour remains, and cool to room temperature.

After stirring the original reaction mixture for 30 mins, add 62.5 cm^3 of saturated NH_4Cl solution, followed by the MnO_2 paste: then stir for 2 hours. Add gradually a solution of $FeSO_4.7H_2O$ (20 g) in 1M H_2SO_4 (125 cm^3), then 150 cm^3 of 50% sulphuric acid. Stir for half an hour and then if necessary cool to room temperature. Filter the black crystals and wash with two 100 cm^3 portions of hot (80 °C) 1M sulphuric acid, and then with 2 × 50 cm^3 ethanol.

Store the product still damp with ethanol: the product should be dried, and a yield obtained, just before the start of the second part of the experiment.

Conversion of $Fe_3(CO)_{12}$ to $Fe_2(CO)_6(SMe)_2$ (to be performed in a fume-cupboard)

Dry the $Fe_3(CO)_{12}$ by washing on a Hirsch funnel with light petroleum (2 × 100 cm^3) and then desiccating it briefly. Record the yield at this point.

Set up a 500 cm^3 3-necked flask with condenser, nitrogen supply, and magnetic stirrer: add $Fe_3(CO)_{12}$ (16.8 g), Me_2S_2 (30 cm^3) and benzene (200 cm^3). Stir the mixture and, using an oil bath, reflux under nitrogen for 5 hours. Cool to room temperature, and filter using a sintered glass funnel. *N.B.* The residue is pyrophoric and should not be allowed to become dry: do NOT suck air through the residue. Wash the residue with benzene (4 × 50 cm^3) and evaporate the combined benzene fractions to dryness: pump the dry product on the oil pump for 2 hr.

Meanwhile dispose of the black pyrophoric residue by washing it down the fume-cupboard sink with plenty of water, having previously removed all flammable chemicals from the fume cupboard. All glassware contaminated with Me_2S_2 should be soaked in sodium hypochlorite solution.

Weigh the crude product, run a t.l.c. plate (use light petroleum), and record its n.m.r. spectrum in $CDC\ell_3$ solution.

Now proceed to either (a) the chromatography of the mixture, or (b) the nitrosylation of the unseparated mixture.

Chromatography

Set up a silica chromatography column (2.8 × 140 cm):[14] dissolve the crude mixture in the minimum volume of light petroleum and apply it to the column, and develop with petroleum. Three bands will be apparent by the time the front of the first band is half-way down the column. Now allow the solvent to drain from the column, and cut the column with a scalpel to separate the bands. Extract each band with petroleum, and remove the solvent on the rotary evaporator *at room temperature*. Check the purity of each fraction by t.l.c.

Record the yield, melting point, infra-red spectrum, and ^1H n.m.r. spectrum ($CDC\ell_3$ solution) of each fraction. (Typical yields of *anti*- and *syn*-$Fe_2(CO)_6(SMe)_2$ and $[MeSFe_2(CO)_6]_2S$ are 20%, 5% and 1% respectively: m.p.s. (/°C); 65-67, 101-103, 163-165 respectively.) Assign the *anti* and *syn* structures to the two major components based upon their ^1H n.m.r. spectra: compare the *anti/syn* ratio deduced from the recovered yields with that from the n.m.r. spectrum of the crude mixture.

Anti $\rightleftharpoons$ *syn* equilibrium

Take a small (*ca.* 100 mg) portion of each of the *anti* and *syn* isomers and reflux each separately for 15 mins in 50 cm^3 of solvent (consult a demonstrator for the solvent to be used): after cooling, and removal of the solvent, examine each sample by t.l.c. and by ^1H n.m.r. spectroscopy. Deduce the equilibrium constant K = [*anti*]/[*syn*].

Nitrosylation of $Fe_2(CO)_6(SMe)_2$

(a) Using NO gas

Set up a 250 cm^3 3-necked flask equipped with reflux condenser, and inlets for both N_2 and NO. Dissolve 3.7 g (10 mmol) of $Fe_2(CO)_6(SMe)_2$ in 50 cm^3 $CH_2C\ell_2$, add this solution to the reaction flask and thoroughly purge the system with N_2. Reflux the mixture for 1 hr during which NO is bubbled through the refluxing solution. Cool, and filter the solution through a sintered glass funnel. (*N.B.* The residue may be pyrophoric; dispose of as previously.) Reduce the volume on the rotary evaporator until crystals just begin to form, then cool in ice and add cold methanol to precipitate the $Fe_2(NO)_4(SMe)_2$. Filter, wash with a little cold methanol and dry *in vacuo*. Note the yield, and check the purity by t.l.c. Record the infrared spectrum and the ^1H n.m.r. spectrum.

(b) Using sodium nitrite

Set up a 250 cm^3 3-necked flask equipped with N_2 supply, reflux condenser, pressure-equalised dropping-funnel, magnetic stirrer, and oil bath. To the flask add 10 mmol $Fe_2(CO)_6(SR)_2$ and 50 cm^3 ethanol. Stir under N_2 for 5-10 mins and then add a solution of 2.8 g $NaNO_2$ in 25 cm^3 water and a solution of 4.6 g NaOH in 25 cm^3 water. Place 50 cm^3 of a 1:1 mixture of glacial acetic acid and water in the dropping-funnel. Reflux the reaction mixture under N_2 for 2 hours: on adding the nitrite and hydroxide the reaction mixture turns a bright orange/yellow; after 15-20 minutes heating it should be almost black.

After 2 hours, allow the mixture to cool, then add the acetic acid solution dropwise with maximum stirring. Vigorous evolution of CO and CO_2 soon begins; continue adding the acid until this stops. Check the pH of the reaction mixture; if it is still alkaline, continue adding the acid until the mixture is neutral or slightly acidic.

(a) <u>*Anti*-$Fe_2(CO)_6(SMe)_2$</u> : $\delta(^1H)$/p.p.m. ($CDC\ell_3$) : 1.63, 2.17.
$\delta(^{13}C)$/p.p.m. ($CDC\ell_3$) : 8.0, 21.6 (CH_3); 208.7 (C
$\nu(CO)/cm^{-1}$: 2085(s), 2050(vs), 2000(vs).

(b) <u>*Syn*-$Fe_2(CO)_6(SMe)_2$</u> : $\delta(^1H)$/p.p.m. ($CDC\ell_3$) : 2.13.
$\delta(^{13}C)$/p.p.m. ($CDC\ell_3$) : 20.3 (CH_3) ; 209.7 (CO).
$\nu(CO)/cm^{-1}$: 2075(s), 2040(vs), 2000(vs), 1990(sh)

(c) <u>$[MeSFe_2(CO)_6]_2S$</u> : $\delta(^1H)$/p.p.m. ($CDC\ell_3$) : 2.15.
$\nu(CO)/cm^{-1}$: 2080(m), 2060(s), 2040(vs),
2010(s), 1990(sh).

(d) <u>$Fe_2(NO)_4(SMe)_2$</u> : $\delta(^1H)$/p.p.m. Very solvent dependent, see discussion.
$\nu(NO)/cm^{-1}$: 1760(s), 1730(s).

<u>Questions</u>

1. Draw the solid-state structure of $Fe_3(CO)_{12}$ and explain the observation[15] that the ^{13}C n.m.r. spectrum shows only one resonance.
2. Draw Newman projections for $Fe_2(CO)_9$, and for the *anti* and *syn* isomers of $Fe_2(CO)_6(SMe)_2$: comment on the observation of only a single carbonyl resonance in the ^{13}C n.m.r. spectrum of each isomer at room temperature, and predict the number of carbonyl resonances at low temperature.

3. How is the nitrosyl complex $Fe_2(NO)_4(SMe)_2$ related electronically to the carbonyl complex $Fe_2(CO)_6(SMe)_2$? Does either obey the 18-electron rule?

DISCUSSION

The reaction sequence carried out in this experiment is;

$$Fe(CO)_5 \longrightarrow Fe_3(CO)_{12} \longrightarrow Fe_2(CO)_6(SMe)_2 \longrightarrow Fe_2(NO)_4(SMe)_2$$

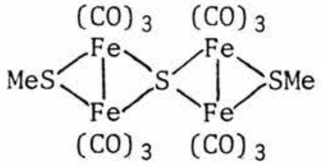
$$+$$

$$[MeSFe_2(CO)_6]_2S$$

All the products are to a greater or lesser extent air-sensitive in solution, so that N_2 atmospheres are required throughout: in addition the two isomers of $Fe_2(CO)_6(SMe)_2$ readily re-form an equilibrium mixture in solution, so that considerable care is required in handling the solutions. Brief reflux of either the *anti* or the *syn* isomer in hydrocarbon solvents yield the equilibrium mixture for which K can readily be determined by ^1H n.m.r. ; this is slightly solvent dependent and typical values of K are, for benzene, 4.0 ± 0.2, and for cyclohexane, 1.6 ± 0.2. Because of the ease of this interconversion, the removal of solvent after chromatography *must* be performed at room temperature.

Our own students are told the molecular formulae of all the products which are formed subsequent to $Fe_3(CO)_{12}$ and are required to use the spectral data to deduce structural formulae. The whole exercise can be made more challenging for more able students by withholding molecular formulae and providing instead mass spectral data. Similarly, the n.m.r. assignment can be made more difficult by substituting ethyl for methyl throughout,[16] although in this case we have never observed a third compound.

The minor product isolated in the chromatographic separation, $[MeSFe_2(CO)_6]_2S$, (V)

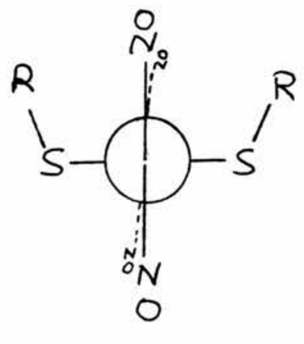


(V)

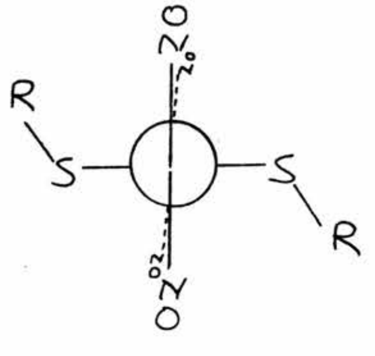
has been observed as a low-yield product in a number of reactions, including those between $Fe_3(CO)_{12}$ and CH_3SCN[13] and $Fe_2(CO)_9$ and cyclooctatetraenyl methyl sulphide, $C_8H_7SCH_3$.[17] A similar compound, $[t\text{-}BuSFe_2(CO)_6]_2S$ is formed along with many other products when t-BuSH reacts over a long period with $Fe_3(CO)_{12}$: less sterically hindered thiols do not appear to react in this way.[18] The mechanism of formation of (V) is uncertain:[19] neither of $Fe_2(SMe)_2(CO)_6$ and (V) is converted to the other on reflux in benzene, nor is (V) formed from the reaction of Me_2S_2 with $Fe_2S_2(CO)_6$ or $Fe_3S_2(CO)_9$, both of which are early products[19,20] in the reaction of $Fe_3(CO)_{12}$ with organo-sulphur compounds.

These tetra-nuclear complexes are of particular interest in having rigid but chiral Fe_4S_3 frameworks: the overall molecular symmetry is only C_2,[13] but the framework is rigid in solution up to at least +150 °C.[21]

The nitrosyl complex $Fe_2(NO)_4(SMe)_2$, like most of the family of complexes $Fe_2(NO)_4(SR)_2$ exists[6] as 1:1 mixture of C_{2v} and C_{2h} isomers (VI and VII respectively) in solution.



(VI)



(VII)

The ^1H n.m.r. spectra of all of these nitrosyl species are solvent dependent,[6,22] and for R = CH_3, the chemical shifts range from 2.20 p.p.m. in toluene-d_8 to 3.54 p.p.m. in DMF-d_7 : in $CDCl_3$ it is 2.83 ± 0.01 p.p.m. for *both* isomers.

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