SYNTHESIS AND CHARACTERISATION OF

HETEROPOLYCYCLIC COMPOUNDS CONTAINING

S-S AND S-N BONDS

by

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The following is a statement of postgraduate courses attended during the period of study.

Molecular rearrangements

Dr. G. Tennant

N.M.R. spectroscopy

Dr. R.K. Harris

Phosphorus in organic synthesis

Prof. J.I.G. Cadogan and Dr. I. Gosney

Organo Sulphur Compounds in general synthesis

Dr. D. Leaver

Chemical aspects of Oil Products research

- Various speakers from Shell Research

S.R.C. Graduate School

- Manchester Polytechnic, 1976

Intra departmental seminars, 1974 - 1977

CONTENTS

ABSTRACT

The synthesis and characterisation of a number of polysulphur heterocycles containing S-S bonds was attempted but only limited success was achieved.

The structure of anthra[1,9,8-bcde:5,10,4-b'c'd'e']bis(thia-thiophthen), first obtained by a previous worker, was conclusively established by reductive methylation to 1,4,5,8-tetra(methylthio) anthracene and 5,10-di(methylthio)anthraceno[1,9-cd:5,10-c'd']bis [1,2]dithiole both of which were more easily characterised than the highly insoluble starting material. Attempts to synthesise the closely related 1,1aλ^4,2,3,4,4aλ^4,5,6-octathiadipentaleno[2,3,4,5-cdef:2',3',4',5'-ijkl]-s-indacene via reaction of hexabromodurene with sulphur gave black intractable solids. A similar intractable solid was obtained from the reaction of 4,8-dihydro-4,8-dioxo-1,3,5,7-tetra(methylthio)benzo[1,2-c:4,5-c']dithiophene with sodium sulphide. The dioxo-compound gave no reaction with phosphorus pentasulphide.

Attempts to synthesise 1,2,5,6-tetrathia-3,4,7,8-tetra-azacyclo-pent[fg]acenaphthylene($C_6N_4S_4$) gave a solid of molecular formula $C_6N_4S_5$. Identification of the solid was not possible but several possible structures are discussed. Attempts to degrade the product to the desired tetrathio-compound or to a more soluble derivative failed.

1,2,3,4,5,6,7,8-Octathiadicyclopenta[cd,ij]-s-indacene was synthesised by reaction of hexachloro-p-xylene with sulphur and sodium N-propoxide in n-propanol. The compound could not be fully characterised owing to its insolubility and the irreproducibility of the reaction.

Several cyclopalladated dithiocarbamato-complexes were synthesised and treated with thiocyanogen or with bromine. With certain exceptions complexes derived from N-donor ligands (e.g. benzo[h]quinoline) or S-donor ligands (e.g. xanthene-9-thione) gave the thiocyanato derivatives of the ligands which were converted into isothiazolium or 1,2-dithiolium salts, respectively, by treatment with perchloric acid. Quinolizine-4-thione and N-methylisoquinoline-1-thione yielded cyclopalladated complexes but these could not be converted into the bromo- or thiocyanato-derivatives of the parent ligands. N,N-Dimethylthiobenzamide yielded a novel type of complex which was cyclopalladated in one of the N-methyl groups.

Reaction of 1,2-dithiole-3-thiones with sodium tetrachloropalladate gave polymeric complexes in which the thione sulphur and S-2 of the dithiole ring were bonded to palladium. No orthopalladation was observed in benzo-1,2-dithiole-3-thione.
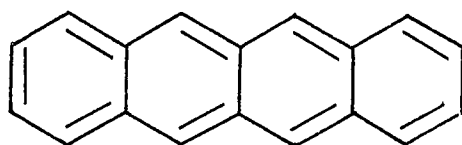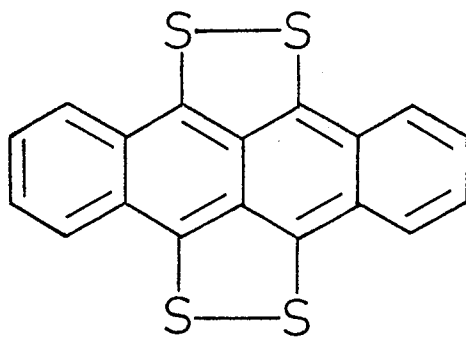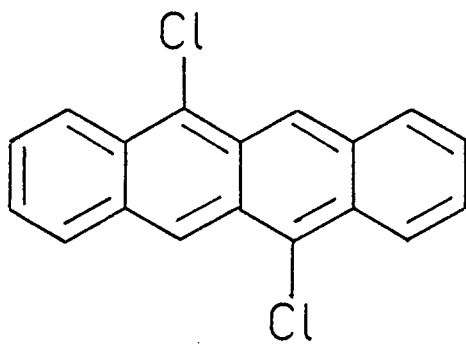
INTRODUCTION
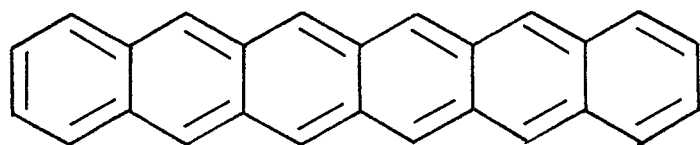
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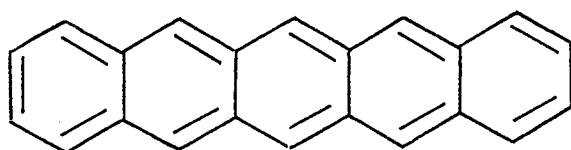
(2)

(3)

(4)

(3)

S_2Cl_2/trichlorobenzene

(5)

(4)

S_8/trichlorobenzene

(3)

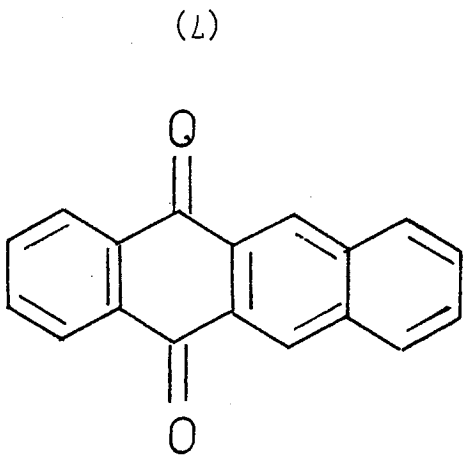__Section one.__   __Acene polysulphides__

Compounds have been reported which contain two or more sulphur atoms bonded to a linear acene system. These compounds are related to the more well known 1,2-dithioles and 1,6,6a-thiathiophthene although the chemical similarity is somewhat masked owing to the acene "backbone". Consequently the linear acene polysulphides are of considerable theoretical importance.

In 1939 Marschalk[1] reported attempts to synthesise heptacene by the dehydrogenation of a mixture of hydroheptacenes using elemental sulphur. No heptacene was obtained and the only isolated product was a green insoluble solid which contained sulphur. Similar products were isolated from the reaction of sulphur with hydrogenated derivatives of hexacene (1) pentacene (2) and tetracene (3) but not from dihydro-anthracene.

No further work was reported on these acene polysulphides until Marschalk etal.[2-6], in a series of papers, described the preparation and properties of tetraceno[9,10-__cd__:11,12-__c'd'__]bis (1,2) dithiole (4), sometimes referred to as tetrathiotetracene.

Tetrathiotetracene (4) was obtained from the reaction of tetracene (3) with elemental sulphur (or more rapidly with disulphur dichloride) in refluxing trichlorobenzene. 9,11-Dichlorotetracene (5) was isolated as an intermediate in the latter reaction and, on further treatment with disulphur dichloride, it reacted to yield tetrathiotetracene[7] (4).

To confirm the structure of tetrathiotetracene (4) Marschalk converted it into 9,10,11,12-tetra(methylthio) and -tetra(benylthio) tetracene (6;R=Me,PhCH$_2$) by reduction with sodium in liquid ammonia

(7)

(6; R=Me or PhCH$_2$)

i) Na/NH$_3$(l)
ii) RCl

i) NH$_3$(l)
ii) [O]

(4)

$(\mathcal{R}_{20}, 5 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1})$

(4)

X^-

$(\mathcal{R}_{20}, 1 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1})$

(8)

$2X^-$

$(\mathcal{R}_{20}, 3 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1})$
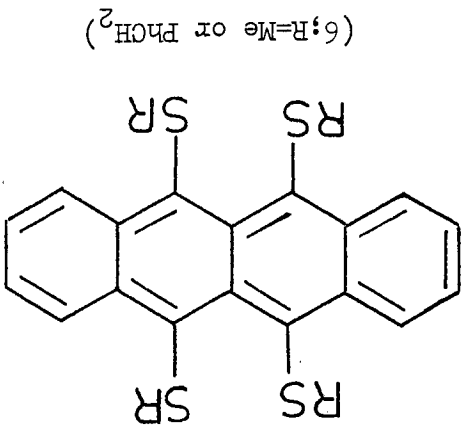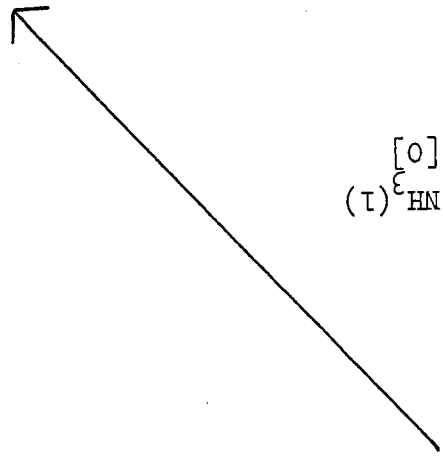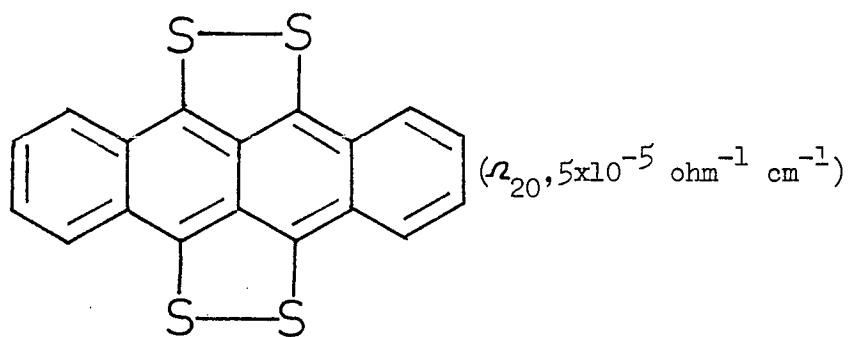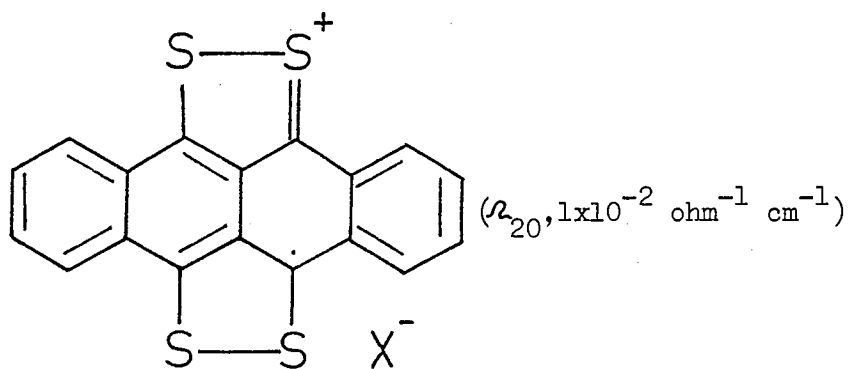
(9)

followed by treatment with the appropriate alkyl halide. The reaction of compound (4) with ammonia in an autoclave followed by oxidation gave tetracene-9,10-quinone (7).

Tetrathiotetracene (4) can be oxidised to a stable radical cation (8) and dication (9) with oxidising agents in an acidic medium. Reduction of compound (8) or (9) with titanium trichloride or sodium dithionite regenerates compound (4).

The formation of a stable radical cation is characteristic of even-numbered polyene or aromatic systems containing electron-pair donor substituents on the first and 2n th. carbon atoms[8,9]. In some such systems, moreover, there is evidence that further oxidation leads to a dication although this is not always stable. The generalised redox equilibria are outlined below:

$$\ddot{X}\text{---}(\text{CH}=\text{CH}\text{---})_n\ddot{X} \underset{+e}{\overset{-e}{\rightleftharpoons}} \overset{+\cdot}{X}\text{---}(\text{CH}=\text{CH}\text{---})_n\ddot{X} \underset{+e}{\overset{-e}{\rightleftharpoons}} \overset{+}{X}\text{---}(\text{CH}-\text{CH}\text{---})_n\overset{+}{X}$$
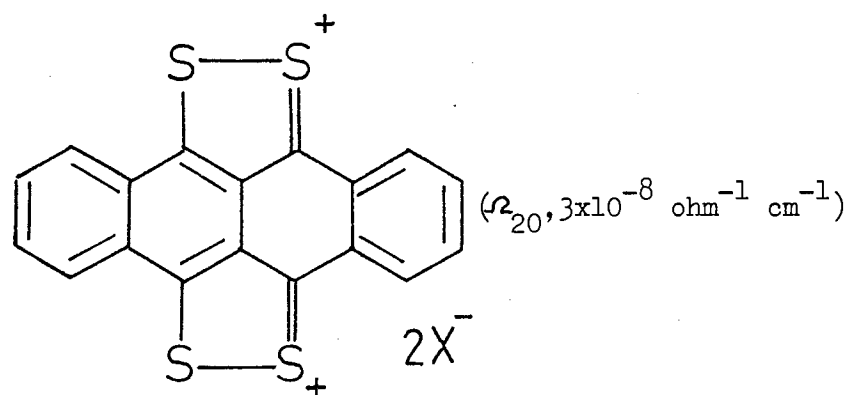
$$\updownarrow$$

$$\ddot{X}\text{---}(\text{CH}=\text{CH}\text{---})_n\overset{\cdot+}{X}$$
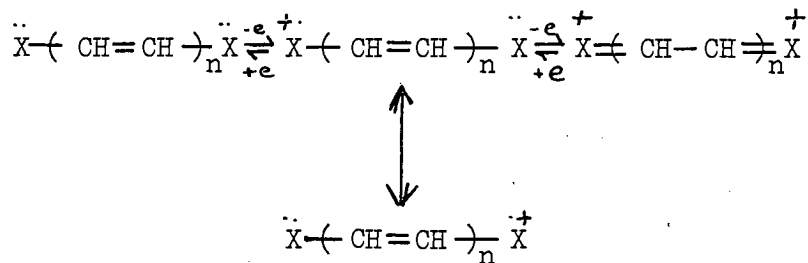
The radical cation of tetrathiotetracene is thought to gain stability from the possible contribution of canonical structures such as (10b) which contain a 1,2-dithiolium ring.
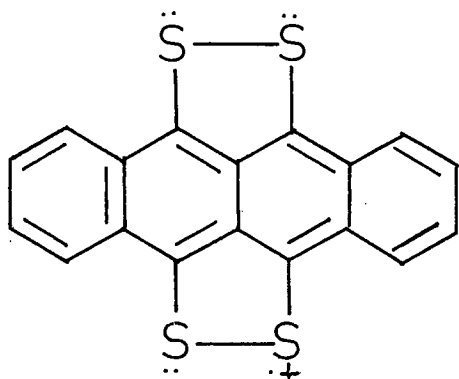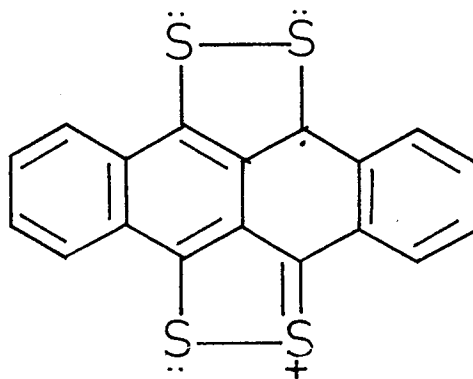
(10a)   (10b)

Similarly the dication (9) can be expected to be stabilised by the contribution of structures containing two 1,2-dithiolium rings (11a,b).
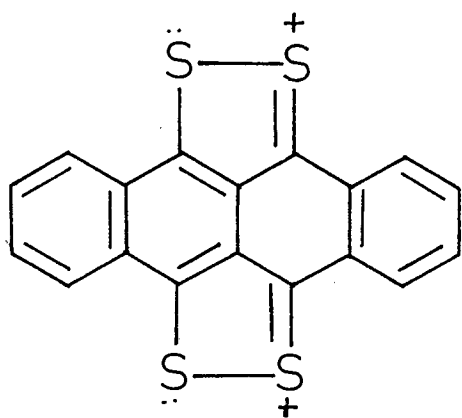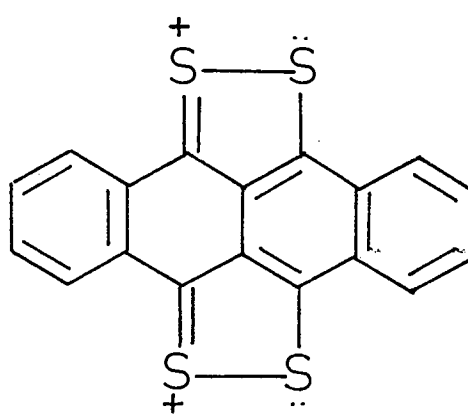
(11a)   (11b)

Tetraselenotetracene (12) was synthesised[10] by the reaction of selenium with 9,11-dichlorotetracene (5) in refluxing diphenyl ether-biphenyl (3:1). Like compound (4), tetraselenotetracene can be oxidised to a stable radical.

The structure of compound (4) was confirmed in 1967 by Troussant[11] who carried out X-ray diffraction studies. Matsunaga[12] was the first to report that tetrathiotetracene (4) formed charge-transfer complexes with strong electron acceptors such as o-chloranil, tetracyanoethylene, etc., and that the complexes showed an unusually high electrical

$(5) \xrightarrow[\Delta]{Se}$ $(\Omega_{20}, 2\times10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1})$

(12)

$(2) \xrightarrow{S_8}$ trichlorobenzene

(13)

$(1) \xrightarrow{S_8}$ trichlorobenzene

(14)
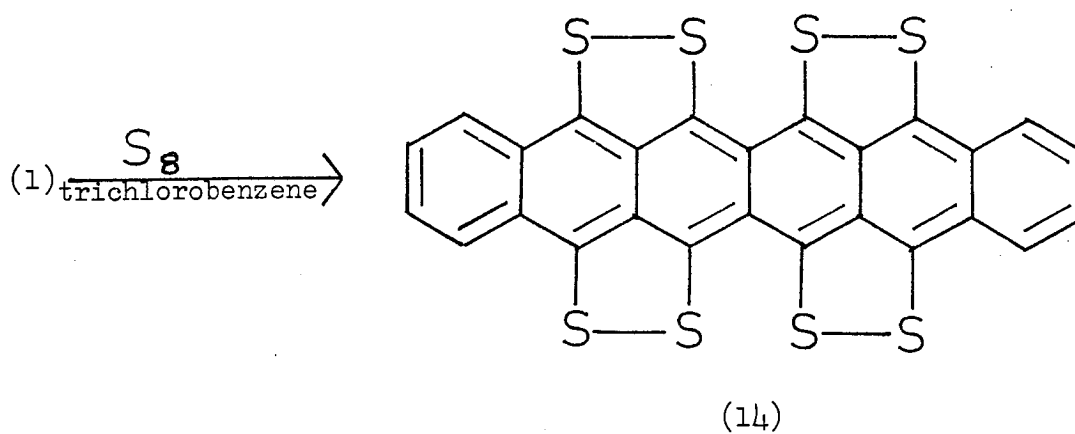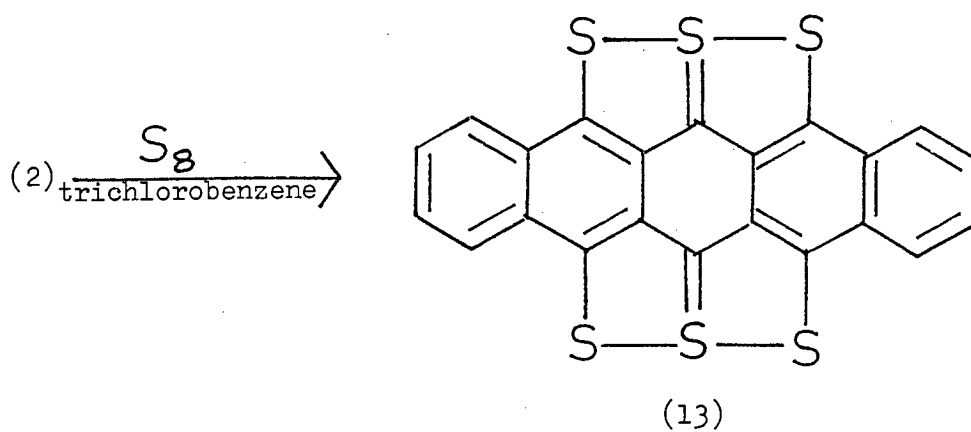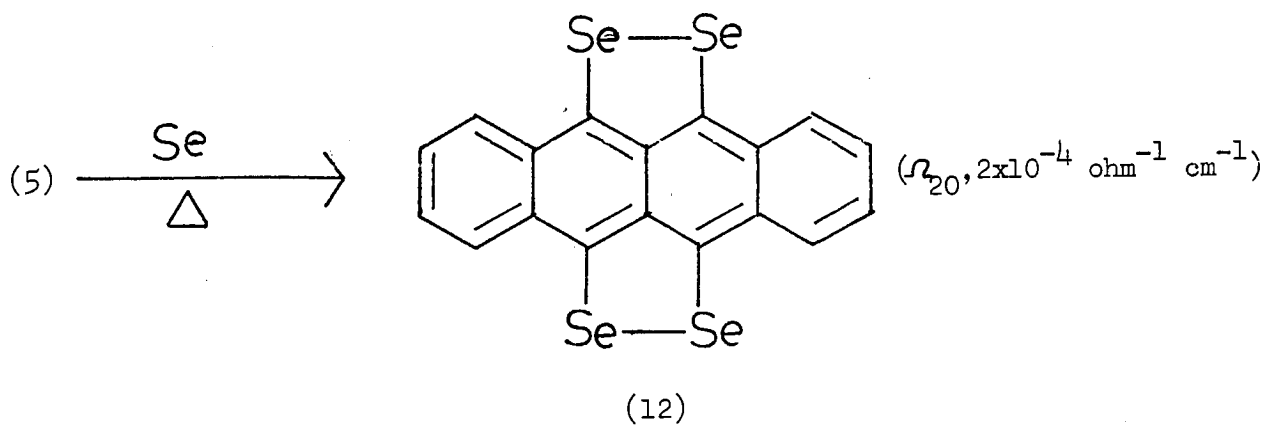
conductivity. Various aspects of this property such as the dependence on pressure[13,14] and temperature[15] have since been reported.

Goodings[16] etal. have reported the electrical conductivities of tetrathiotetracene itself and of some related compounds (the values are given in parenthesis alongside the relevant formulae) and found that they were comparable to those reported for the charge-transfer complexes. Goodings etal. further reported the characterisation of the acene polysulphides reported by Marschalk[1].

Pentacene (2) was treated with elemental sulphur in refluxing trichlorobenzene and dark green needles were isolated. The needles, although not very soluble, were characterised and found to be hexathio-pentacene which was formulated as (13). The electrical conductivity of (13) was in the insulator range, and attempts to isolate a radical cation failed. The poor conductivity and resistance to oxidation were attributed to the enhanced stability associated with the presence of two thiathiophthen ring systems in the molecule. Unlike the 1,2-dithioles, which are easily oxidised to generate cations containing one or more aromatic dithiolylium rings, the fused-ring thiathiophthens do not readily lose electrons since this would rupture the stable 10π aromatic system.

Since tetracene, with four reactive meso-positions, formed a tetrasulphide (4) and pentacene, with six meso-positions, formed a hexasulphide (13), Goodings attempted to synthesise octathiohexacene (14). However, the reaction of hexacene (1) with sulphur produced a black insoluble solid with an empirical formula, $C_{26}H_{10}S_6$ established by analysis and high resolution mass spectroscopy. All attempts to form an octasulphide failed indicating the high stability of the six-sulphur
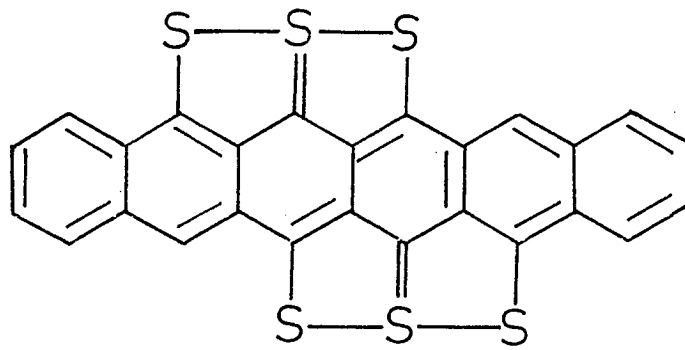
(15a)
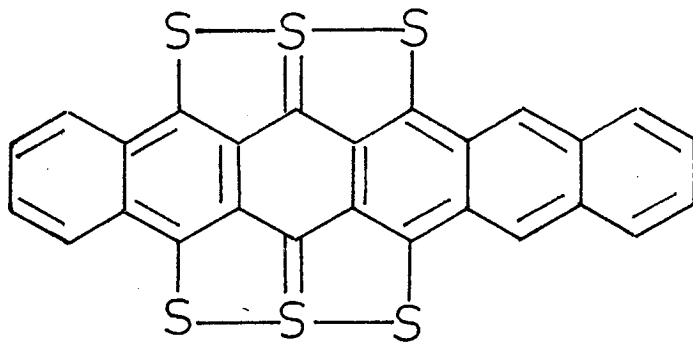
(15b)
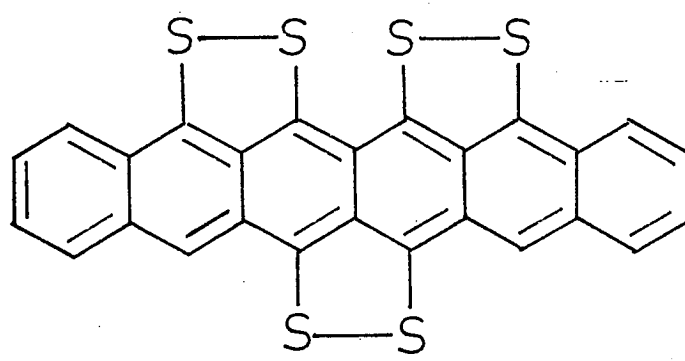
(16)

system. Conductivity measurements showed that the compound was a semi-conductor. The hexasulphide (15) could not be oxidised to a radical cation and no n.m.r. spectrum could be obtained owing to the insolubility of the compound. Goodings suggested structures (15a,b) for the hexathiohexacene but by analogy with hexathiopentacene (13) such structures containing a thiathiophthen ring system would be expected to be insulators i.e. to possess a low conductivity. A third possible structure (16) containing three 1,2-dithiole rings may be formed in small amounts and by analogy with tetrathiotetracene (4) this would be expected to be a semiconductor. There must, however, be some doubts concerning the validity of the conductivity measurements since Goodings (9) etal. found that small amounts(<1 ppm) of other oxidation states present as an impurity in an otherwise pure sample can increase the electrical conductivity by five or six order of magnitude. The failure to synthesise octathiohexacene (14) can be attributed to the stability of the thiathiophthen ring system; assuming a step-wise introduction of sulphur atoms, the formation of the stable hexasulphide (15) presumably precludes the formation of any of the desired octasulphide (14).

At the same time that Goodings reported his studies on acene polysulphides, Davidson[7] also reported the synthesis of a series of polysulphides. It is well known[17] that chlorine atoms in the 1,4,5 and 8 positions in anthraquinone are susceptible to nucleophilic displacement owing to the activating effect of the quinone carbonyl groups and so Davidson treated 1,8-dichloroanthraquinone (17) with sodium sulphide in dimethyl formamide and, on acidification, obtained 5-oxo-5H-anthra(1,9,8-bcde)thiathiophthen (18). In a similar reaction 1,4,5,8-tetrachloroanthraquinone (19) gave a dark green microcrystalline

(17)   i) Na₂S   ii) HCl   (18)

(19)   Na₂S   (20)

(21)

(22)

(23)

(24)

(25)

(26) or the 1,5-diMeS isomer

H_2O

(21) and/or (22)

disulphoxide (s)

monosulphoxide(s)
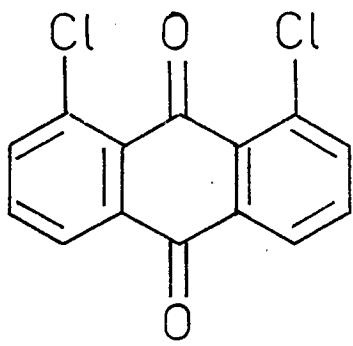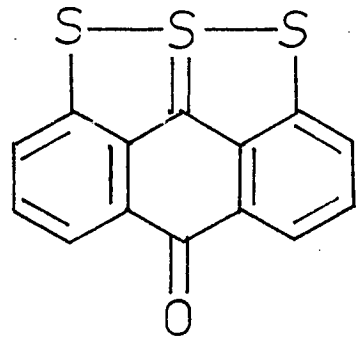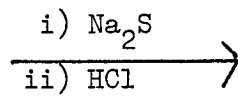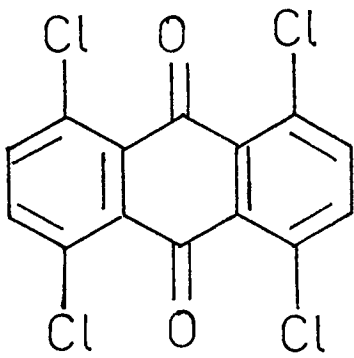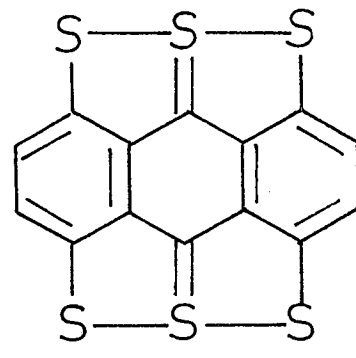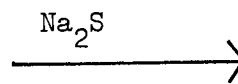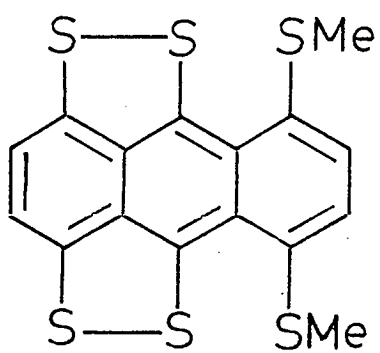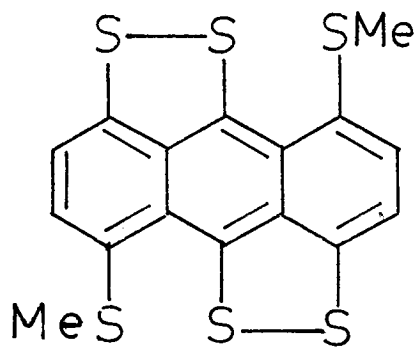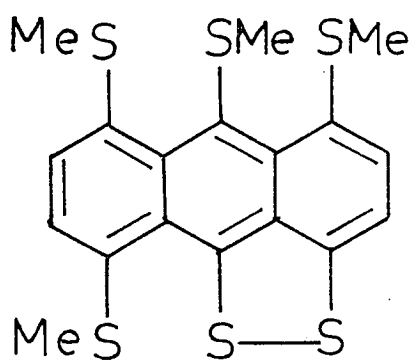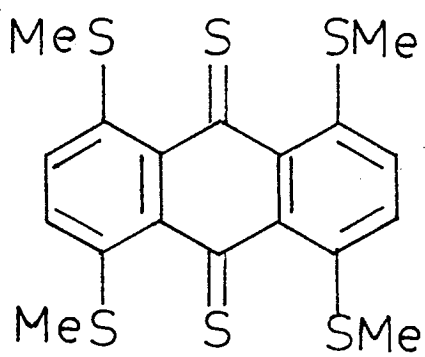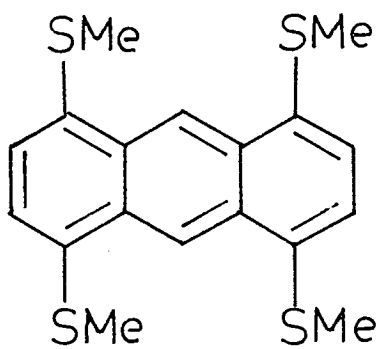
solid with a metallic lustre to which Davidson assigned the structure
(20). Anthra(1,9,8-bcde:5,10,4-b'c'd'e')bis(thiathiophthen) (20) was
not obtained pure, however, and the evidence for its structure rested
solely on the mass spectrum and an exact mass measurement.

Steven[18] repeated Davidson's synthesis of "hexathioanthracene"
(20) and isolated it in a pure state. Since hexathioanthracene (20)
is insoluble in most solvents, proof of its structure is dependent on
chemical degradation into more soluble and characterisable products.

Accordingly, hexathioanthracene (20) was reduced with alkaline
dithionite and the reduced product was methylated. Steven thus isolated
a mixture of products in a low yield which he attempted to characterise
by mass spectroscopy. A mass spectrum of the mixture contained peaks
at ^{m}/e values 424, 394 and 362 (hexathioanthracene, ^{m}/e = 364) and
Steven suggested structures (21-25) as some of the possible products.
Since the products were isolated in a low yield Steven did not attempt
to separate the mixture.

The reaction of hexathioanthracene (20) with methylfluorosulphonate
("Magic Methyl") followed by water also gave a mixture of at least
three products (shown by H.P.L.C.) with peaks at ^{m}/e 426, 410, 394 and
364, as the possible parent ions. It was suggested that these products
might be formed from a di(methylthio)anthracenobis(1,2-dithiolium) salt
such as (26) by reaction with water and disproportionation to give an
anthracenobis(1,2-dithiole) (21 and/or 22), ^{m}/e 394 and its mono- and
disulphoxides, ^{m}/e 410 and 426.

Since Steven could not isolate any products in a pure form none
of the structures suggested could be confirmed. Thus the structure
of hexathioanthracene (20) has yet to be established unambiguously.
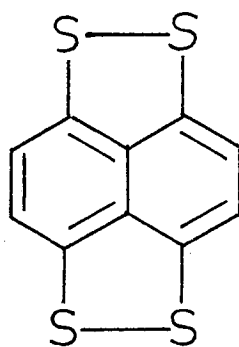
(27)
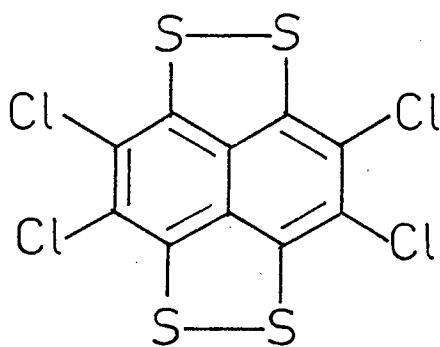
(28)

chromic acid

Raney nickel
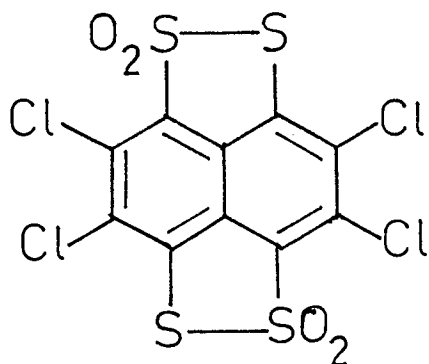
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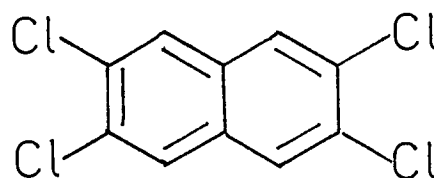
(30)

A compound closely related to tetrathiotetracene (4) is naphtho [1,8-cd:5,4-c'd']bis[1,2]dithiole (27) and Wudl[19] has recently synthesised this "tetrathionaphthalene", in yields of 6-10% by the reaction of naphthalene-1,5-dithiol with sulphur dichloride under Friedel-Crafts conditions followed by a reductive work-up. The reaction of tetrathionaphthalene (27) with 7,7,8,8-tetracyanoquinodimethane in trichlorobenzene gave a charge-transfer complex. Conductivity measurements on the complex gave a value of approximately $40 \, \Omega^{-1} cm^{-1}$ compared to $1 \, \Omega^{-1} cm^{-1}$ for the corresponding tetrathiotetracene (4)-TCNQ complex.

The 2,3,6,7-tetrachloro derivative (28) of tetrathionaphthalene (27) was reported by Klingsberg[20] in 1972 who isolated it from the fusion of octachloronaphthalene with sulphur at $310°C$. The only reported[21] reactions of compound (28) are the oxidation with chromic acid to give the bis(disulphoxide) (29) and the reduction with Raney nickel to produce 2,3,6,7-tetrachloronaphthalene (30).

The related naphthalene-1,8-disulphide (31) was first synthesised by Lanfrey[22] and more recently by Price and Smiles[23] and by Zweig and Hoffman[24].
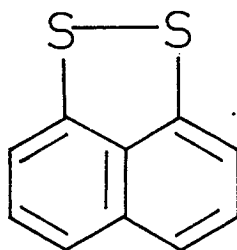
(31)

Naphthalene[1,8-cd](1,2)dithiole (31) is reported to readily form charge-transfer complexes with electron acceptors[24] and the radical cation has been isolated and studied by electron-spin resonance[24,25] and ultra-violet spectroscopy.

Section two.   4-Thioacyl-1,2-dithiole-3-thiones

In 1925 Arndt[26] investigated the reaction of diacetylacetone
(32) with phosphorus pentasulphide in benzene and on the basis of
elemental analysis and molecular weight determinations assigned the
structure (33) to the product.

(32)   (33)
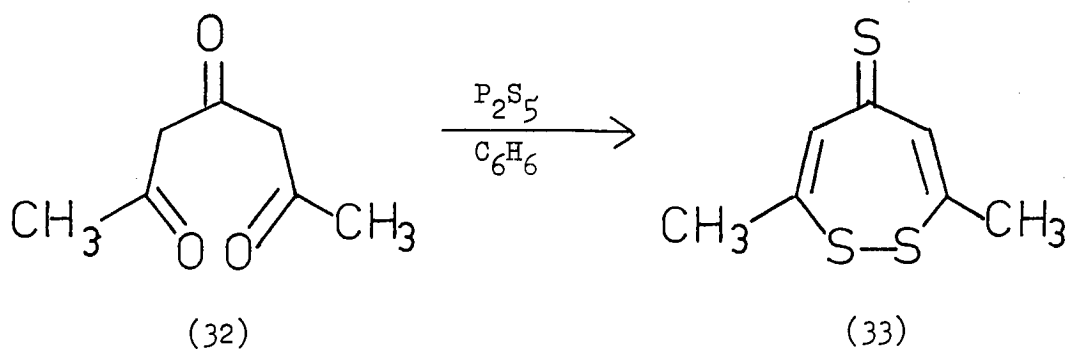
The structure was not disputed until 1958 when Bezzi etal.[27-29]
carried out an X-ray analysis and established that the product was
2,5-dimethyl-6a-thiathiophthen (34). The X-ray analysis established
that the compound was planar, and that the three-sulphur atoms were
co-linear. The S-S bond length (2.36Å) was considerably shorter than
twice the Van der Waals radius of sulphur (3.70Å) but longer than the
normal disulphide bond (2.04Å).

(34)
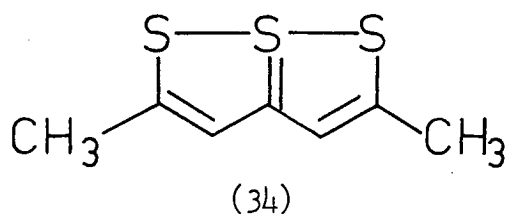
The result was explained by postulating resonance between two equivalent structures (34a,b) which exemplify a type of electron delocalisation known as "single bond - no bond resonance".

(34a)   (34b)
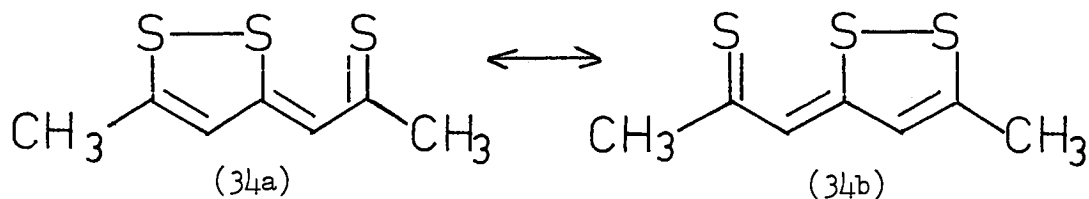
Since the report by Bezzi numerous 6a-thiathiophthens have been synthesised[30] and a great deal of controversy has arisen concerning the fine structure of the system. They have been represented as "single bond - no bond" resonance hybrids (34a,b), as structures containing a central tetravalent sulphur (35) or as an "electron-rich three-centre bond" stabilised to some extent by π-electron conjugation (36).

(35)   (36)
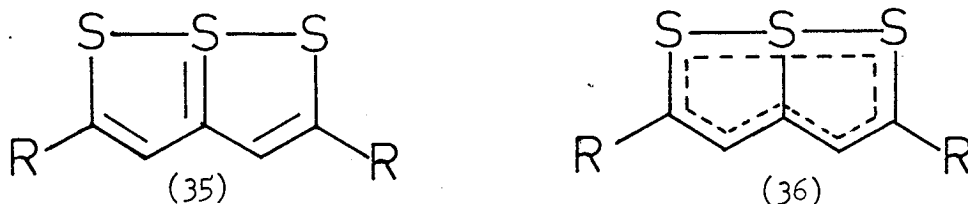
Leaver[31] etal. sought related examples of tautomeric, or mesomeric structures, and investigated the four-sulphur system of 4-thioacyl-1,2-dithiole-3-thione (37).

Employing Teste's[32] procedure for the synthesis of (37a), by the action of phosphorus pontasulphide on (38a) in refluxing xylene, Lever etal. synthesised the compounds (37b-f).
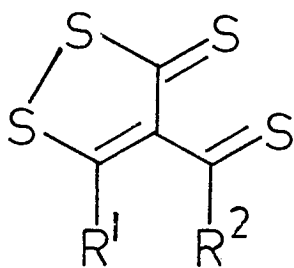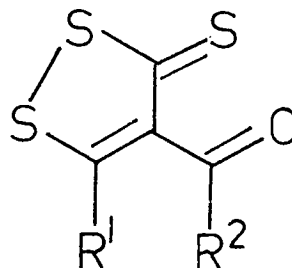
(37)   (38)

	R^1	R^2
a)	Ph	Ph
b)	p-MeC$_6$H$_4$	p-MeC$_6$H$_4$
c)	Ph	p-MeC$_6$H$_4$
d)	p-MeC$_6$H$_4$	Ph
e)	Ph	p-MeOC$_6$H$_4$
f)	p-MeOC$_6$H$_4$	Ph

The 'H n.m.r. spectrum of compound (37b) contained two methyl singlets at 2.35 and 2.30 δ indicating that the two aryl groups were not rendered equivalent by single bond - no bond resonance. Attempts to synthesise (37c) and 37d) gave identical products which, as shown by the presence of two methyl signals in their n.m.r. spectra, were mixtures of the two isomeric thioacyl compounds. A similar result was obtained for the isomers (37e) and 37f). The authors concluded that the isomeric thioacyl compounds (37;$R^1 \neq R^2$) were interconvertible but that the taut-omeric equilibrium was not rapidly established on the n.m.r. time scale at ambient temperature.

Davidson[7] suggested that the observations made by Leaver etal. might not be giving a valid indication of whether or not single bond -

(44)　　　　　　　(43)　　　　　　　(45)

P_2S_5

(41)
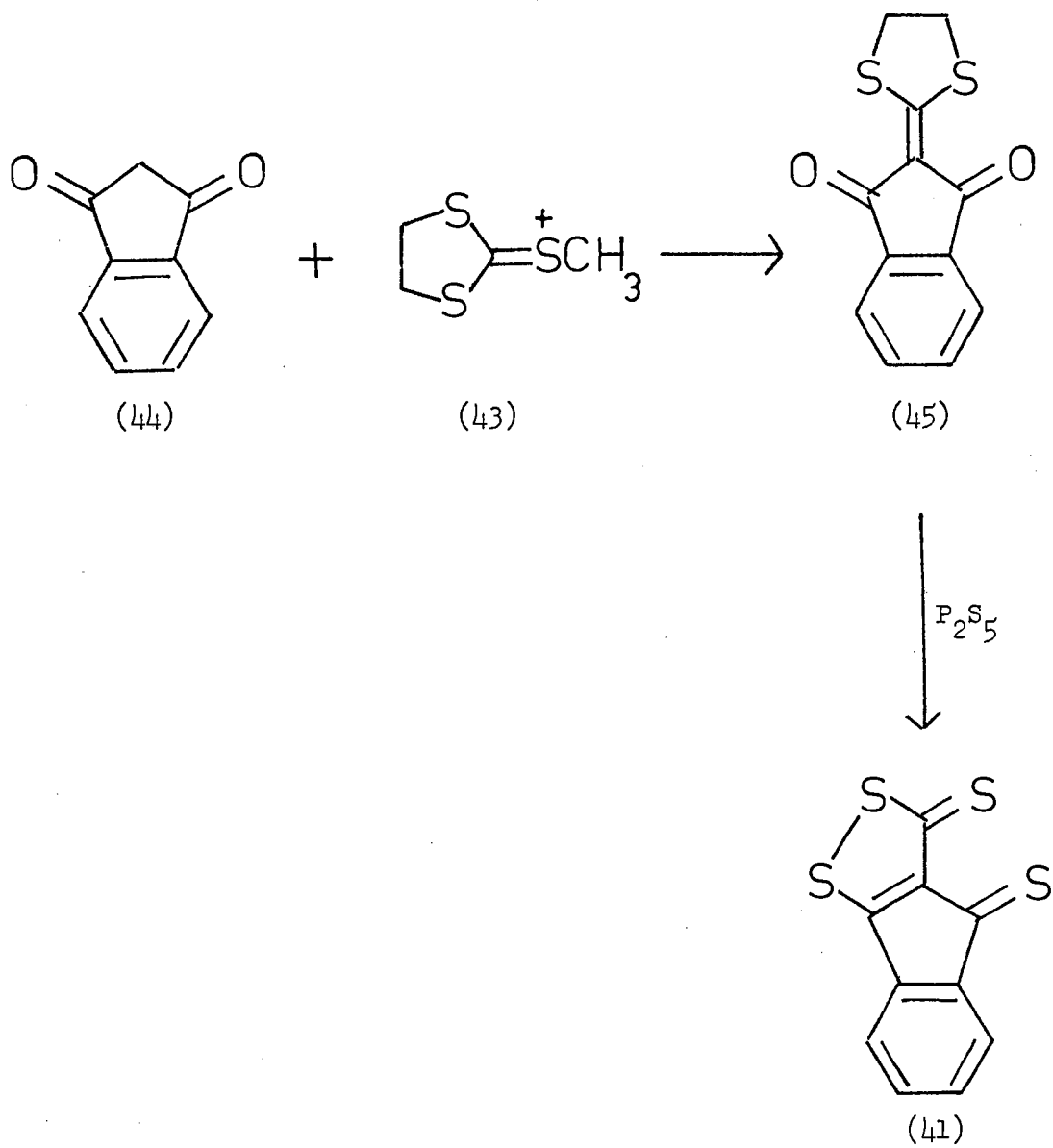
Scheme 1

no bond resonance was occurring in this system since it was possible that the preferred conformations of the compounds were such that there was no interaction between the two thione sulphur atoms (39).
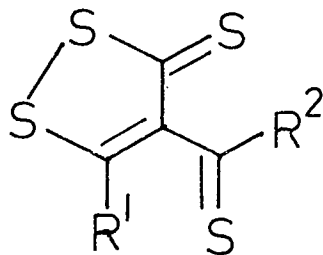
(39)

Davidson then attempted to synthesise the compounds (40-42) which were fixed in the most favourable conformation for single bond - no bond resonance to occur.
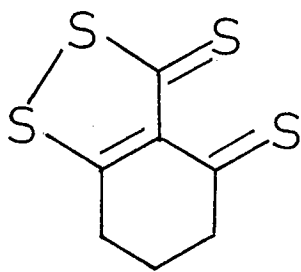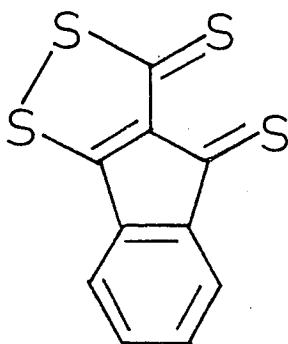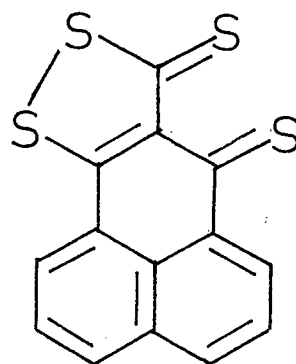
(40)   (41)   (42)

The attempted synthesis involved the reported reaction of 2-methyl-thio-1,3-dithiolanium methosulphate (43) with compounds containing an activated methylene group[33] and then treatment of the condensation product with phosphorus pentasulphide. It was expected that this procedure, in addition to replacing oxygen by sulphur, would remove the ethylene bridge, as in Raoul and Vialle's[34] synthesis of 1,2-dithiole-3-thiones from dithiolanylidene ketones. The proposed synthesis is shown in scheme 1 exemplified by using indan-1,3-dione (44).
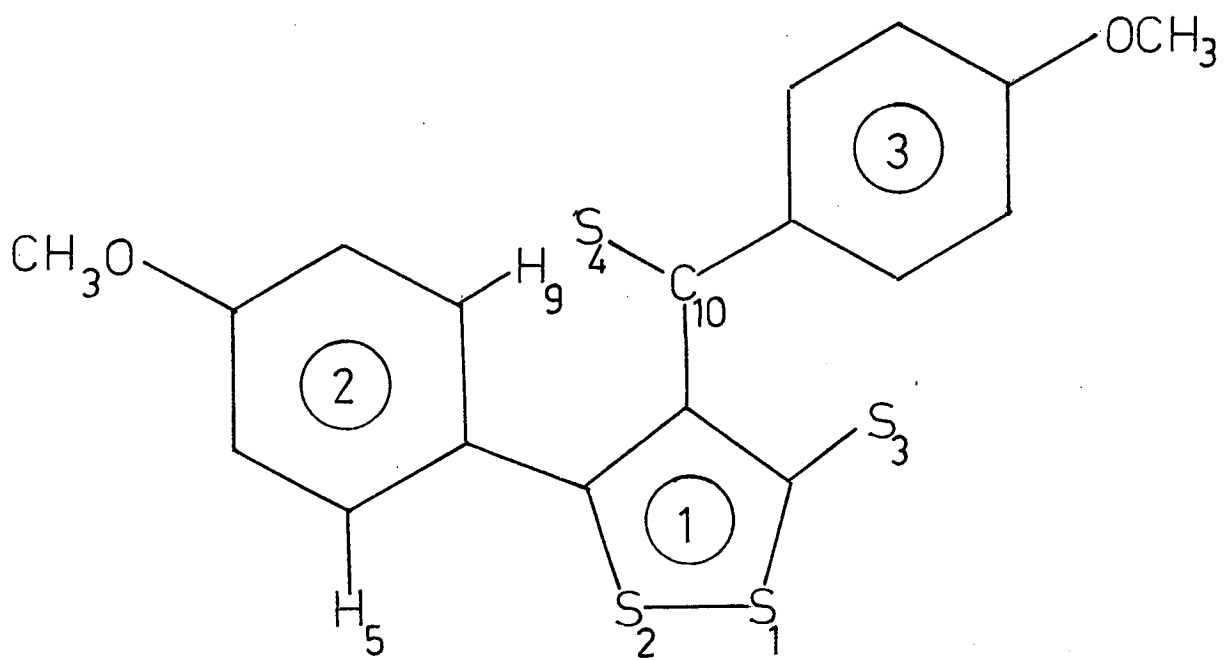
In all cases the condensation product (45) was isolated (and characterised) but treatment with phosphorus pentasulphide did not produce any of the desired compounds. Davidson suggested that this was possibly due to lack of a stable aromatic ring system in the case of (40) and possibly due to sterio hindrance in examples (41,42).

Davidson's suggestion that the preferred conformations may not allow any interaction between the two thione sulphur atoms (39) has recently been confirmed by Nyburg[35].

Nyburg etal. carried out a crystal structure analysis on compound (37b) and established that the sulphur atoms, S_1 and S_2, are single-bonded, 2.044Å, and that the sulphur atoms, S_3 and S_4, are non-bonded and so the molecule is without mirror symmetry. The structure is a compromise between attempts to obtain mutual coplanarity of rings 1 and 2, (to yield maximum π- conjugation) and to avoid interactions between H_9 and C_2 and C_{10}, and H_5 with S_2.

Calzaferri and Gleiter[36] have carried out extended Hückel cal-culations on 4-thioformyl-1,2-dithiole-3-thione (46) and its valence tautomerisation.

(46a)   (46b)
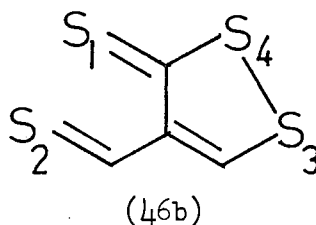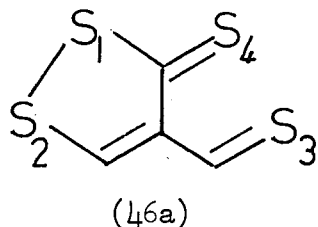
The valence tautomerism is complicated as there are at least two non-synchronous and one synchronous path for the narcissistic reaction[37]
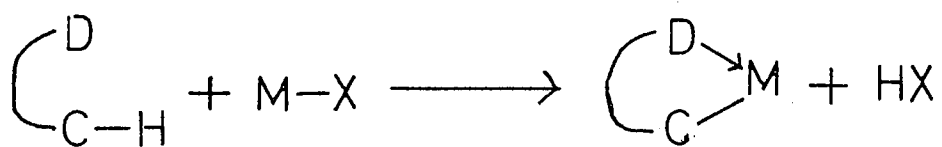
D = donor atom

M = transition metal

X = leaving group

fig. (i)

(48)

(47)

$PdCl_4^{2-}$

(49)
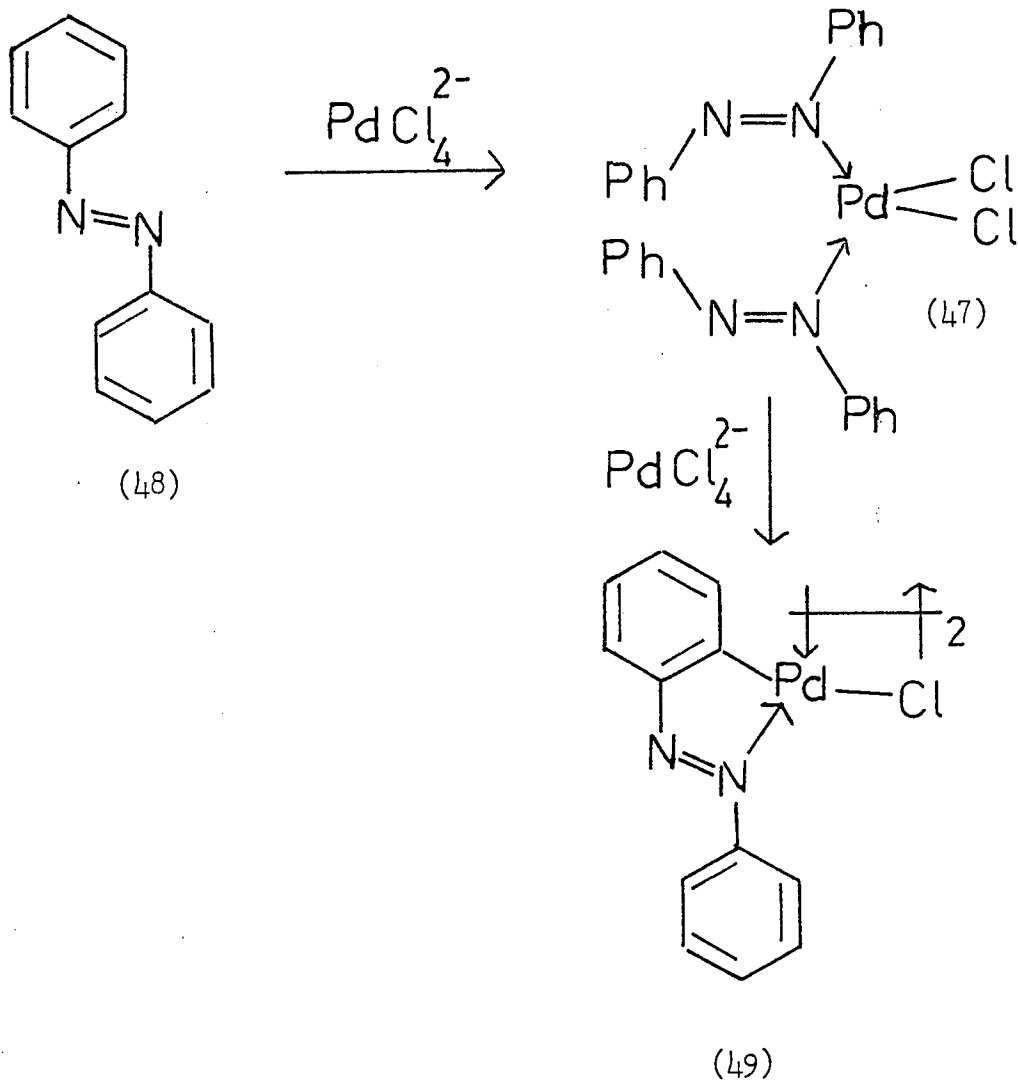
fig. (ii)

providing that all carbon-carbon and carbon-sulphur bond lengths are not changed. The three paths are:

(i) From (46b), the S_3-S_4 bond is lengthened until the S_1-S_2 and S_3-S_4 distances are equal (C_2v symmetry) then the S_1-S_2 bond is shortened to give isomer (46a).

(ii) A concerted path is followed and while S_3-S_4 is lengthened S_1-S_2 is shortened.

(iii) The distance S_1-S_2 is shortened until the S_1-S_2 and S_3-S_4 distances are equal, then the S_3-S_4 bond is lengthened.

They calculated that path (iii) will show a crossing between a low-lying empty π-orbital and the antibonding lone pair combination at S_1 and S_2 thus making this the less favourable path.

Calzaferri and Gleiter further calculated the activation energy for compound (46) to be 1.5 eV, a value that is consistent with the experimental findings of Leaver et al.[31]

Section three.   Cyclometallation reactions and their use
in organic synthesis

Although a number of compounds with transition metal-carbon bonds has been known for a long time it is only comparatively recently that it has become recognised that the formation of bonds to carbon is a general, and characteristic, property of all d-group transition metals.

Trofimenko[38] introduced the term "cyclometallation" to describe those reactions of transition metal complexes in which a ligand under-goes an intramolecular (or more rarely, intermolecular) metallation with the formation of a chelate ring containing a metal-carbon σ-bond. The

chelate ring is usually 5-membered and a variety of transition metals in groups VI - VIII have been reported to form cyclometallated complexes. The general reaction is shown in figure (i).

Cyclometallation reactions have recently been comprehensively reviewed by Bruce[39] and so only those aspects which are relevant to the present study will now be described. Thus the discussion will be limited to (a) the formation and general reactions of cyclopalladated complexes, and (b) the use of cyclometallated complexes in heterocyclic synthesis.

(a)   The formation and general reactions of cyclopalladated complexes

Normally the formation of the palladium-carbon σ-bond occurs instantaneously by the direct interaction of the donor ligand and palladium reagent, the eliminated aryl hydrogen combining with a suitable leaving group - see figure (i).

(i)   Palladium reagents

The commonest palladium reagents are sodium (or lithium) tetrachloropalladate and palladium acetate. Bis(benzonitrile)palladium dichloride has been used in the palladation of a limited number of ligands. In the formation of a cyclopalladated complex an intermediate ligand-metal complex without a palladium-carbon σ-bond (47) is initially formed, this complex is normally not isolable, and then cyclisation occurs with the elimination of the aryl-hydrogen. This process is illustrated in figure (ii) exemplified with azobenzene (48).

Occasionally palladation occurs on heating (50-150°C) the reaction mixture with an inert solvent as the reaction medium and heat transfer agent.

(50)

a: R = H
b: R = CH$_3$O

(51)

a: R = H
b: R = CH$_3$O

(52)

$\dfrac{\text{Na}_2\text{PdCl}_4}{\text{CH}_3\text{OH}}$
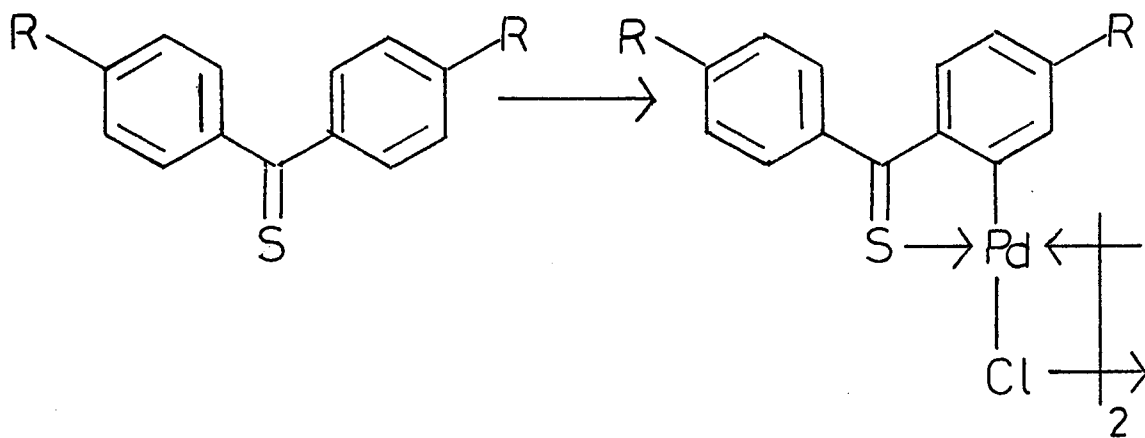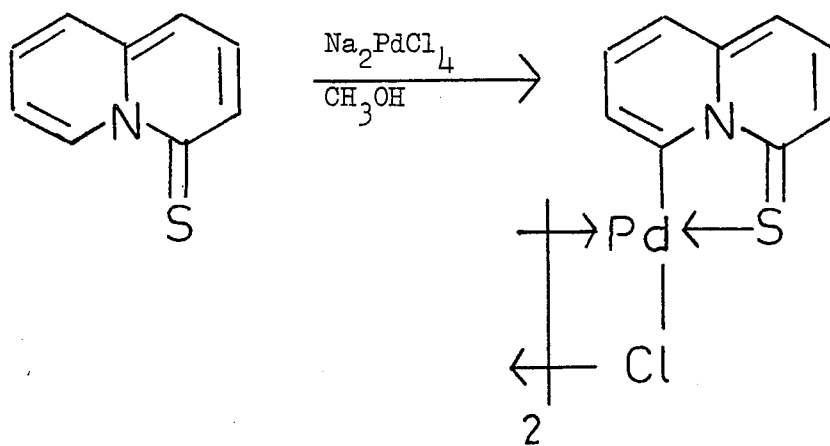
(53)

(ii)   Types of ligands that undergo cyclopalladation

The type of ligands that may be cyclopalladated can be classified according to the nature of the donor atom, the commonest donor atoms being phosphorous, nitrogen and sulphur. The remaining discussion will be limited to ligands containing sulphur or nitrogen as the donor atom since only these types were used in the present work.

Cyclopalladated sulphur donor ligands

Alper[40] in 1973 reported the first orthopalladation of a sulphur donor ligand, namely the reaction of thiobenzophenone (50a) with sodium tetrachloropalladate in methanol. At ambient temperature a complex containing no palladium-carbon σ-bond (similar to 47) was obtained, but on reflux cyclisation occurred with loss of hydrogen chloride to give the ortho-palladated complex (51a).

Davis[41] carried out a similar cyclopalladation reaction with quinolizine-4-thione (52) and obtained di-μ-chlorobis(4-thionoquino-lizin-6-yl)dipalladium (II), (53). However, he reported that attempts to repeat the reaction failed and a variety of uncharacterisable complexes was isolated. At present no further work has been reported on cyclopalladated sulphur donor ligands but cyclometallated iron complexes of thiobenzophenones have been reported and some of their reactions will be discussed later.

Cyclopalladated nitrogen donor ligands

The majority of work reported on cyclopalladation is concerned with the use of nitrogen donor ligands and, as a consequence, numerous cyclopalladated complexes with a variety of different nitrogen ligands are known. Cyclopalladated nitrogen donor complexes can be classified
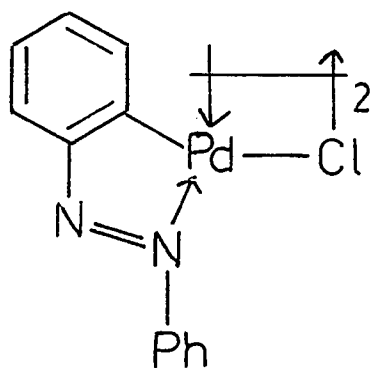
(49)
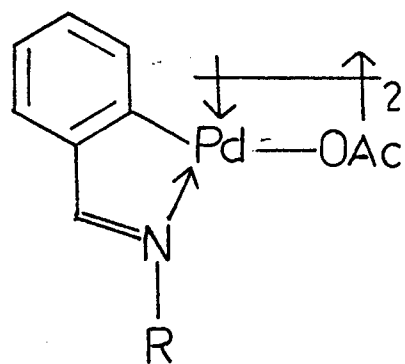
(54)
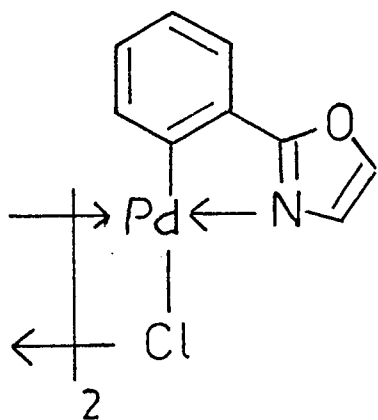
(55)
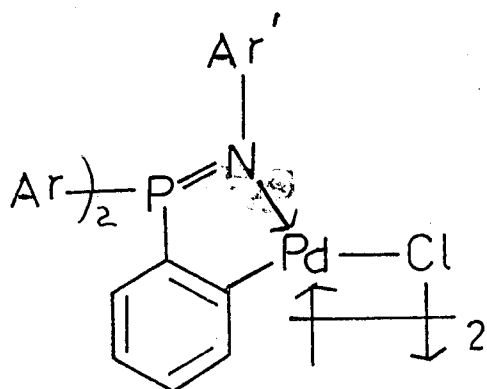
(56)
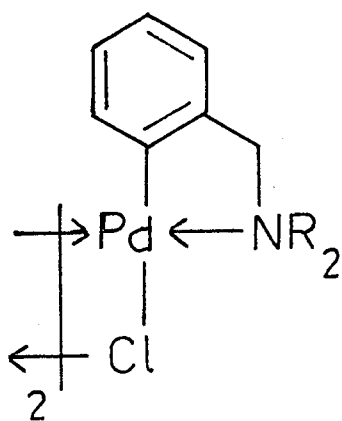
(57)

into five main groups according to the nature of the nitrogen donor:

(1)   azobenzene and its derivatives,

(2)   the isoelectronic, and isostructural, Schiff bases and

        related azomethines such as oximes and hydrazones,

(3)   suitably phenyl-substituted nitrogen heterocycles,

(4)   phosphinimines,

(5)   N,N-dialkyl benzylamines and N,N-dialkyl-1-naphthylamines.

These groups are illustrated by the cyclopalladated complexes (49,54-57) shown opposite.

(1)   Azobenzene and its derivatives as nitrogen donor ligands

The first cyclometallation involving a nitrogen donor ligand was reported in 1963 by Kleiman and Dubeck[42] who found that treatment of azobenzene (48) with nickelocene produced the orthometallated nickel complex (58).

(58)
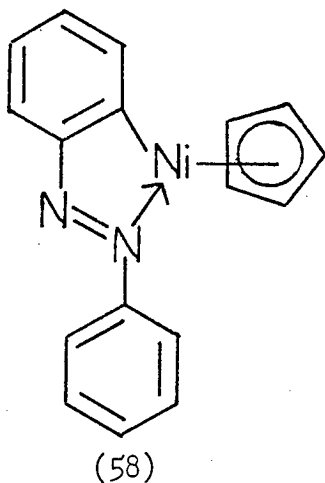
Since 1963 many cyclometallated azobenzene complexes have been reported. Cope[43], in 1965, reported the reaction of azobenzene and sodium tetrachloropalladate which gives the orthopalladated complex, di-μ-chlorobis[2-(phenylazo)phenyl]dipalladium(II), (49). Substituted azobenzenes react in the same way.

(59)

a: R = H
b: R = CH₃O

(61)

$\xrightarrow[\text{Me}_2\text{CO}]{\text{NaCl}}$
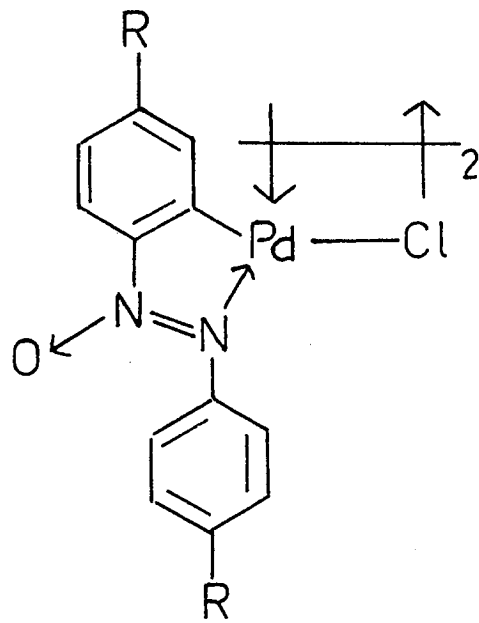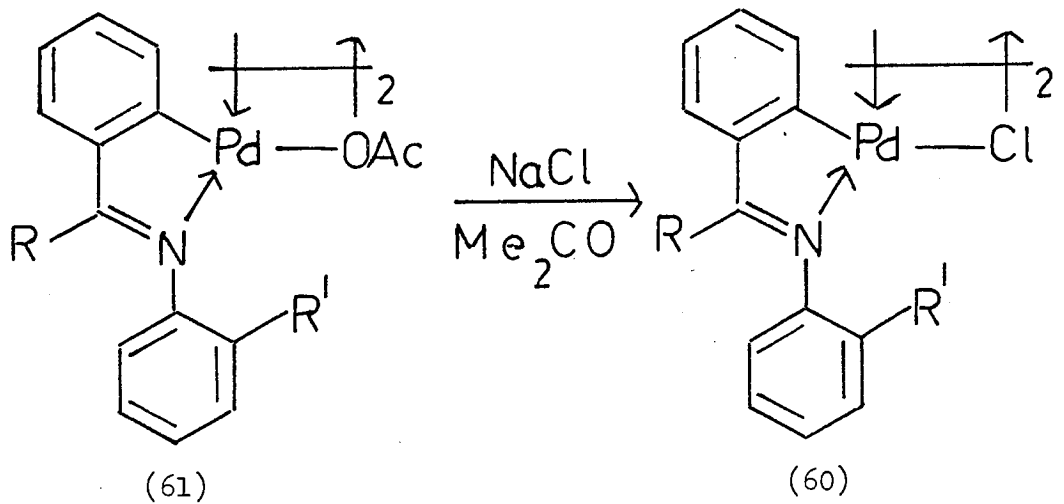
(60)

a: R = R' = H
b: R = H, R' = CH₃
c: R = CH₃, R' = H

Balch and Petridis[44] in 1969 reported the orthopalladation
of azoxybenzene (59a). In contrast to the reaction of azobenzene
which occurs immediately on mixing the reagents, the palladation of
azoxybenzene occurs over a period of 48 hours in refluxing methanol.
The relative resistance of azoxybenzene to palladation is presumably
due to electron-withdrawal by the azoxy-group (which is isoelectronic
with the nitro group) from the phenyl group which is undergoing
substitution. Bruce[45] and his co-workers later reported the
synthesis of the orthopalladated 4,4'-dimethoxyazoxybenzene (59b)
and confirmed the structure by characterising the monomeric ortho-
palladated complexes formed by "bridge-splitting" reagents. The
bridge-splitting reactions will be referred to later and discussed
in more detail.

(2) Schiff bases as nitrogen donor ligands

In 1969 Molnar and Orchin[46] reported that treatment of a number
of Schiff bases with bis(benzonitrile)palladium dichloride in methanol
gave orthopalladated complexes of the type (60). Many authors[47-49]
have since disputed this work.

Onoue and Moritani[48], on repeating Molnar's work, isolated no
cyclopalladated products and reported that the major product (69%) was
dichlorodianiline palladium (II). These workers and Lewis and his
co-workers[49] concluded that the aniline complex was formed by
hydrolysis of the N-benzylidene aniline ligand after co-ordination
to palladium.

Onoue further reported the synthesis of the acetate-bridged ortho-
palladated Schiff base complexes (61) which were converted into the
chloride-bridged complexes (60) by a metathetical reaction with sodium
chloride in acetone.
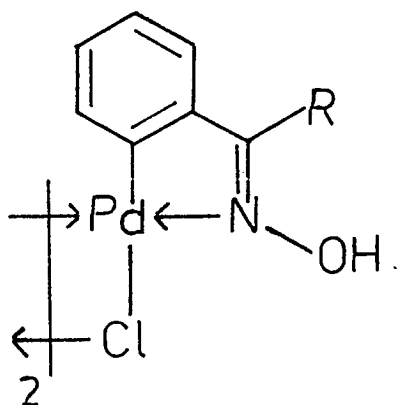
(62)
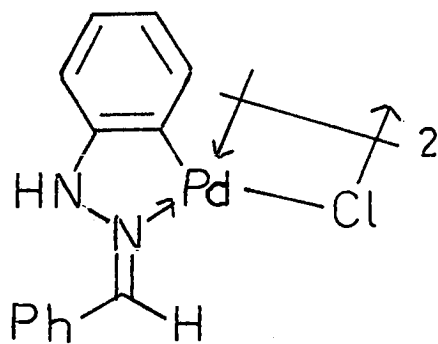
(63)
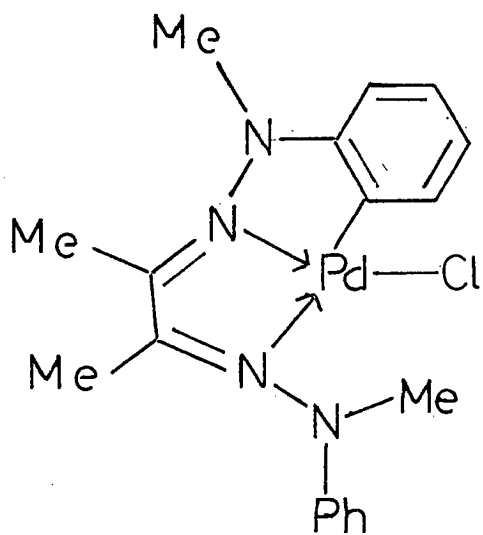
(64)
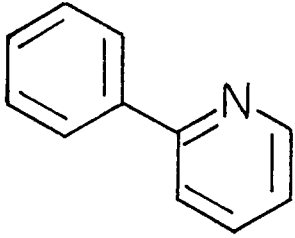
(65)
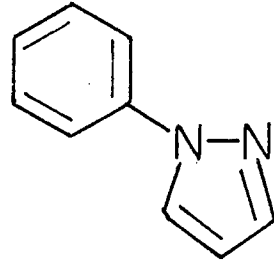
(66)
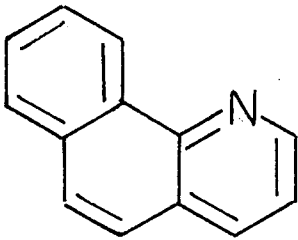
(67)
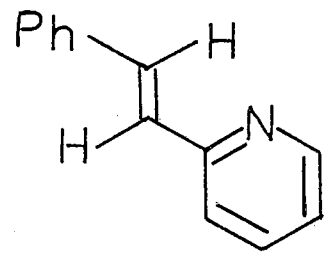
(68)

Heck[50] has also reported the <u>cyclopalladation</u> of a series of novel Schiff bases and the results of various carbonylation reactions performed on the resultant complexes.

A limited number of related azomethines has been reported to undergo cyclopalladation, examples include aromatic oximes[51,52] (62), phenyl hydrazones[49] (63) and osazones[53] (64).

(3) <u>Phenyl-substituted nitrogen heterocycles as nitrogen donor ligands</u>

A consideration of the geometry of many nitrogen heterocycles containing a phenyl substituent α to nitrogen suggests that easy metallation of the phenyl ring should occur to form a 5-membered chelate ring.

Many phenyl-substituted nitrogen heterocycles have been reported to undergo cyclopalladation including 2-phenylpyridine[41,54,55] (65), 4-phenyl pyrimidine[54] and 1-phenylpyrazole[38,54] (66). Related to these <u>ortho</u>metallations are the metallation reactions of benzo[<u>h</u>]quinoline[49,56,57] (67) and 2-styryl pyridine[41] (68), the latter being an example in which an olefinic carbon is bonded to the metal instead of an aromatic carbon.

The first examples of this type were the reactions of 2-phenylpyridine and 2-phenylquinoline to give the cyclopalladated complexes, illustrated by structure (69a), on treatment with sodium tetrachloropalladate in methanol at ambient temperature. Nonoyama and Yamasaki[58,59]
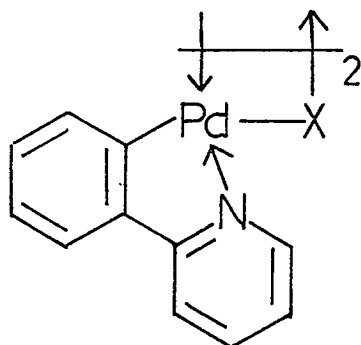
(69)

a: X = Cl

b: X = OCOCH₃
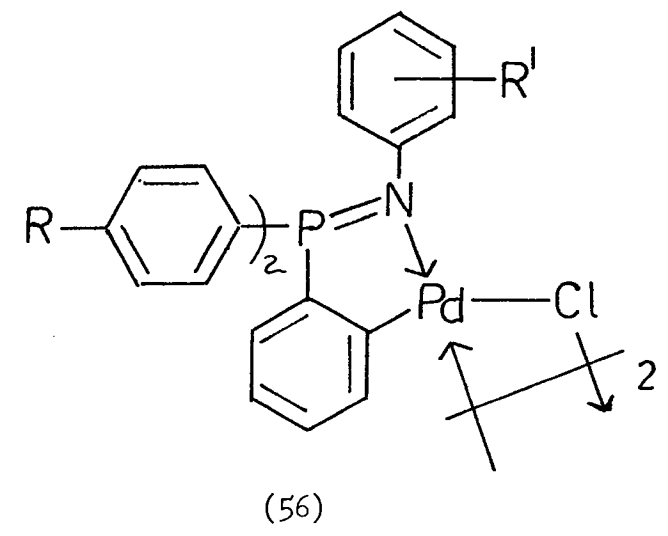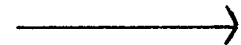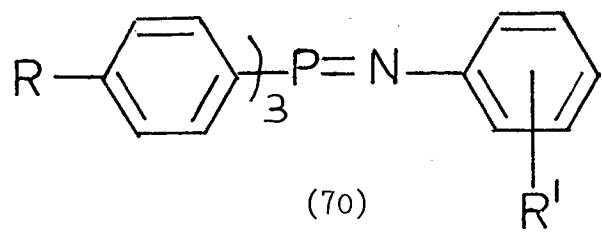
R = H, R' = m-Me, p-Me, p-MeO
R = Me, R' = p-MeO

PhCH₂NH—R $\xrightarrow{\text{Na}_2\text{PdCl}_4}$
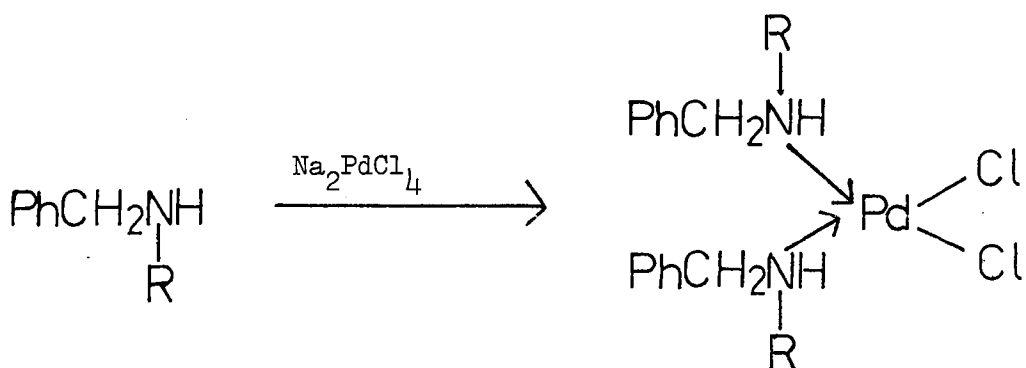
(71)

a: R = H
b: R = CH₃
c: R = C₆H₅
d: R = C₆H₅CH₂

(73)

a: R = H
b: R = CH₃
c: R = C₆H₅
d: R = C₆H₅CH₂
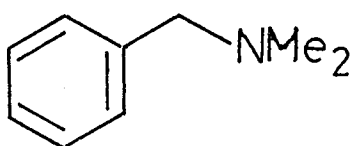
(72)
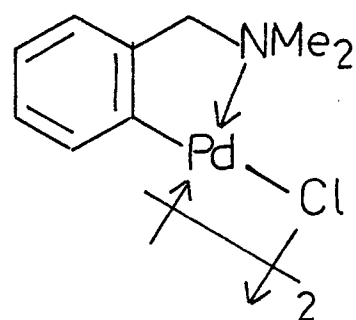
(74)
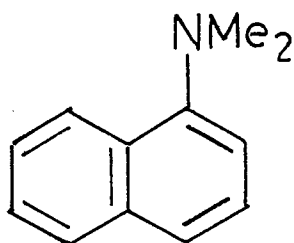
(75)

later reported the synthesis of the cyclopalladated benzo[h]quinoline complex and the results of some ligand exchange reactions on the complex.

The palladation of 1-phenylpyrazole (66) is of a different type to that of 2-phenylpyridine (65), since in the latter case palladation of a carbon-phenyl group occurs whereas the former is palladation of a nitrogen-phenyl group. The course of palladation is not altered, or affected, by the change of carbon for nitrogen, but is dependent on the geometry of the molecule.

Nonoyama[60] and Sokolov[61] and his co-workers have reported the palladation of 8-alkylquinoline derivatives. These reactions are different to the preceding type since it is an alkyl hydrogen that is replaced by palladium. This type of reaction will be discussed in greater detail later.

(4)   Phosphinimines as nitrogen donor ligands

Alper[62] has recently reported the cyclopalladation of a series of phosphinimines (70). The phosphinimines were treated with sodium tetrachloropalladate in methanol at ambient temperature and yields of 56-97% of the cyclopalladated complexes (56) were obtained. The structures were confirmed by elemental analysis and a study of the 'H n.m.r. spectra.

(5)   N,N-Dialkylbenylamines and N,N-dialkyl-1-naphthylamines as
       nitrogen donor ligands

Cope[63] and his co-workers in 1968 investigated the reaction of a series of substituted benzylamines with palladium (II), and platinum (II), complexes. They reported that primary and secondary benzylamines (71)

Scheme 2

(76)

a: R = H

b: R = Me

(77)

(78)

(79)
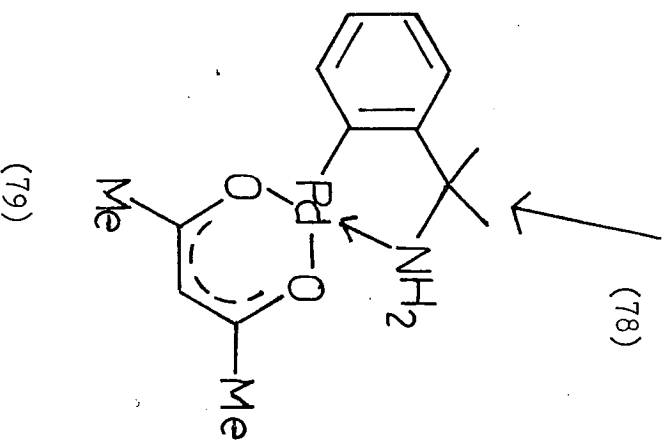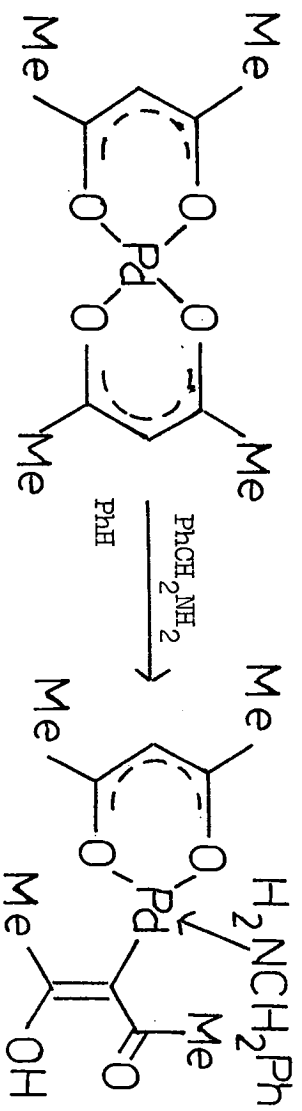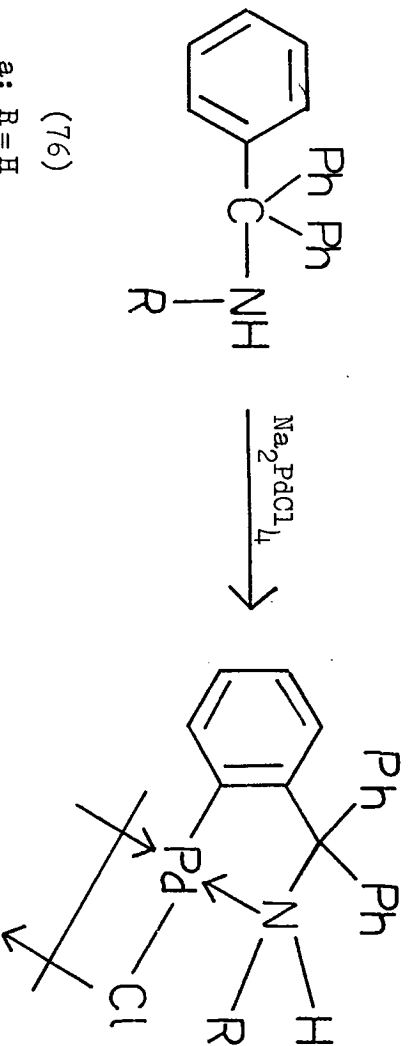
reacted with the metals to give the diaminodichloropalladium (II) complexes (73) whereas cyclopalladated complexes (74) were obtained from the reaction with tertiary amines (72). N,N-Dimethyl-1-naphylamine (75) also reacted to give a cyclopalladated product and Cope suggested that palladation had occurred in the 8-position thus permitting the formation of a 5-membered chelate ring.

To ascertain whether the formation of a 5-membered chelate ring was essential for palladation to occur Cope studied the reaction of lithium tetrachloropalladate with N,N-dimethyl-2-phenylethylamine and N,N-dimethyl-3-phenylpropylamines. Had cyclopalladation occurred in these compounds, complexes containing 6- and 7- membered chelate rings would have been formed but, in practice, only complexes of type (73) were isolated.

Lewis[49] et al. reported that substitution of the α-benzyl position (in benzylamines) with bulky groups favoured the formation of cyclopalladated complexes. They further reported that triphenylmethylamine (76a) and N-methyltriphenylmethylamine (76b) reacted with sodium tetrachloropalladate to give the cyclopalladated complexes (77). This was the first reported cyclopalladation of a primary and secondary amine.

Baba and Kawaguchi[64], in 1975, reported the cyclopalladation of benzylamine and 1-aminonaphthalene by treatment with palladium acetylacetonate in refluxing benzene. They further reported that if the reaction was carried out at ambient temperature, a non-cyclised complex (78) was isolated. The complex (78), (2,4-pentanedionato-0,0') (2,4-pentanedionato-C^3)(benzylamine)palladium (II) cyclised rapidly to the cyclopalladated complex (79) in refluxing benzene (Scheme 2).

Et$_2$N —⟨benzene ring⟩— NEt$_2$

(80)

Na$_2$PdCl$_4$

(81a)

Cl—Pd
Et\N→Pd
Et
⟨aromatic ring with two CH$_2$NEt$_2$ groups coordinated to Pd-Cl⟩
Et—N←Pd—Cl
Et

(81b)

Et\N→Pd
Et   Cl
⟨aromatic ring⟩
Et—N←Pd
Et   Cl Cl

$$\xrightarrow{\text{Na}_2\text{PdCl}_4}$$
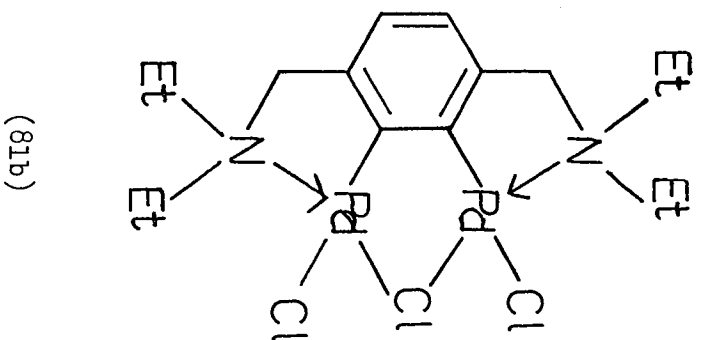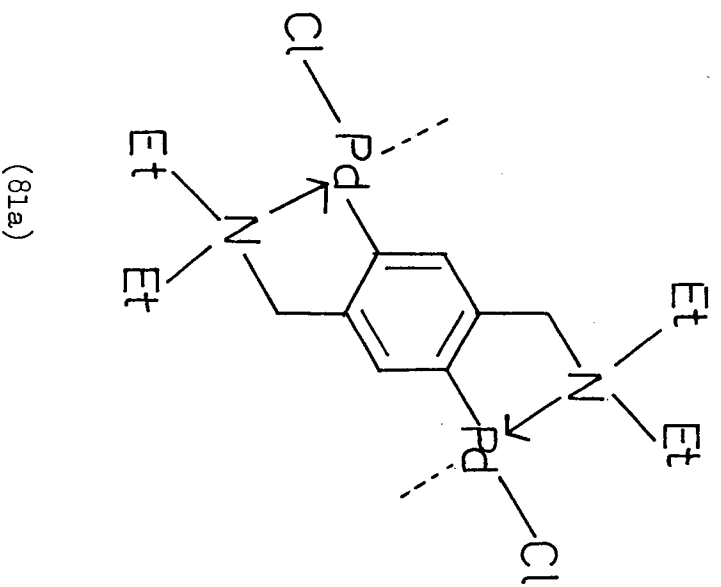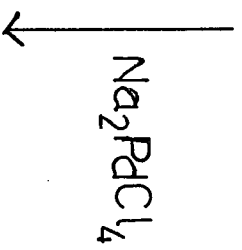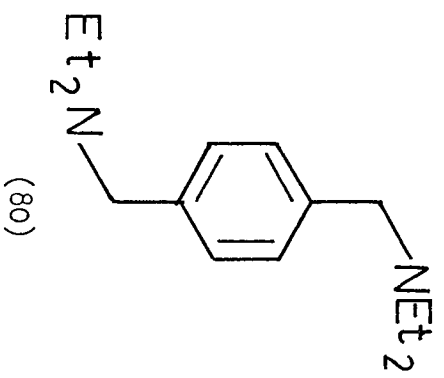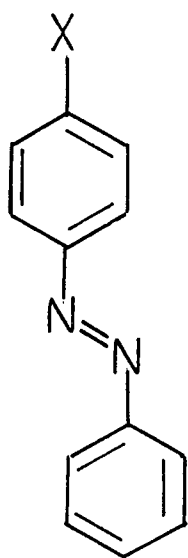
(82)
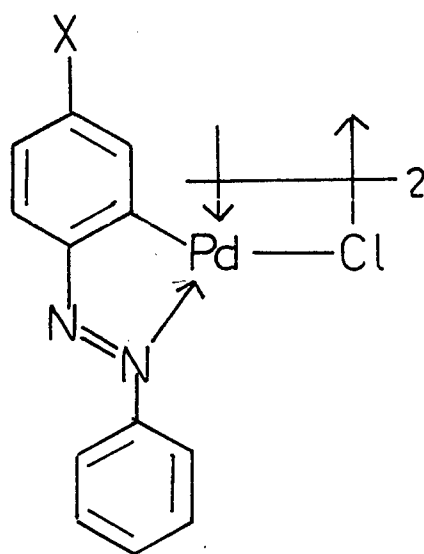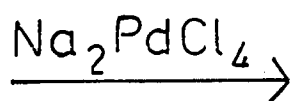
a: X = MeO
b: X = Me
c: X = H
d: X = Cl

(83)

a: X = MeO
b: X = Me
c: X = H
d: X = Cl
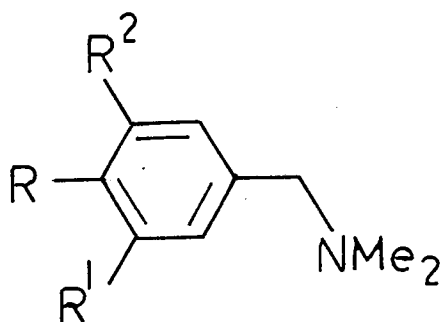
(84)

a: $R^1 = R^2 = H$, R = MeO
b: $R^1 = R^2 = MeO$, R = H
c: $R^1 = R^2 = H$, R = NO_2
d: $R^1 = R^2 = Me$, R = H

The secondary amine, N-methylbenzylamine (71b) reacted with palladium acetylacetonate to yield a complex of the same type as (78) which, however, decomposed on being heated, depositing metallic palladium. N,N-Dimethylbenzylamine (72) was found to be unreactive with palladium acetylacetonate and Kawaguchi attributed this to the steric effect of the methyl groups which hinder the approach of the nucleophilic nitrogen to the palladium centre.

In 1973 Trofimenko[38] reported the first di-cyclopalladation of a nitrogen donor ligand. N,N,N',N'-Tetraethyl-p-xylylene α,α'-diamine (80) was treated with an excess of tetrachloropalladate(II) and the two possible cyclopalladated complexes (81a,b) were isolated. The complexes were separated and characterised via solubility, ligand exchanged products and X-ray photo-electron spectroscopy (ESCA) measurements.

(iii) The mechanism of cyclopalladation reactions

The palladation of aromatic compounds generally proceeds with the elimination of an ortho-hydrogen together with the group, or atom, leaving the metal.

Early studies of substituent effects on the orthopalladation of azobenzenes suggested that the mechanism probably involved electrophilic attack by palladium on the aromatic ring. Takahashi and Tsuji[65] investigated the orthopalladation of mono-p-substituted azobenzenes (82) and showed that the choice of aromatic ring to be substituted was dependent on electronic effects and that the preference for palladation into the substituted ring decreases in the order MeO>Me>H>Cl, thus confirming palladation of the more electron-rich ring. 4-Methoxyazobenzene (82a) produced only one product (83a) and that was the complex from

palladation of the p-anisyl ring, whereas palladation of 4-chloro-
azobenzene occurred in both aromatic rings with a preference (3:1)
for the unsubstituted phenyl ring.

Bruce[66] investigated the palladation of a series of m-sub-
stituted azobenzenes and his findings clearly demonstrated that palla-
dation occurred via an electrophilic process.

Cope[63] carried out the competitive orthopalladation of N,N-
dimethylbenzylamine and azobenzene and isolated only one complex, (74),
demonstrating that the tertiary amines reacted at a much faster rate
than azobenzene.

Cope further, reacted lithium tetrachloropalladate with a series
of substituted N,N-dimethylbenzylamines (84) and from compounds (84a,b)
obtained orthopalladated complexes (74) whereas from (84c) a complex
of type (73) was isolated. From these results Cope postulated that Pd(II)
is only a weak electrophile and that the reaction probably occurs via an
initial rapid co-ordination of the nitrogen to the metal followed by
attack of the metal at an ortho position of the aromatic ring. The
difference in reaction of primary, secondary and tertiary amines was
unclear but Cope proposed, on purely steric grounds, that primary and
secondary amines would co-ordinate more strongly to the palladium than
tertiary amines, and that the stronger co-ordination would decrease the
electrophilic character of the palladium sufficiently to prevent sub-
sequent attack on the aromatic ring.

Lewis[49] et al. later obtained results consistent with those of
Cope apart from the reaction of N,N,3,5-tetramethylbenzylamine (84d)
which, in contrast to the similarly hindered, but more activated (84b),
gave a complex of type (73) rather than a cyclised complex.
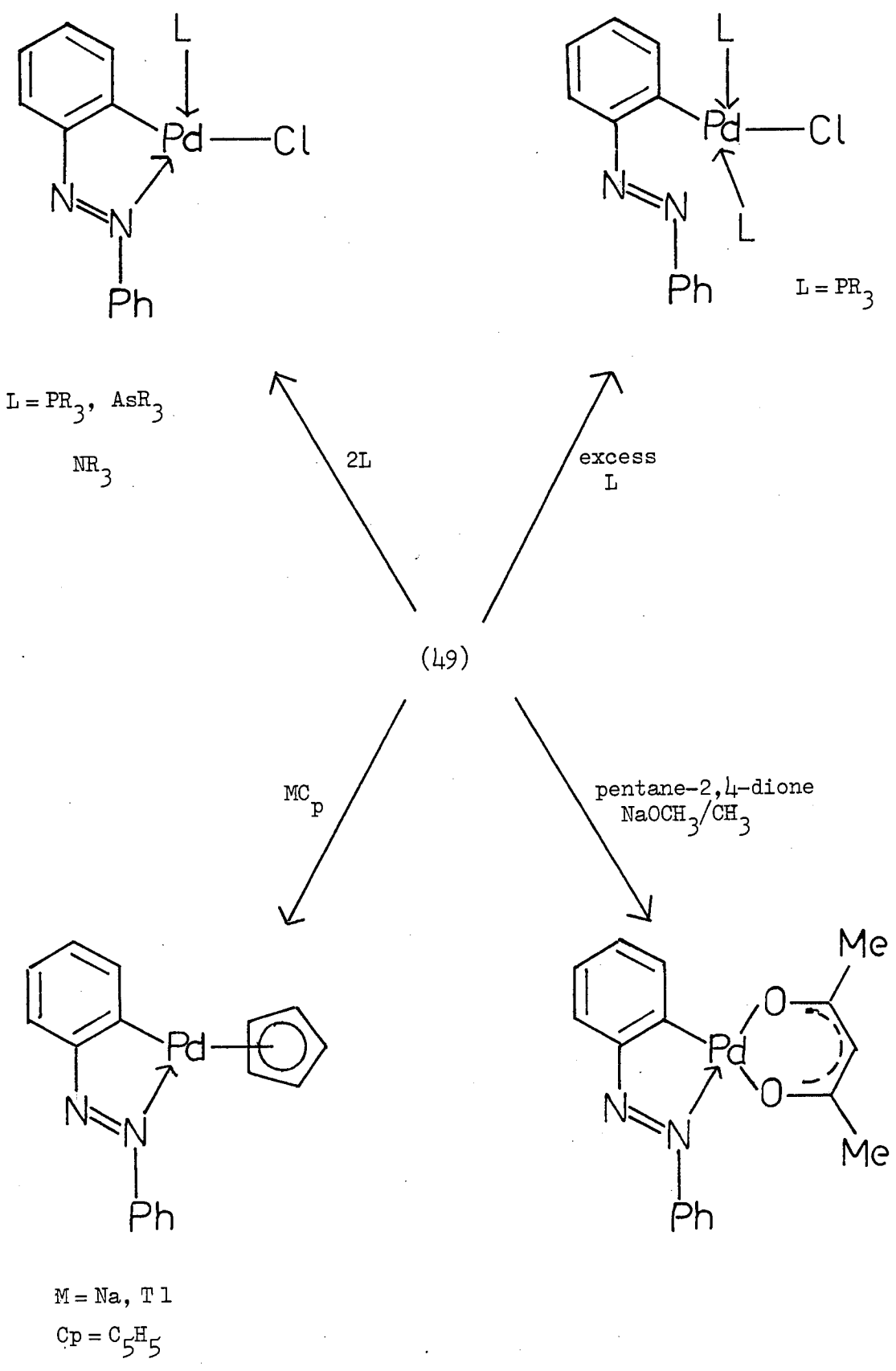
fig. (iii)

All the above results point essentially to the same mechanism i.e. electrophilic attack by palladium but reaction may be prevented by steric factors. (Evidence for other metals such as manganese points to nucleophilic attack.)

(iv) Ligand exchange reactions

Ligand exchange reactions of cyclopalladated complexes have been limited generally to the cleavage of the halogen-bridged dimers, these reactions being sometimes referred to as "bridge-splitting" reactions. The dimeric halide complexes (e.g. 49,51,60,etc.) tend to be high melting, insoluble and involatile compounds and thus they cannot be easily characterised. The ligand-exchanged complexes are monomeric and much more amenable to characterisation and crystallographic studies[67] owing to their increased solubility in common organic solvents. The commonest "bridge-splitting" reagents are phosphines, amines, acetyl acetonate and cyclopentadienide. All the bridged dimeric cyclopalladated complexes previously discussed have been reported to undergo ligand-exchange reactions, and these reactions are illustrated in figure (iii) exemplified by the ortho-palladated azobenzene complex (49).

The carbon-palladium σ-bond has been demonstrated to be a reasonably strong bond[68] and it remains intact during ligand exchange. However, phosphines, when present in excess, have been reported to cleave not only the halogen bridges but also in some instances, the nitrogen-palladium co-ordinate bond, thus forming complexes of type (85).

(85)   (86)
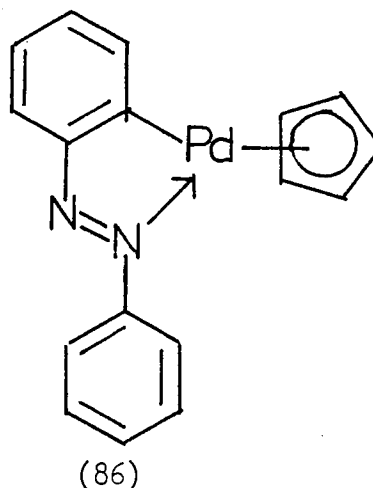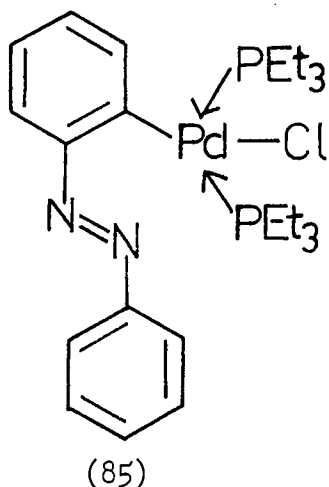
The structures of the phosphine complex (85) and the π-cyclo-
pentadienyl complex[69] (86) have been confirmed by X-ray crystal-
lography.

Occasionally it is possible to prove the presence of a <u>cyclo-
palladated</u> ligand by a ligand-exchange reaction with pyridine.
Trofimenko[38] described the reaction of pyridine with various benzyl-
amine-palladium complexes of the type (74). When the reaction was
performed in organic solvents, insoluble monosubstitution products of
the type (87) were obtained. In water, however, the bis(pyridine)
cations (88) were readily obtained and isolated as hexafluorophosphate
salts.

(87)   (88)
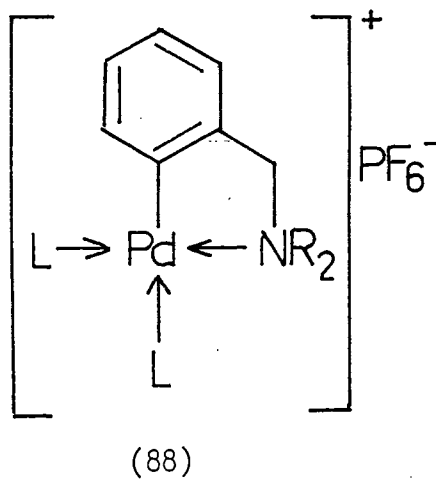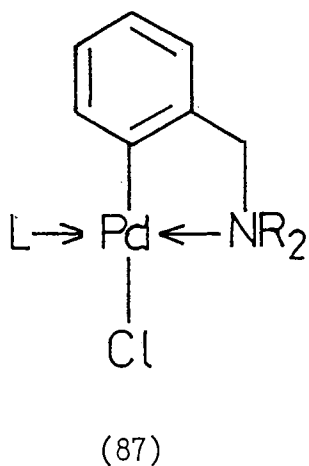
L = pyridine

The formation of these cations could be used in distinguishing chemically between complexes of the type (74) and, for example, bis (benzylamine)palladium dichloride (73a) which contains no carbon-palladium bond. Under these conditions the pyridine simply displaced the co-ordinated benzylamine ligand in (73) but not the carbon-bonded ligand in complex (74). Thus the ligand exchange reaction with pyridine can be used to establish the presence of a cyclopalladated ligand.

Lewis[49] and his co-workers reported the standard bridge-splitting reactions of the halogen-bridged N,N-dimethylbenzylamine complex (74). They also reported the metathetical exchange reactions with thiocyanate, acetate and trifluoroacetate, (further examples of ligand exchange) to produce the bridged complexes (89).

(74) + X$^-$ $\longrightarrow$

X = SCN, CH$_3$CO$_2$,

CF$_3$CO$_2$

+ Cl$^-$

(89)

a: R = Me

b: R = Et

c: R = $\{CH_2\}_4$
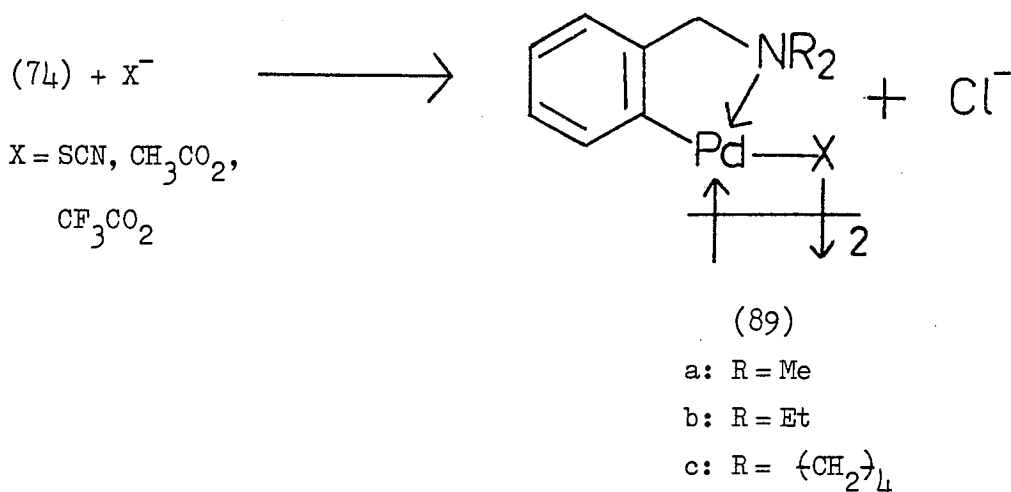
(v) Replacement of palladium by non-metallic atoms or groups

The earliest, and perhaps, simplest reactions of cyclopalladated complexes involving the replacement of the palladium by a non-metallic atom, or group, are the degradative reductions with lithium aluminium hydride whereby the palladium is replaced by hydrogen. The reductions were initially carried out to prove that orthopalladation had occurred;
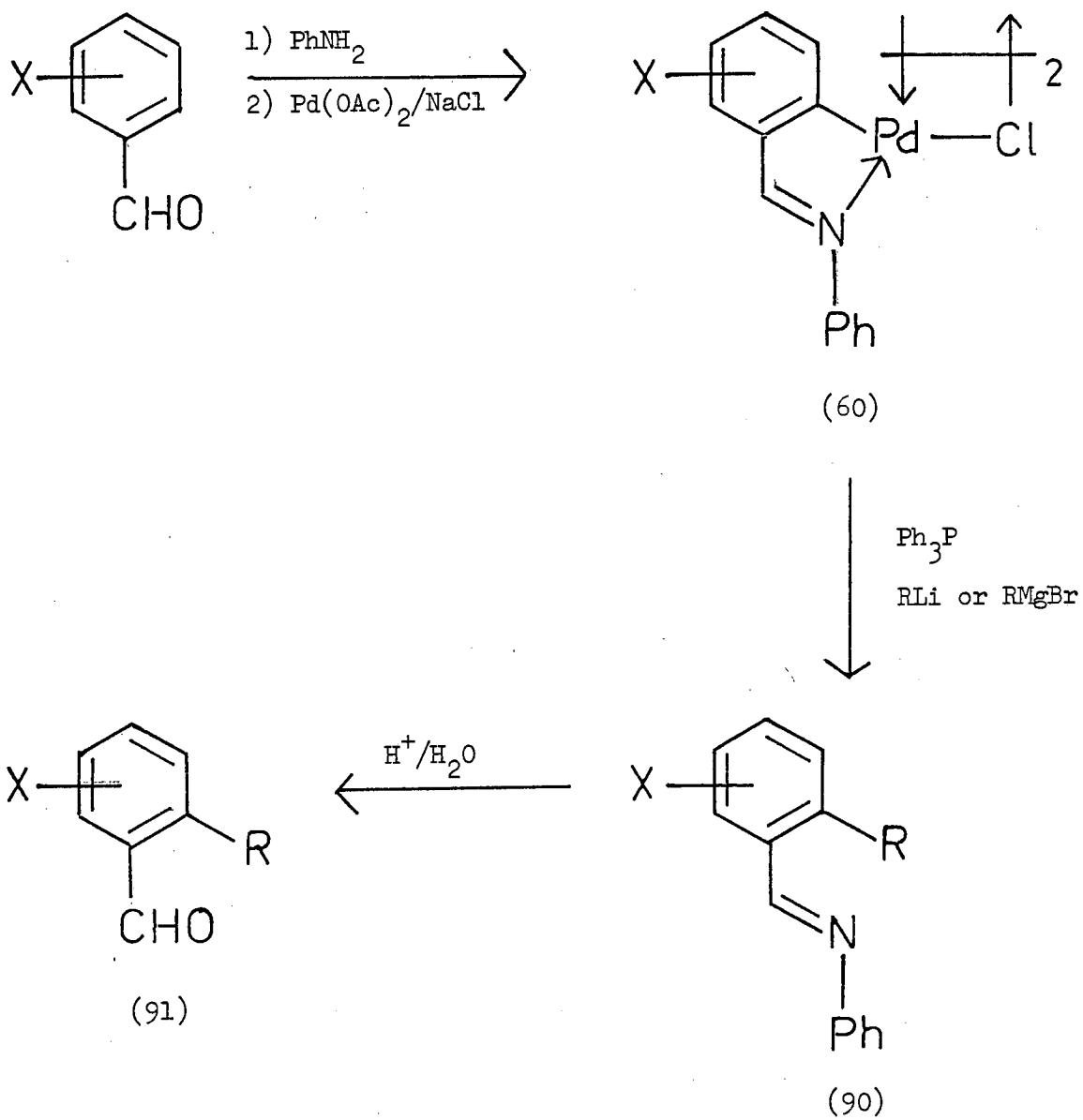
Scheme 3

reduction of complex (49), for example, with lithium aluminium deuteride led to the isolation of ortho-deuterioazobenzene[43], thus confirming that the original complex had contained an ortho carbon-palladium bond.

(74)   (92)
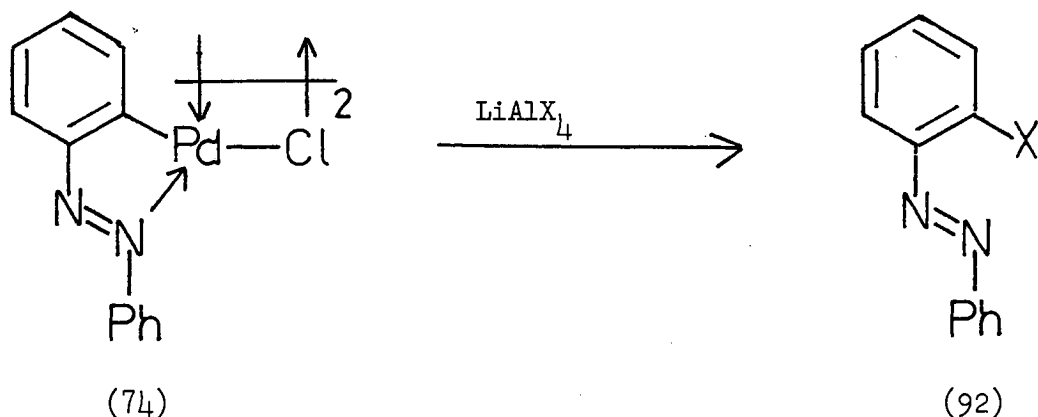
In 1971 Fahey[70] reported that azobenzene was halogenated by chlorine, or bromine, selectively ortho to the azo function, when its solutions were treated with the respective halogen in the presence of a Pd(II) catalyst. Since exhaustive chlorination yielded 2,2', 6,6'-tetrachloroazobenzene as the major product, and di-μ-chlorobis[2-(phenylazo)phenyl]dipalladium(II), (49), was isolated from the reaction, Fahey postulated that a carbon-palladium-σ-bond was initially formed and that the halogen then replaced the palladium. The process could be repeated until the tetrachloroazobenzene was formed.

Murahashi[71] and his co-workers used the ortho-specificity of the palladation reaction to synthesise a series of ortho-alkyl-benzaldehydes. The ortho-palladated Schiff bases (60) were reacted with alkyl-lithiums, or Grignard reagents, in the presence of triphenyl-phosphine and high yields of ortho-alkyl Schiff bases (90) were obtained. Subsequent acid hydrolysis gave the appropriate ortho-alkylbenzaldehyde (91). The reaction sequence, illustrating the replacement of palladium by an alkyl group, is given in Scheme 3. The process can be repeated

and disubstituted benzaldehydes formed e.g. 2,6-dimethylbenzaldehyde
(91;R=Me,X=o-Me) was synthesised in 72% yield from benzaldehyde via
o-methylbenzaldehyde.

The arylation of olefins in the presence of palladium(II) species
has been a topic of interest[72,73] but conclusive proof of the assumed
intermediacy of an aryl-palladium complex has been neglected. However,
Holton[74] has recently reported the reaction of the ortho-palladated-
N,N-dimethylbenzylamine complex (74) with methyl vinyl ketone, in
refluxing benzene or toluene, in the presence of excess triethylamine.
In the reaction the ketone displaced the palladium and an ortho-dimethyl-
aminomethylenone (92) was isolated.
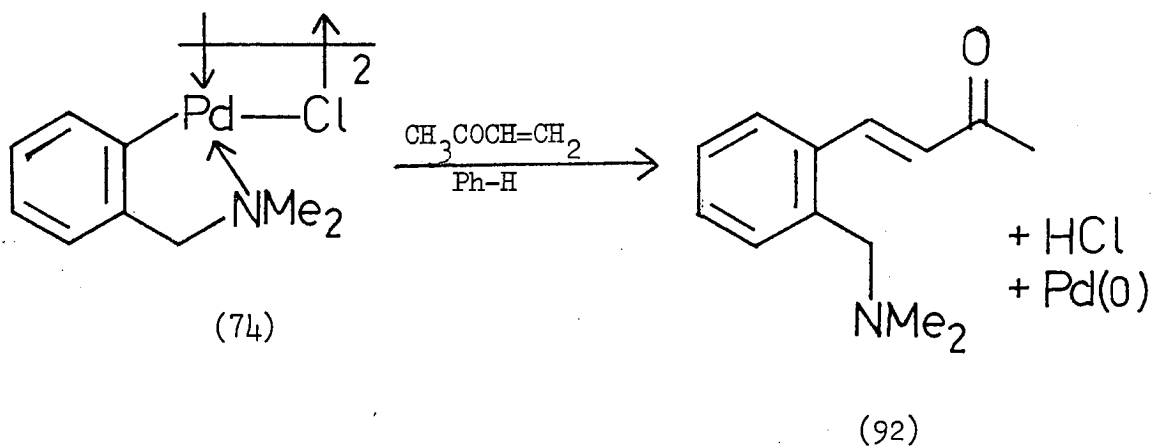
Holton further reported that the reaction appeared to be general
for all vinyl ketones, and that only the trans-enones were isolated.
Compounds of the type (92) are useful precursors for the synthesis of
alkaloids.

(83)

(93)

(94)

(95)
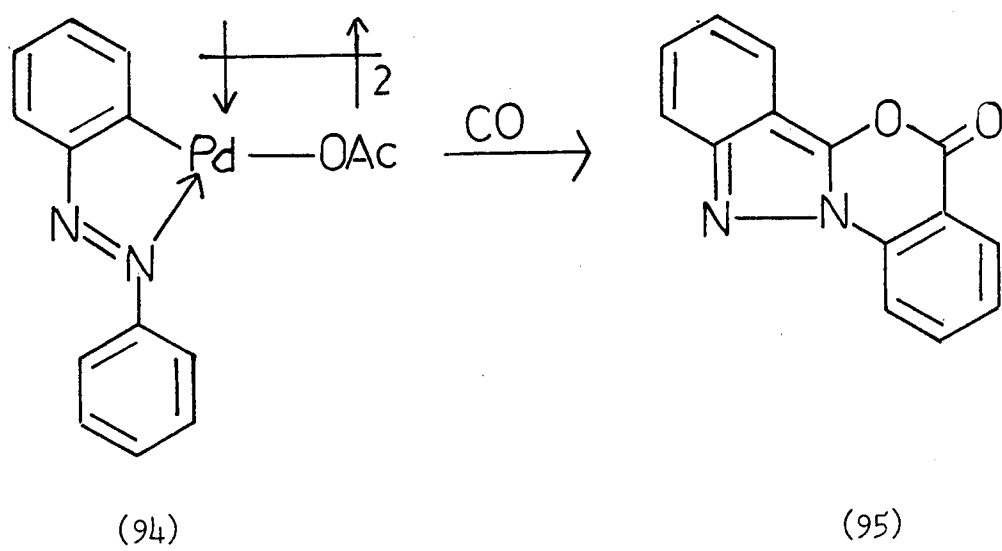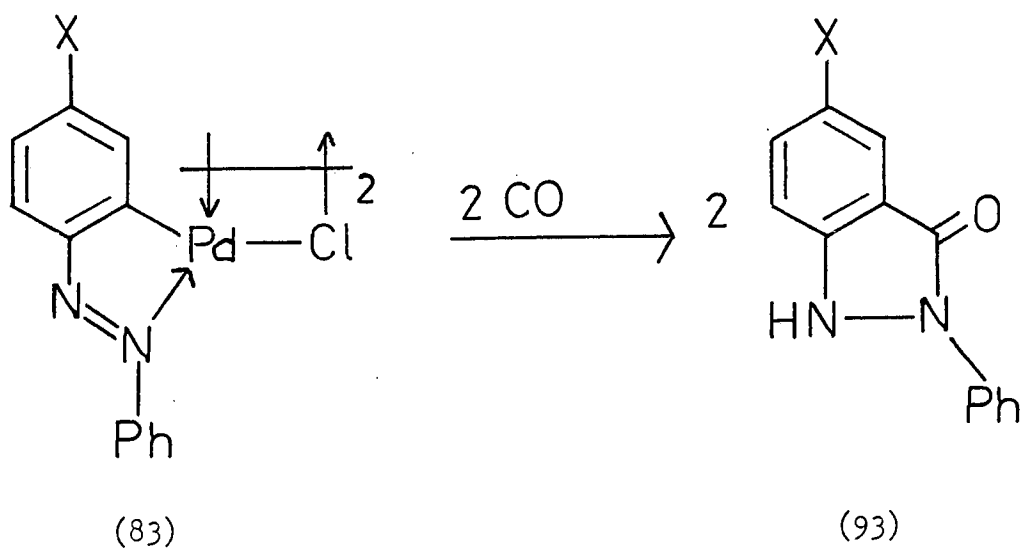
½ (61)

↓ 2CO

(99)

R = R' = H
R^2 = Me, Et

(100)
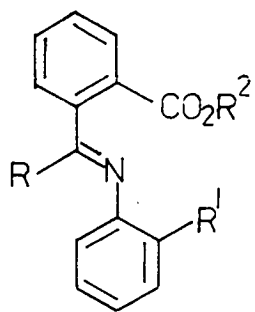
R^2OH
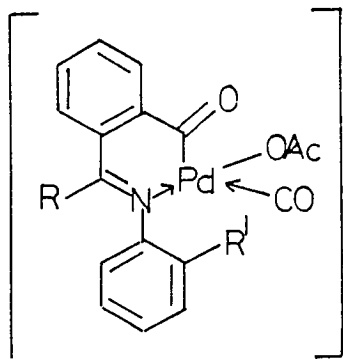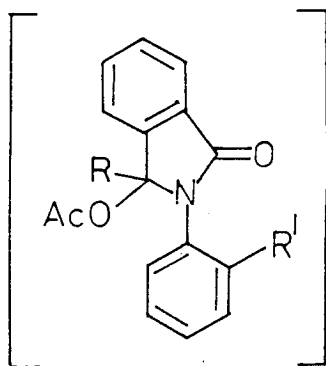
(101)
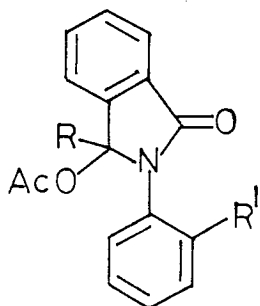
(96)

R = H
R' = H.Me
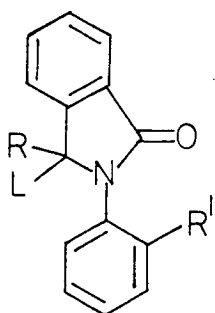
(97)

R = R' = H
L = PhNH, MeO, EtO
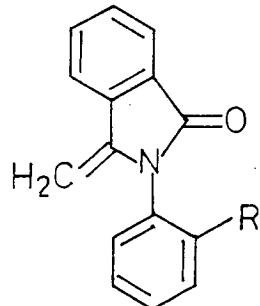
(98)

R = Me
R' = H

(b) <u>The use of cyclometallated complexes in heterocyclic synthesis</u>

(i) <u>Carbonylation and related reactions</u>

Takahashi and Tsuji[65] first reported the potential of <u>cyclo</u>-palladated complexes in synthesis when they carried out a series of carbonylations of 4-substituted <u>ortho</u>-palladated azobenzenes (83) in ethanol at 100°C and 150 atm. and isolated indazolone derivatives (93) in reasonable yields. These reactions are thought to involve initial insertion of a carbonyl group into the carbon-palladium bond followed by displacement of palladium and ring closure.

Heck[50] extended the carbonylation reaction when he carbonylated di-μ-acetatobis[2-phenylazo)phenyl]dipalladium(II), (94) in xylene at 100°C under 1 atm. of carbon monoxide, and isolated the heterocyclic lactone (95) as well as the indazolone derivative (93;X=H). The lactone (95) had been reported earlier by Prichard[75] who isolated it from the high temperature carbonylation of azobenzene with nickel tetracarbonyl.

In 1975 Heck[50] reported the results of a comprehensive study of the carbonylation of a series of <u>ortho</u>-palladated Schiff base complexes. Unlike the azobenzene complexes (83,94) which have a tendency to react at both aromatic rings, the Schiff base complexes (61) showed more straightforward behaviour.

From the study Heck postulated a possible mechanism for carbonylation taking account of all isolated products. These reactions, and postulated mechanism, are summarised in Scheme 4. Complex (61a) was readily carbonylated in xylene at 100°C with 1 atm. of carbon monoxide to give only 3-acetoxy-2-phenylphthalimidine (96), and the <u>ortho</u>-methyl complex (61b) reacted in an analogous manner. The carbonylation of complex (61a) was

(102)

2 CO

R=H

R=CH₃

(103)

(104)

HC—OAc
Ph

H₂C=C—Ph

Pd—OAc

R   Ph

(89)

(105)

R = Me, Et

(106)

R = Me, Et

(107)

Scheme 5

(83)   (110)

(93)   (109)
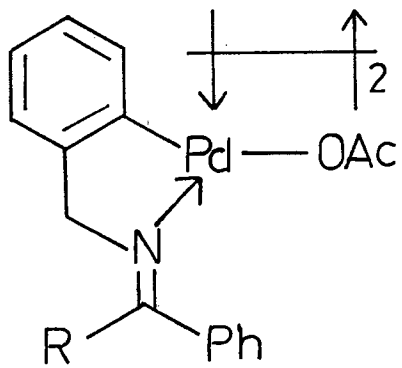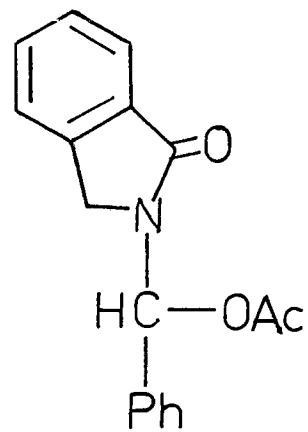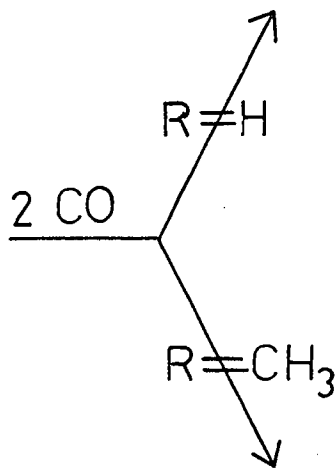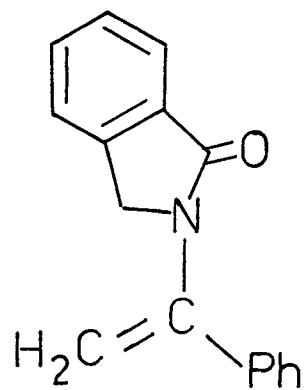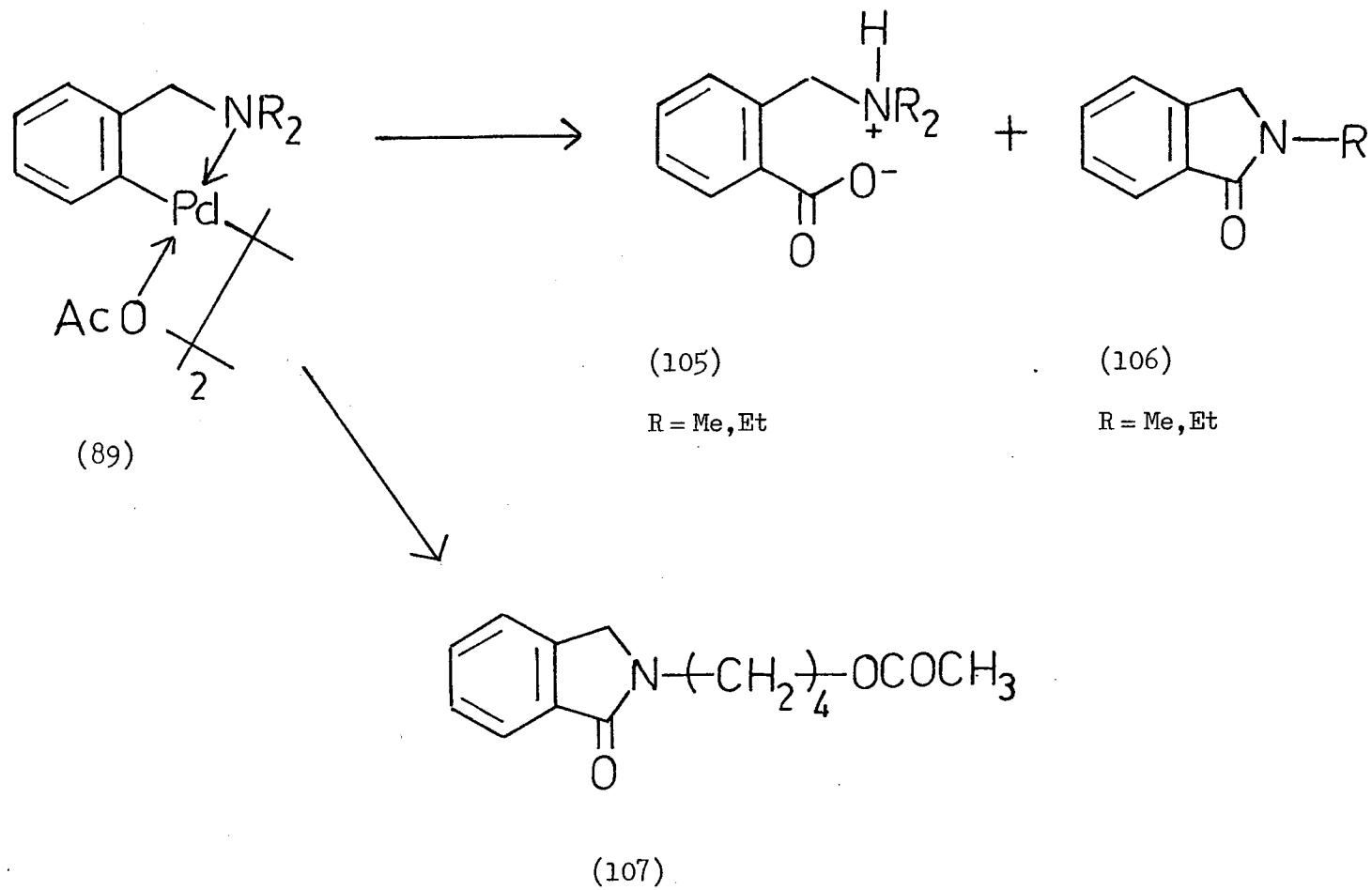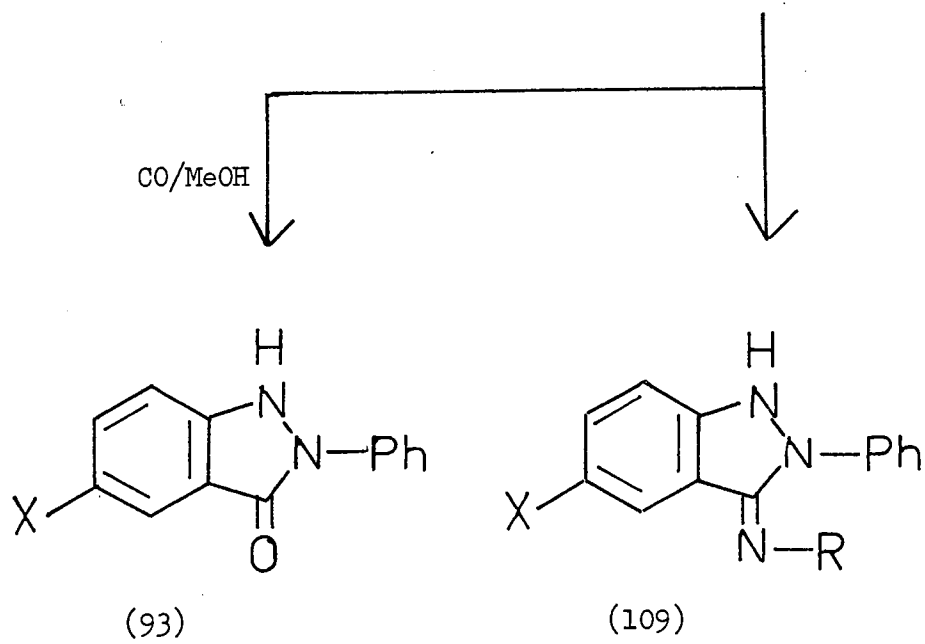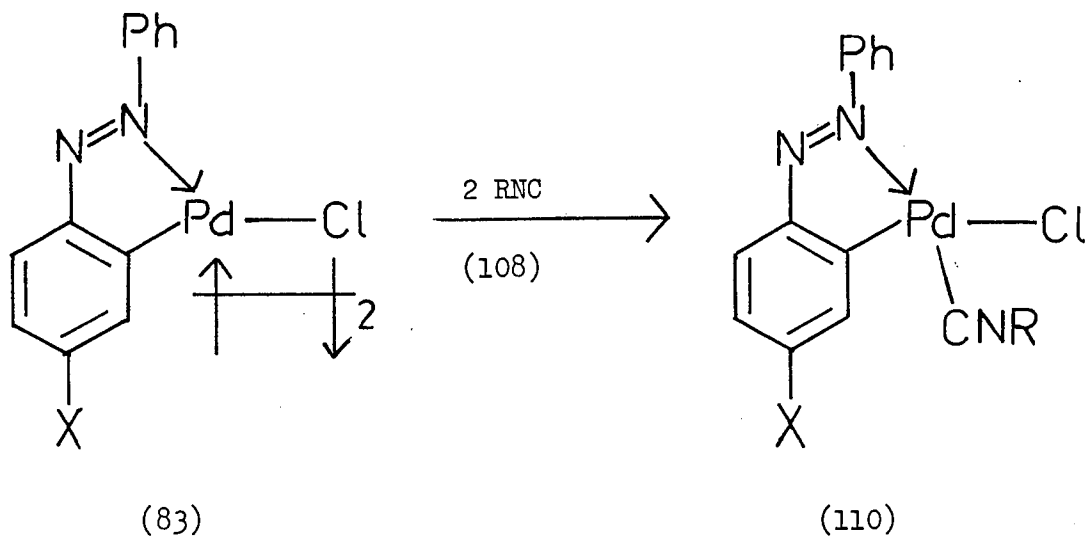
<u>Scheme 6</u>

also carried out in the presence of added nucleophiles and products incorporating the nucleophiles (97) were obtained. However, when L=methoxy or ethoxy the uncyclised Schiff base ester (99) was also isolated. The carbonylation of complex (61c) gave exclusively the methylenephthalimidine (98) rather than the expected tertiary acetate. Heck postulated compounds (100,101) as possible intermediates although no evidence (except for the products isolated) was reported. Heck further carbonylated the novel benzylamine Schiff base complex (102) and obtained the corresponding products (103,104). Rather interestingly the carbonylation of complex (102;R=Me) yielded the methylene derivative (104) and not the tertiary ester.

Heck has also reported the carbonylation reaction of the ortho-palladated complex (89a,b;X=CH$_3$CO$_2$). The only products isolated were hydrolysis products (105) of the mixed anhydride and phthalimidine derivatives (106). These reactions are summarised in Scheme 5. The formation of phthalimidine derivatives was interesting since it involved cyclisation and loss of one of the N-alkyl groups, presumably as the alkyl acetate since complex (89c;X=CH$_3$CO$_2$) gave 2(4'-acetoxybutyl) phthalimidine (107).

Pauson[76,77], Murahashi[78,79], and Heck[68] have obtained products similar to those previously described by carbonylation of cyclometallated azobenzene and Schiff base iron and cobalt complexes or by direct carbonylation of the free ligands using metal carbonyl catalysts which are assumed to cause metallation prior to carbonylation.

Yamamoto and Yamazaki[80] have recently reported the synthesis of substituted indazolines (109) by treatment of ortho-palladated azobenzenes (83) with isocyanides (108) as illustrated in Scheme 6. The ortho-palladated complexes (83) reacted with isocyanides (108) with cleavage

(112)

(112) + (112)
X = S   X = 0

(vii)

(i),(ii)

(vi)

R
HC—OCH₃
CO₂CH₃
R

(114)

+ (112)
X = 0

R

(v)

HC—OCOCH₃
Hg(OCOCH₃)₂
R

(116)

R
S—Fe(CO)₃
Fe(CO)₃
R

(111)

(iii)

(iv)

R
CH—CH
R
R

(113)

R
HC—OCH₃
Hg(OCOCH₃)₂
R

(115)

(i) $\bar{O}H$, $\bar{M}eO$, $\bar{N}_3$, $\bar{S}CN$

(ii)   Ce(IV)/acetone; h /EtOH

(iii) KOBu^t/Bu^{t}OH

(iv)   Hg(OAc)₂/MeOH

(v)   Hg(OAc)₂/THF

(vi)   Hg(OCOCF₃)₂/THF

(vii) H₂O₂/$\underline{m}$ClC₆H₄CO₃H
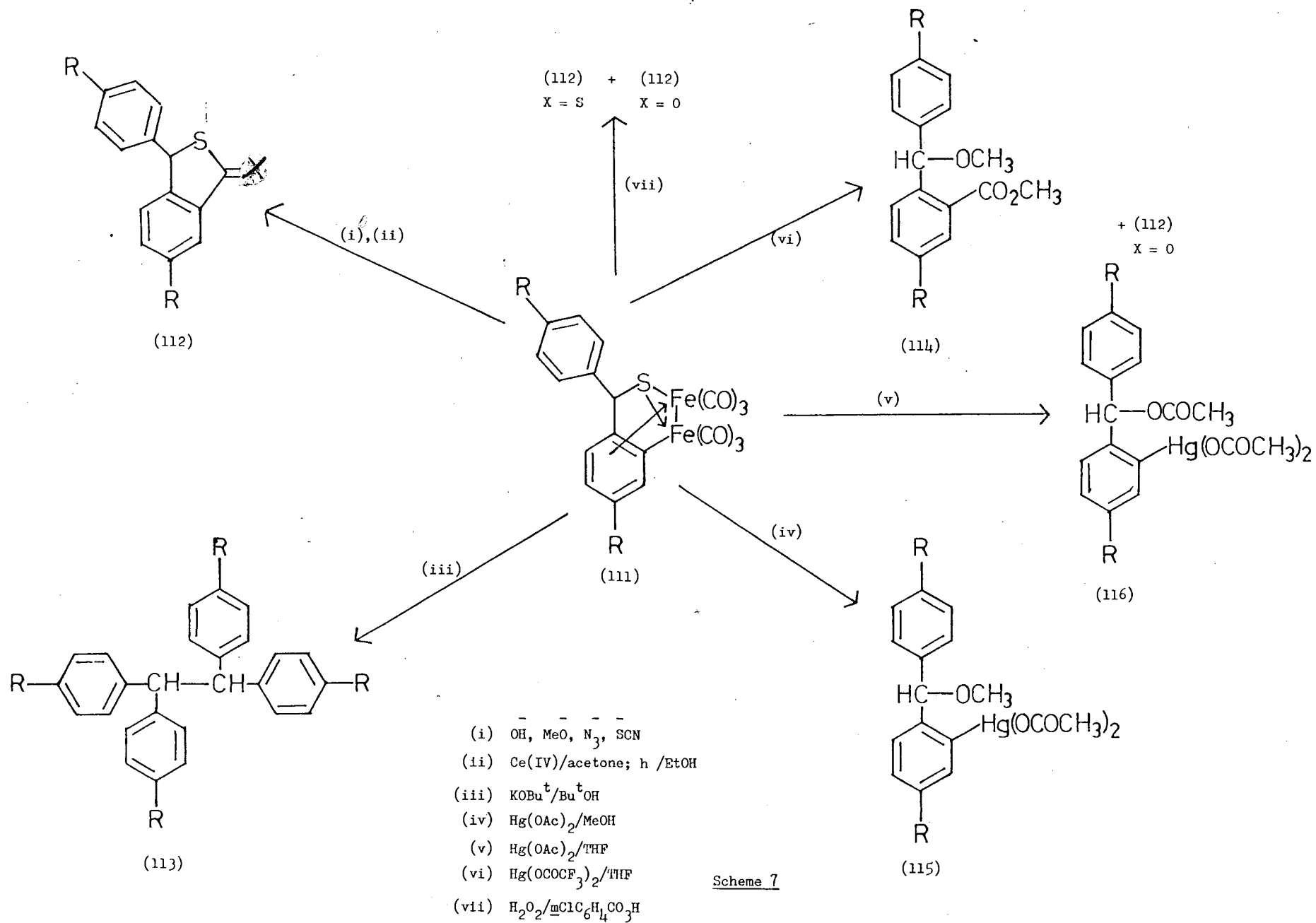
Scheme 7

of the chloride bridges to give the monomeric complexes (110) which were thermally degraded at 100-130°C to yield the 3-imino-2-phenyl-indazolines (109) and metallic palladium. This reaction was analogous to Takahashi's[65] synthesis of indazolones from compound (83) and carbon monoxide. Substituted indazolones (93) can be synthesised from complex (110) by treatment with carbon monoxide in methanol at 40°C under a pressure of 100 atm^{-1}.

Alper[81-83] and his co-workers have demonstrated the possibilities of the <u>cyclo</u>metallated thiobenzophenone iron complexes (111) in organic synthesis, and their results are summarised in Scheme 7. Treatment of the complex (111) with a variety of anions or cyanogen bromide yielded the carbonyl inserted thiolactone (112;X=S) which was also isolated from the reaction of (111) with Lewis acids or cerium (IV) salts or by photolysis.

The reaction of (111) with potassium-<u>t</u>-butoxide in <u>t</u>-butanol gave 1,1,2,2-tetra-arylethanes (113). Lactones (112;X=0) and esters (114) were isolated from treatment of (111) with mercuric trifluoroacetate whereas the reaction with mercuric acetate gave <u>ortho</u>-mercurated methyl ethers (115) and esters (116).

Treatment of the iron complexes (111) with peroxide produced a mixture of lactone (112;X=0) and the thiolactone (112;X=S).

To determine whether oxidative cyclisation occurred in the formation of (112;X=0,S) Alper[81] synthesised the pentadeuterio iron carbonyl complex (117) and treated it with Ce(IV). The resultant thiolactone (118) still retained the d_5-phenyl substituent demonstrating that carbonyl insertion only occurred into the ring originally containing the carbon-iron σ-bond.

(119)

(120)

(121)

(58)

PhCO₃H

(122)

X = OH

(123)

(117)   (118)
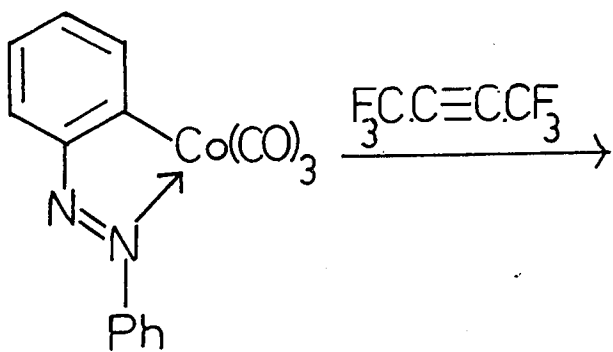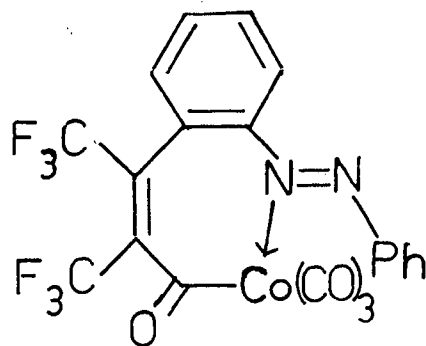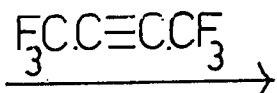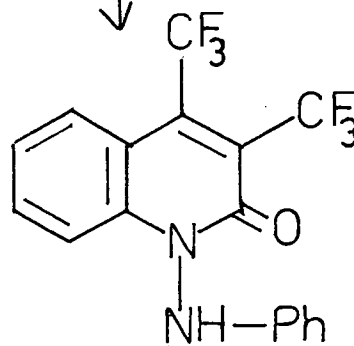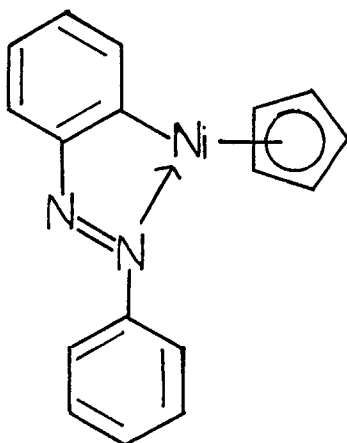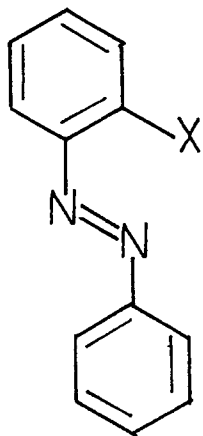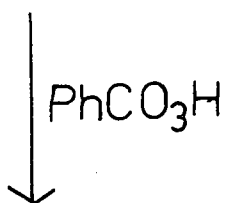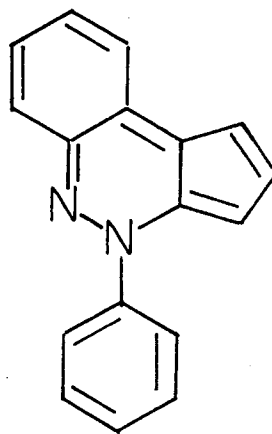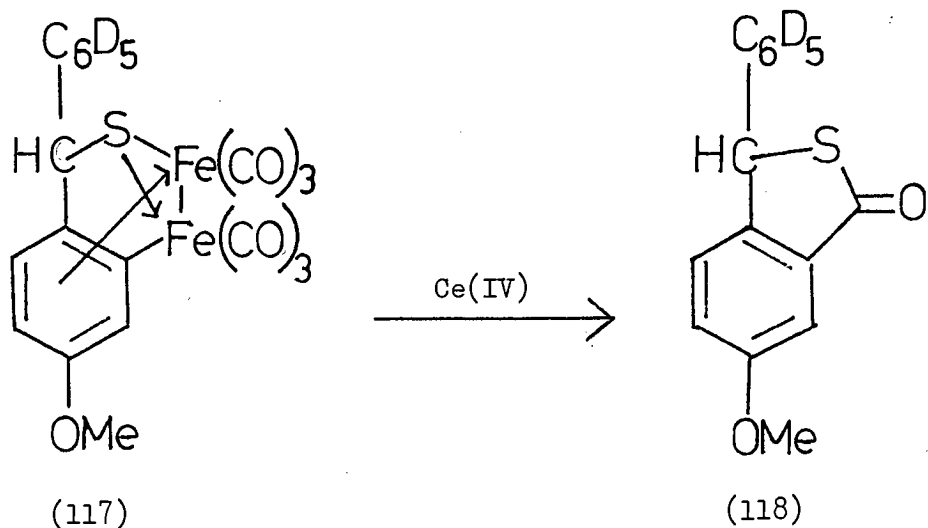
Bruce[84] et al. reported a novel synthesis of substituted

quinolin-2-ones (121) via isolable organocobalt intermediates. The

ortho-metallated azobenzene cobalt complex (119) was treated with hexa-

fluorobut-2-yne whereby a "three-carbon-unit" (the alkyne and carbon

monoxide) was inserted into the carbon-cobalt σ-bond to yield the

isolable intermediate (120) which was characterised and then treated

with carbon monoxide to yield the quinolin-2-ones (121).

Since Kleiman and Dubeck's[42] report on the synthesis of the

cyclometallated azobenzene complex (58) Ustynyuk[85,86] and his co-

workers have studied the complex in great detail. Treatment of the

complex with perbenzoic acid gave a mixture of two products, 2-hydroxy-

azobenzene (122;X=OH) and a novel pseudo-azulene, 4-phenyl-4H-cyclo-

penta[c]cinnoline (123). Ustynyuk further reported that treatment of

o-halogenoazobenzenes (122;X=halogen) with nickelocene gave initially

the ortho-metallated complex (58) which then reacted with excess o-

halogenoazobenzene to yield the cinnoline derivative (123).
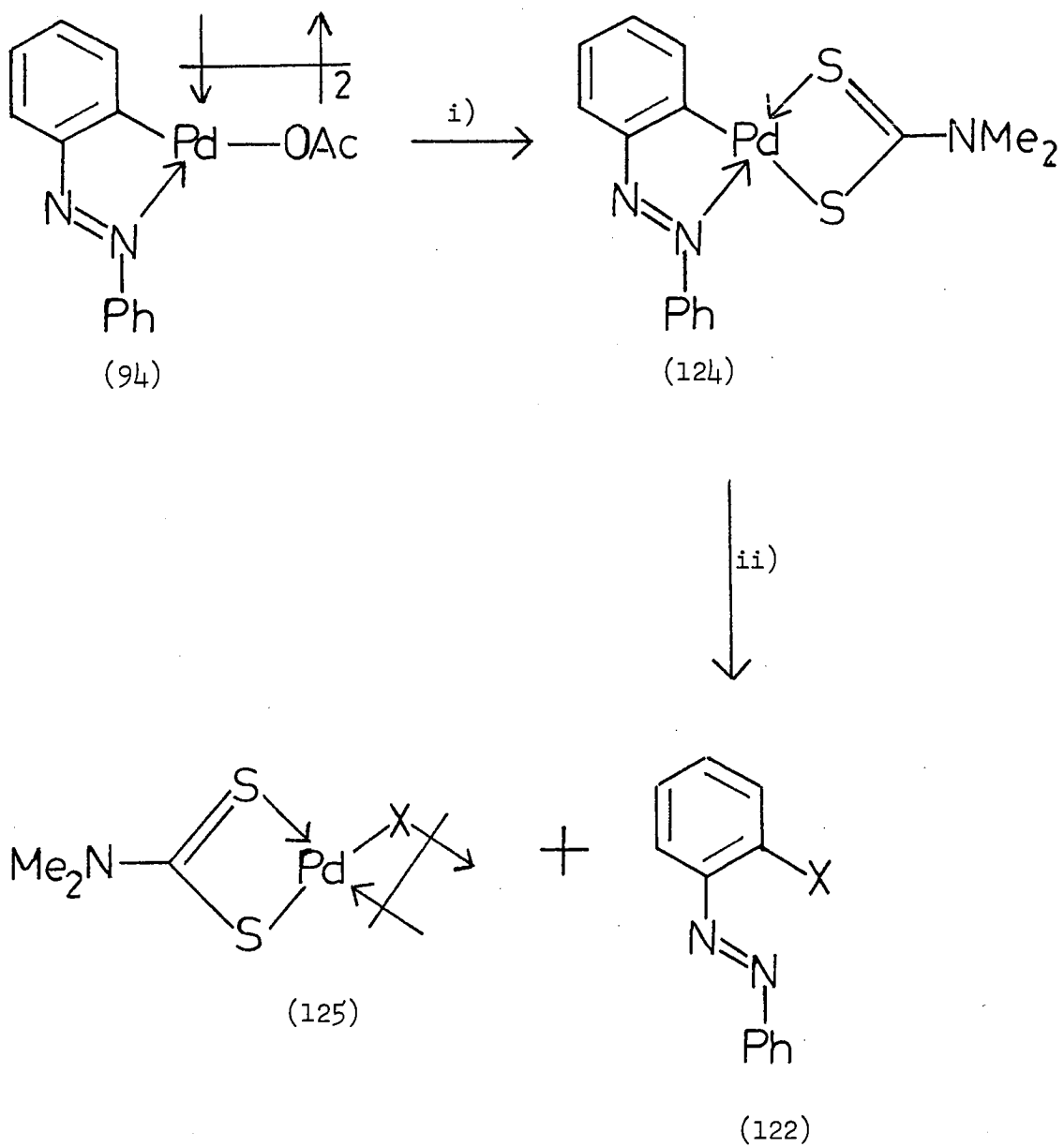
Scheme 8

i) $Et_4NSCSNMe_2 - CH_2Cl_2$

ii) X_2 (X=Br,SCN)

(126)

(127)
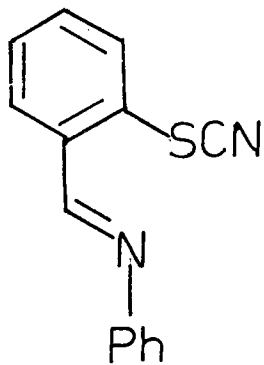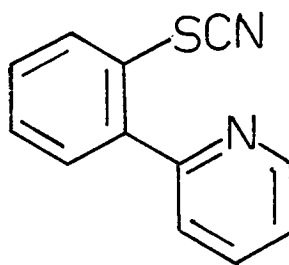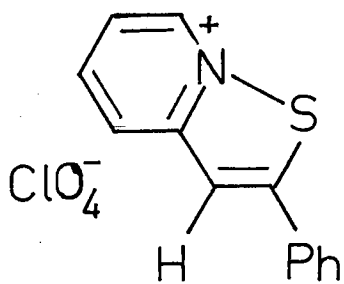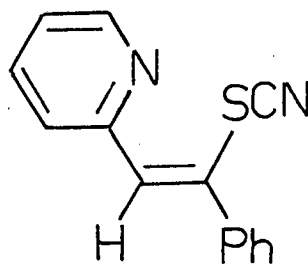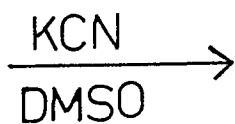
(129) $\xrightarrow[\text{DMSO}]{\text{KCN}}$ (128)

Cross[87] obtained the same cinnoline by heating the corresponding ortho-palladated complex, under vacuum, in a sublimation apparatus. In Cross's reaction the palladium was replaced by a cyclopentadienyl ring with the loss of two hydrogen atoms.

(ii) Heterocyclic synthesis via replacement of palladium
      by a thiocyanato group

Davis[41] has recently reported a study on the potential of cyclo-palladated complexes as intermediates in the synthesis of heterocyclic compounds. He used the ortho-specificity of the palladation reaction and replaced the palladium with a suitable atom, or group, that could be used in a subsequent cyclisation step.

To avoid possible re-palladation of the ortho-substituted azobenzene in the depalladation step Davis synthesised 2-(phenylazo)phenyl(N,N-dimethyldithiocarbamato)palladium(II), (124) by reaction of the complex (94) with tetraethylammonium N,N-dimethyldithiocarbamate in dichloro-methane. The reaction of the dithiocarbamate complex (124) with bromine, or thiocyanogen (a pseudo halogen) resulted in replacement of palladium by bromine, or thiocyanate. The resulting o-substituted azobenzene (122;X=Br,SCN) remained dissolved in the dichloromethane and was easily separable from the insoluble and inert by-product, di-μ-halobis(N,N-dimethyldithiocarbamato)dipalladium(II), (125). The reactions are illustrated in Scheme 8. The o-substituted azobenzenes (122) were obtained in high yield and the structures confirmed by standard spectro-scopic procedures and by comparison with authentic samples.

Using the same procedure Davis synthesised 2-(N-phenylformimidoyl) phenylthiocyanate, (126), 2-(2-thiocyanatophenyl)pyridine, (127) and 2-(2-phenyl-2-thiocyanatovinyl)pyridine (128). The structure of

$$\text{C} \diagdown \underset{\text{N}}{\overset{\text{C}}{\Big(}} \quad \equiv \quad \text{nitrogen donor ligand}$$
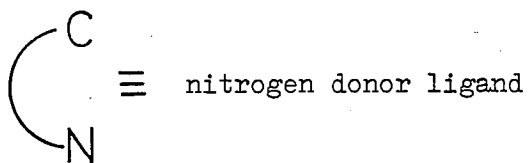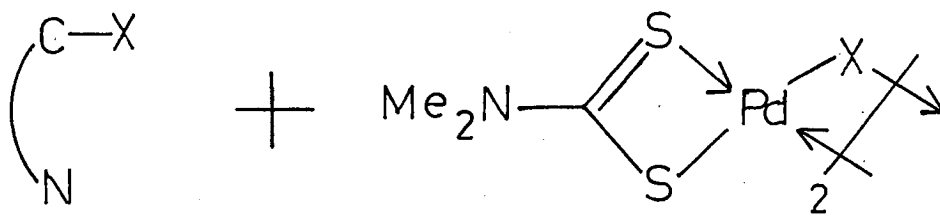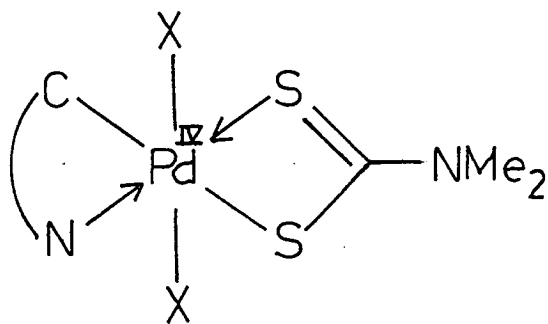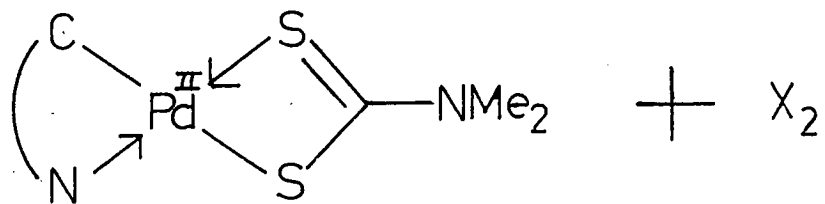
compound (128) was confirmed by the reaction of potassium cyanide on 2-phenylisothiazolo-[2,3-a]pyridinium perchlorate (129), the thiocyanato-stilbazole obtained from this reaction being identical with that obtained from the cyclopalladated 2-vinyl pyridine.

Davis had demonstrated that it was possible to singularly mono-functionalise certain compounds by the use of isolable cyclopalladated complexes. He then exemplified their use as precursors in heterocyclic synthesis by the reaction of 2-(2-thiocyanatophenyl)pyridine (127) with bromine in ethanol to yield the novel, cyclised compound,[1,2]benzo-thiazolo-[2,3-a]pyridinium perchlorate (130).
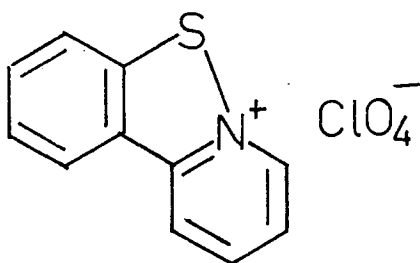
(130)

Davis proposed two possible mechanisms for the replacement of palladium by bromine or thiocyanate. The replacement could occur either by an oxidative addition of the halogen to the central palladium atom of the complex to give an unstable Pd(IV) species which then under-goes reductive elimination or by the direct electrophilic attack of halogen at the carbon-palladium bond. The observation that addition of bromine or thiocyanogen to clear solutions of the dithiocarbamato-complexes gave very dark coloured solutions which slowly lightened and formed a precipitate led Davis to favour the first of these possible mechanisms, shown opposite.

DISCUSSION

(20)

(i)

(132)

(iii)

(133)

(131)

(iv)

(25)

(ii)

(i) $Na_2S_2O_4$–NaOH

(ii) $(CH_3)_2SO_4$

(iii) hydrolysis

(iv) nitrobenzene, reflux

<u>Scheme 9</u>
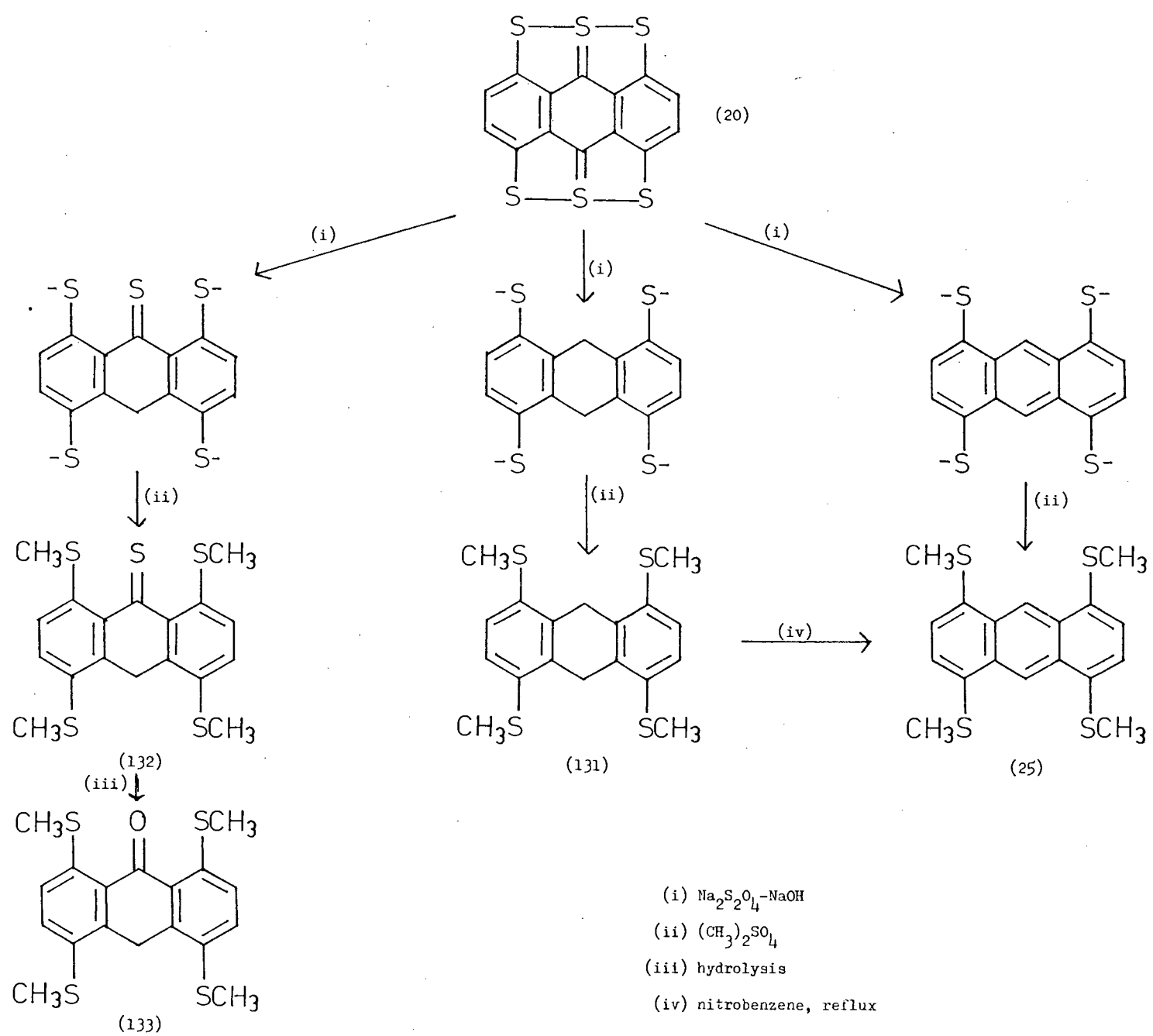
Section one.   The Synthesis of Acene Polysulphides

Davidson[7] and Steven[18] reported the synthesis of hexathio-anthracene (20), but the structure was not conclusively established owing to the insolubility of the compound in common organic solvents. Steven[18] attempted to synthesise soluble derivatives of hexathio-anthracene by reduction and methylation but was only able to isolate a low yield mixture of products which could not be separated (see introduction). Using procedures adapted from Steven's work two approaches to the preparation of characterisable derivatives of compound (20) were attempted; (i) reduction with alkaline sodium dithionite followed by methylation, and (ii) direct methylation followed by reduction.

(i)   Reduction of Hexathioanthracene followed by Methylation

Hexathioanthracene (20) reacted with an excess of alkaline sodium dithionite to form a homogeneous solution. The process of dissolution was accompanied by a series of colour changes (green ⟶ blue ⟶ purple ⟶ red ⟶ orange) attributed to the progressive reduction of the sulphur-sulphur bonds. Treatment of the resulting orange solution with dimethyl sulphate gave a yellow solid which appeared to be homogeneous by t.l.c. and crystallised as yellow plates from ethyl benzoate.

The mass spectrum of the yellow solid showed a parent ion peak at $^m/e$ 362 with an extremely small higher mass peak at $^m/e$ 378. The mass spectrum contained fragment ion peaks at $^m/e$ 347,332,317 and 302 corresponding to four successive losses of methyl groups from the parent ion and indicating that the product was a tetra(methylthio)anthracene (25). A close analysis of the mass spectrum showed that the peak at $^m/e$ 364 (M+2)

was approximately 33% of the parent ion instead of the expected 16% (^{34}S has a natural abundance of 4.2%) and there were smaller peaks at $^m/e$ 365 and 366. These peaks and intensity of the M+2 ion, indicated that there was some dihydroanthracene derivative (131) present as an impurity. The peak at $^m/e$ 378 was attributed to a small amount of 1,4,5,8-tetra(methylthio)anthrone (133) formed, presumably, by hydrolysis of the corresponding thioanthrone (132), (Scheme 9).

The yellow solid was recrystallised from nitrobenzene, as it was thought that nitrobenzene would dehydrogenate the dihydro-derivative to the fully aromatic anthracene derivative (25). The mass spectrum of the purified product showed a single parent ion at $^m/e$ 362 (364=ca.16%) and elemental analysis gave values in agreement with the proposed structure (25). The 'H n.m.r. spectrum contained three singlets at δ9.3, 7.5 and 2.6, with an integration ratio of 1:2:6 respectively, consistent with the proposed structure.

The spectroscopic results clearly showed that reduction of hexa-thioanthracene (20) with alkaline sodium dithionite had not only cleaved the sulphur-sulphur bonds, but had also reduced the resultant anthracene-9,10-dithioquinone derivative to anthracene and dihydroanthracene deriv-atives. This is analogous to the reduction of anthraquinone which, depending on the actual reagent and conditions, yields anthrone, anthracene or dihydroanthracene. Sodium dithionite is not normally used to reduce anthraquinone to dihydroanthracene; but reduction of the dithioquinone would be expected to occur more readily owing to the reduced bond strength of C=S compared with C=O.

Scheme 10
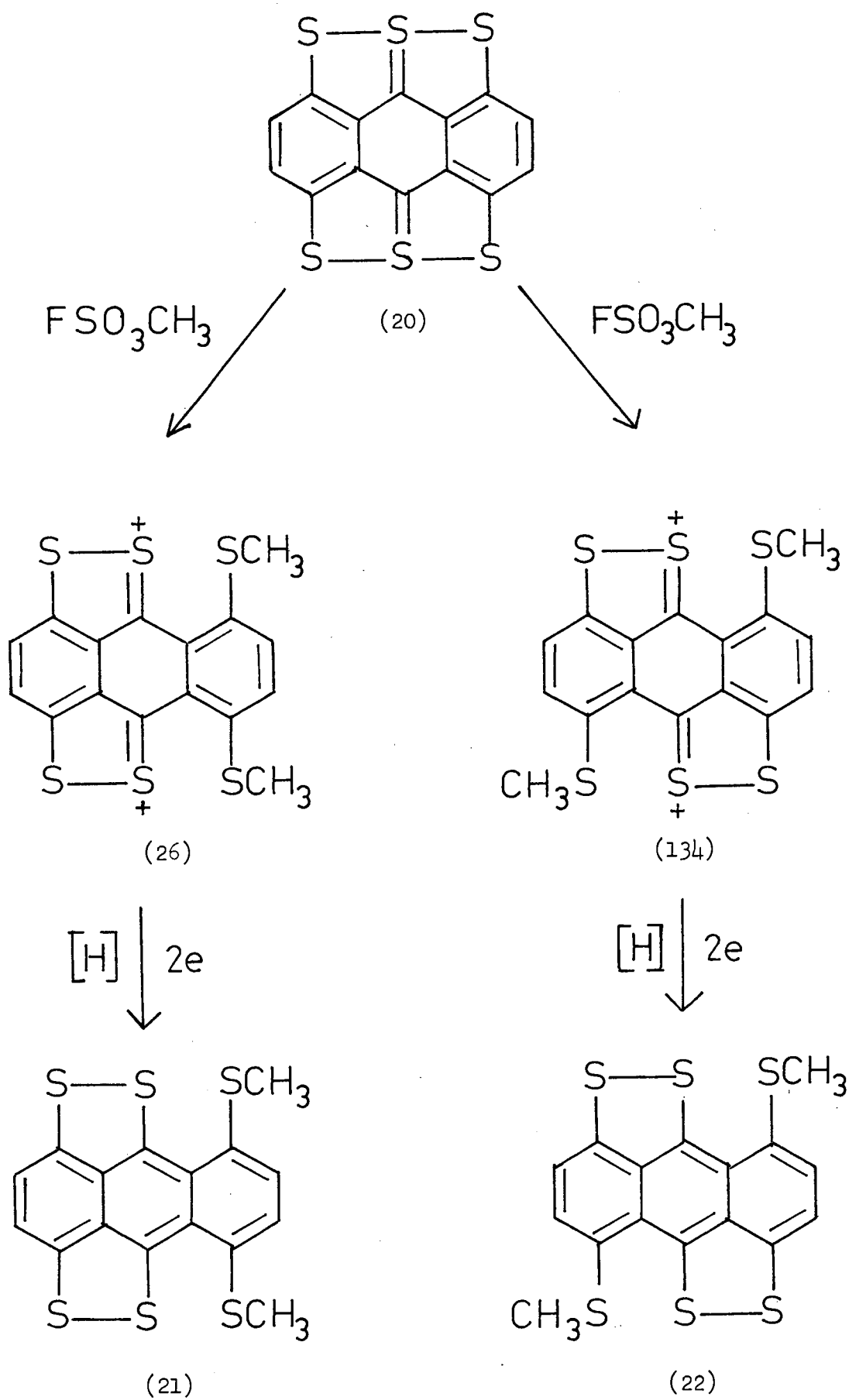
(ii) Direct Methylation followed by Reduction

Steven[18] reported that dimethyl sulphate did not react with hexathioanthracene whereas methyl fluorosulphonate gave a green solid believed to be a di(methylthio)anthracenobis(1,2-dithiolium)salt (26 and/or 134).

The methylation was repeated, under Steven's conditions, and the green salt was treated with an aqueous solution of sodium dithionite at ambient temperature in order to reduce the uncharacterised and unstable salt to a more amenable neutral compound. Reduction gave a dark coloured solid which proved to be a mixture in which one component was soluble and the other insoluble in 1,1,2-trichloroethane.

The mass spectrum of the insoluble product gave a parent ion peak m/e 364 and fragmentation consistent with the product being hexathioanthracene (20). A comparison of the infra-red spectra confirmed the identity of the compound. Since it is difficult to envisage a mechanism for the formation of hexathioanthracene from the salt (26 and/or 134), it seems likely that the hexathioanthracene was present as an impurity in the salt, and not produced from it.

The mass spectrum of the soluble fraction showed the presence of two compounds: (i) a volatile compound which showed peaks at m/e 255, 192,160,149,121 and 73, and (ii) a compound with a parent ion at m/e 394 and fragment ions at m/e 379,364,320 and 182. The identity of the volatile component could not be determined and remains unsolved. The mass spectrum of the second compound was similar to that of Steven's product and indicated that the product was one, or both, of the di(methylthio)anthracenobis(1,2-dithiole)s (21,22), (Scheme 10).
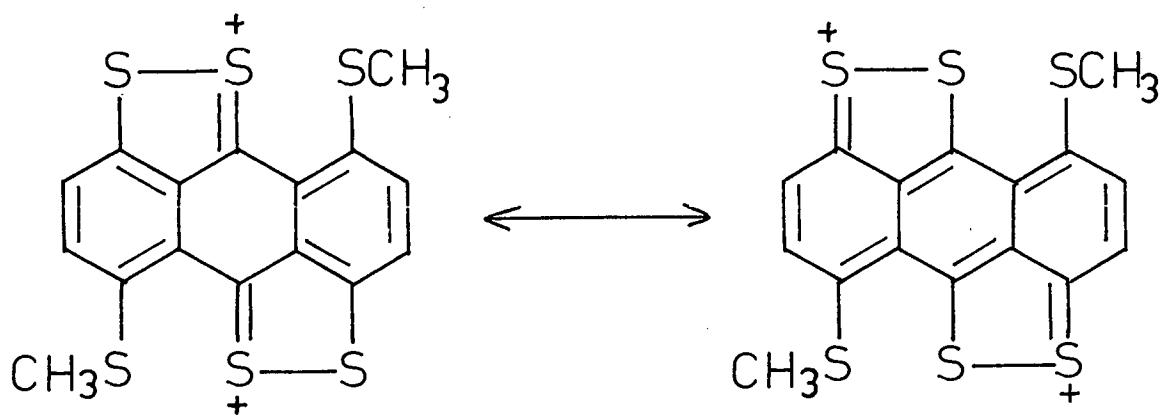
(134)
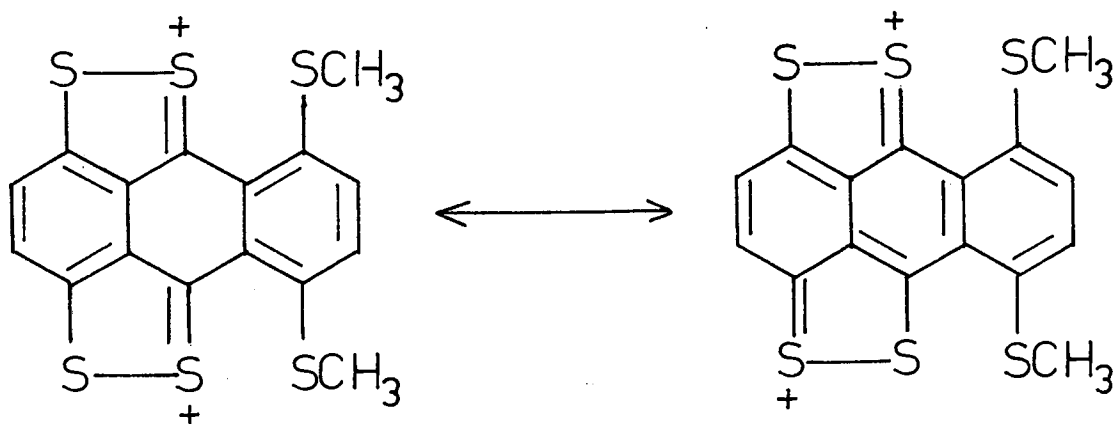
(26)

Chromatography of the soluble fraction gave a purple compound with a metallic lustre which was free from the volatile component. Since recrystallisation of the purple solid was not possible it was purified by vacuum sublimation. The elemental analysis and mass spectrum were then consistent with the proposed structures (21,22). Owing to the low solubility of the sublimate the 'H n.m.r. spectrum had to be obtained by the Pulsed Fourier-Transform method. The spectrum showed three resonances at δ7.4(d;J=8Hz), 6.9(d;J=8Hz) and 2.4(s) indicating that the purple solid was 5,10-di(methylthio)anthraceno[1,9-cd:5,10-c'd'] bis(1,2-dithiole) (22). No evidence for the presence of the isomer (21), which would have shown three singlet resonances, was found.

A possible reason for the isolation of only one isomer could be the increased stability of salt (134) as opposed to (26) owing to the larger charge separation. In compound (134) canonical structures can be drawn with the charges on sulphur atoms at position 1 and 5 (anthracene numbering) whereas in compound (26) the charges can only be separated over sulphur atoms at positions 1 and 10.

Attempts to oxidise hexathioanthracene (20) to a stable radical cation failed, yielding only black uncharacterisable products. The failure was in agreement with the results reported by Goodings[16] et al. in their studies of hexathiopentacene, (see introduction).

(iii) <u>Attempted synthesis of 1,1a λ^4,2,3,4,4a λ^4,5,6-octathiadi-</u>
  <u>pentaleno[2,3,4,5-cdef;2',3',4',5'-ijkl]-s-indacene</u>

As an extension of the study of acene polysulphides, the synthesis of the related compound (137) was attempted. Compound (137) is an interesting compound since it consists entirely of carbon and sulphur

O

(135)

$CS_2/NaH/CH_3I$

CH_3S O SCH_3

S S

CH_3S O SCH_3

(136)

$(EtO)_2PS_2H$ | P_2S_5

S—S—S

S   S

S—S—S

(137)
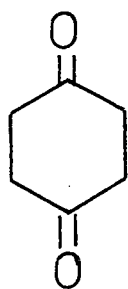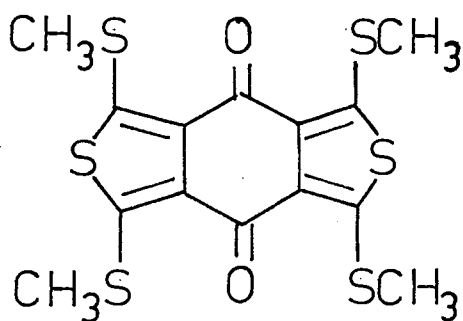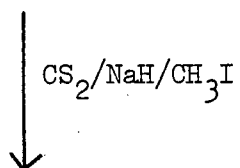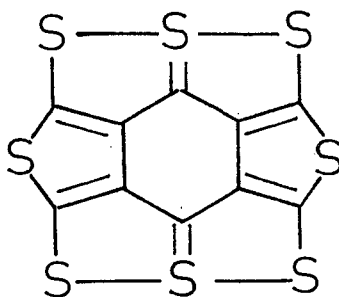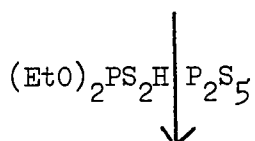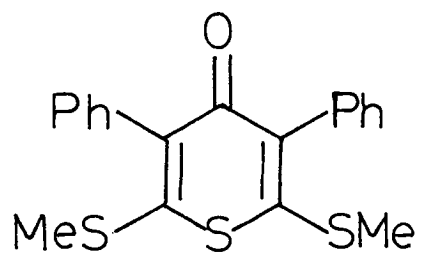
Scheme 11

(139)
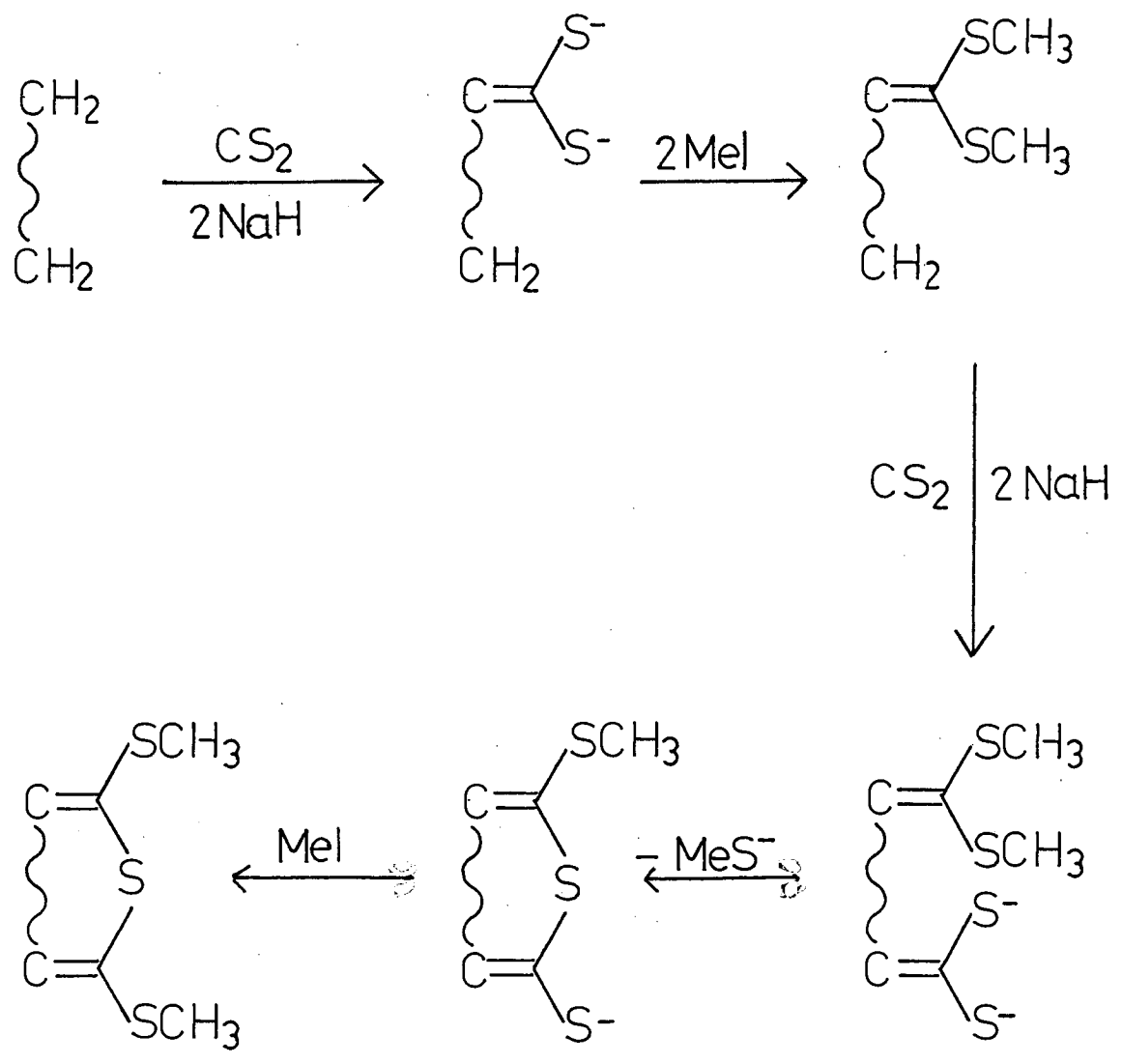
atoms and is isoelectronic with hexathioanthracene (20). The first
proposed synthesis for compound (137) is illustrated in Scheme 11.

Cyclohexane-1,4-dione (135) reacted with carbon disulphide and
methyl iodide in the presence of sodium hydride and dimethylacetamide
to give a dark green solid which precipitated from the toluene used
as reaction solvent. The mass spectrum of the solid showed a parent
ion at ^{m}/e 404 with fragment ions at ^{m}/e 389,371,356,339,323,305 and
202 all consistent with the proposed structure (136) (see experimental).
The mass spectrum also showed a peak at ^{m}/e 258, which might have been
the parent ion of a second compound, together with fragment ions suggest-
ing the structure (138a) or (138b).

(138a)   (138b)
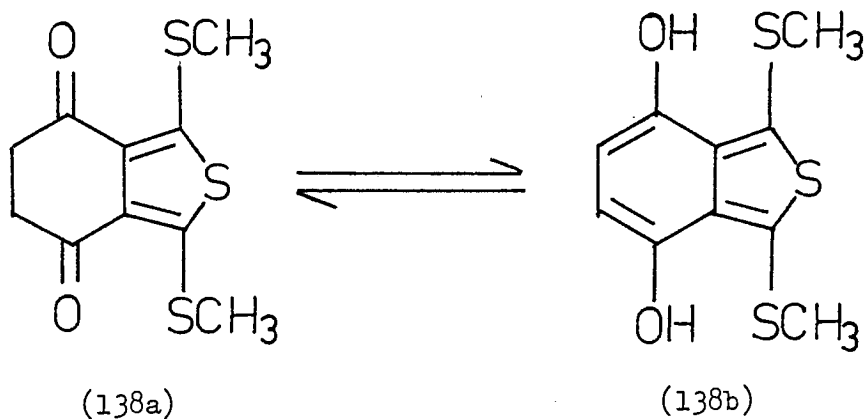
The formation of compounds (136) and (138) is analogous to Shahak
and Sasson's[88] synthesis of 2,6-di(methylthio)-3,5-diphenylthiopyran-
4-one (139) from dibenzyl ketone by reaction with carbon disulphide
and methyl iodide in the presence of sodium hydride. A generalised
scheme for the course of such reactions is shown opposite.

The dark green solid was purified by Soxhlet extraction with
acetonitrile and a small sample of the residue was recrystallised from
pyridine. Elemental analysis then gave values in agreement with structure
(136). Since compound (136) was insoluble in common organic solvents
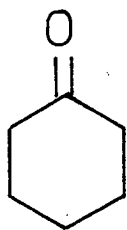
CS$_2$/NaH/CH$_3$I
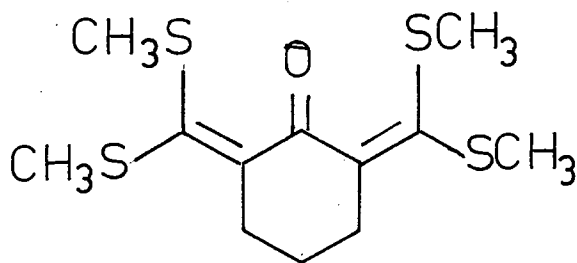
(140)

P$_2$S$_5$/xylene
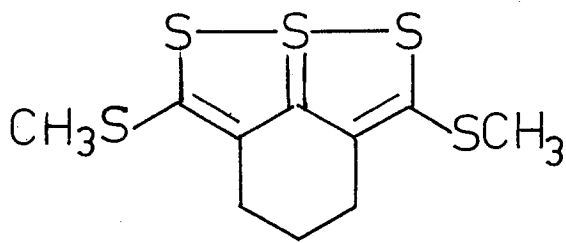
(141)

Scheme 12

no n.m.r. spectra could be obtained to confirm the proposed structure;
however, an exact mass measurement was correct to within 2 p.p.m.

The conversion of compound (136) into the bisthiathiophthen ring
system (137) was attempted by treatment with phosphorus pentasulphide
in various solvents. However, all the attempted thionations failed
and the starting material (136) was recovered quantitatively.

The failure of phosphorus pentasulphide to convert compound (136)
into the thiathiophthen derivative (137) was unexpected since Thuiller
and Vialle[89] reported the synthesis of compound (141) and related
thiathiophthens by a similar method; Scheme 12. Possibly in the
rigid molecule (136) the carbonyl groups are more hindered than that
in the cyclohexanone (140) and, since phosphorus pentasulphide is a
large molecule, no reaction occurs.

The more recent thionation procedure reported by Oae et al.[90]
was equally ineffective, compound (136) being recovered quantatively
after treatment with 0,0-diethyldithiophosphoric acid for 50 hours at
80°.

With one irreproducible exception, attempts to convert (136) into
(137), in dimethylformamide, using sodium sulphide nonahydrate or sodium
hydrogen sulphide and sulphur produced black involatile solids that did
not show infra-red absorptions (as Nujol mulls) and were insufficiently
volatile for mass spectra to be obtained. In the one exceptional
reaction, compound (136) was treated with sodium sulphide in refluxing
aqueous dimethylformamide and a dark green solid was isolated. The
mass spectrum showed a parent ion at $^m/e$ 390 with fragment ion peaks
at $^m/e$ 375,358 and 344 suggesting that the solid might be compound (142)
in which a thiathiophthen unit had been formed from one side of compound

(136) but not from the other. The mass spectrum also showed small peaks at $^m/e$ 404 and 376 corresponding to compounds (136) and (137) respectively.
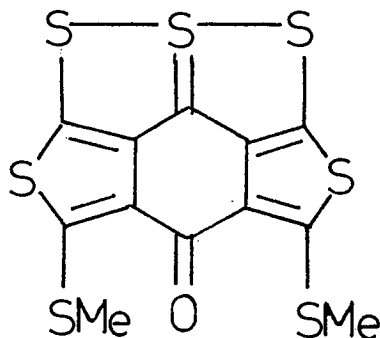
(142)

Further reaction of (142) with sodium sulphide gave black degradation products, similar to those previously described. Attempts to repeat the synthesis of compound (142) failed yielding only black involatile solids which could not be identified.

An entirely different approach to the synthesis of compound (137) via the sulphurisation of 1,4-dibromo-2,3,5,6-tetra(bromomethyl)benzene (143) was also investigated. The starting hexabromo-compound was synthesised by the method of Smith[91] and Hopff[92] by successive bromination of durene.

i) $Br_2-CH_3CO_2H$

ii) Br_2-CCl_4
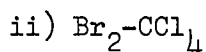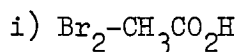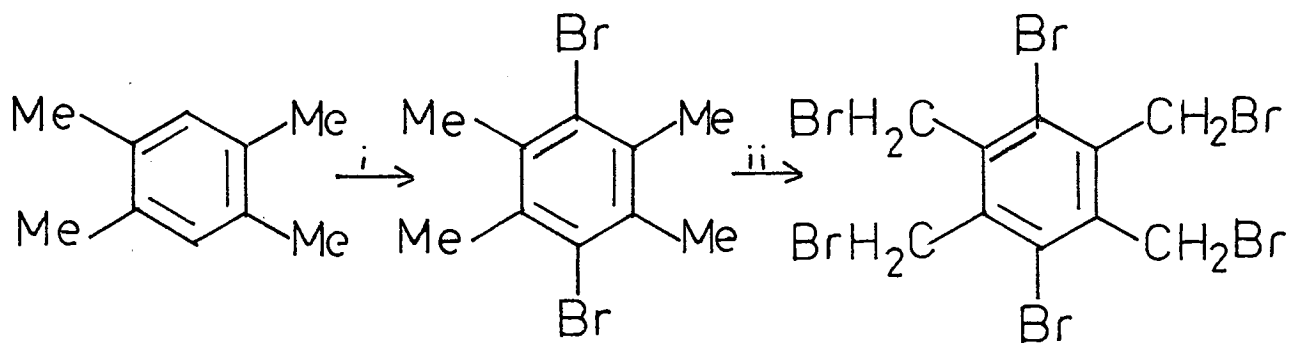
(143)

The synthesis of polysulphur compounds by the reaction of sulphur with benzylic halides in dimethylformamide has been reported by several authors[18,93]. Unfortunately the reaction generally produces a mixture of products, some of which contain N-methyl groups and are believed to be formed by reaction with dimethylamine produced by decomposition of dimethylformamide. A procedure for sulphurisation avoiding dimethylformamide was sought in order to avoid the often difficult separation of the desired product from nitrogenous by-products.

A report by Becke[94] that dithiobenzoic acid (144) may be obtained from benzyl chloride by treatment with sulphur in methanolic sodium methoxide suggested that reaction of the hexabromodurene (143) under similar conditions might yield compound (137). [In view of results obtained in similar reactions with hexachloro-p-xylene (described later) it seemed likely that replacement of methanol by n-propanol would be advantageous].

(144)
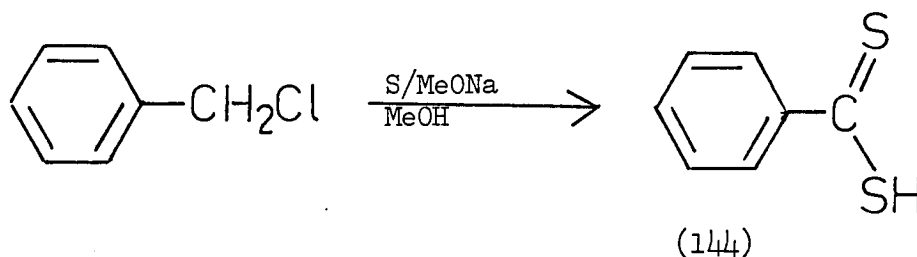
It was envisaged that the progressive conversion of the bromomethyl groups into dithioacid groups would occur first and that prolonged treatment with the reagent would displace the bromine atoms in the 1- and 4- positions. Loss of two molecules of hydrogen sulphide and dehydrogenation could then yield compound (137). Unfortunately, the only isolated product was a black involatile solid, similar to those obtained previously. A similar product was obtained by reaction of the hexabromodurene with sulphur in dimethylformamide.

(iv) Synthesis of a polysulphide derived from pyridazino

[4,5-d]pyridazine

There is a great deal of interest in the conductivity of radical

cations and charge-transfer complexes derived from acene polysulphides.

Many of the initial studies were carried out on tetrathiotetracene (4),

and recently interest has focussed on the closely related naphtho[1,8-cd:

4,5-c'd']bis[1,2]dithiole (27) ("tetrathionaphthalene").

(4)

(27)
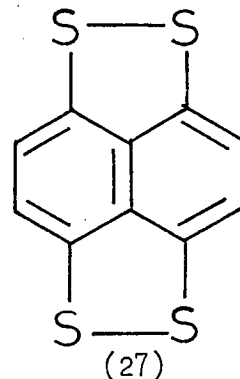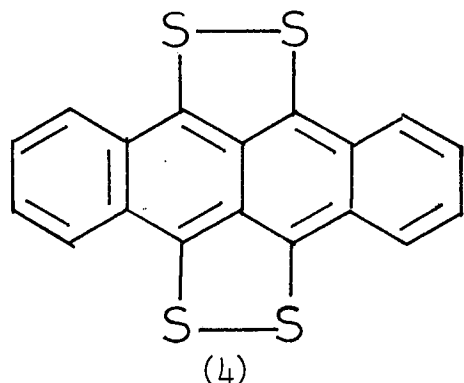
When this study started tetrathionaphthalene (27) had not been

reported, although Davidson[7] and Steven[18] both reported unsuccessful

attempts to synthesise it. Recently, however, Wudl[19] has reported

the synthesis of tetrathionaphthalene and some initial conductivity

measurements (see introduction).

Pyridazino[4,5-d]pyridazine (145) is isostructural with naphthalene

and it seemed possible that its tetrathio-derivative (146) would resemble

tetrathionaphthalene and might be more easily synthesised.

(145)

(146)

Scheme 12

(147)

(148a)　　　　　　　　　　　　(148b)
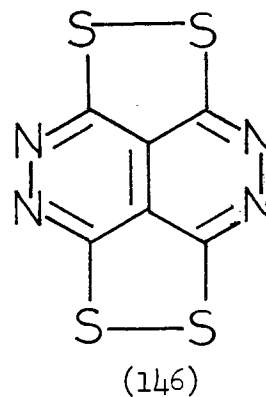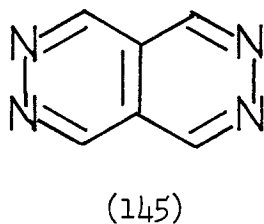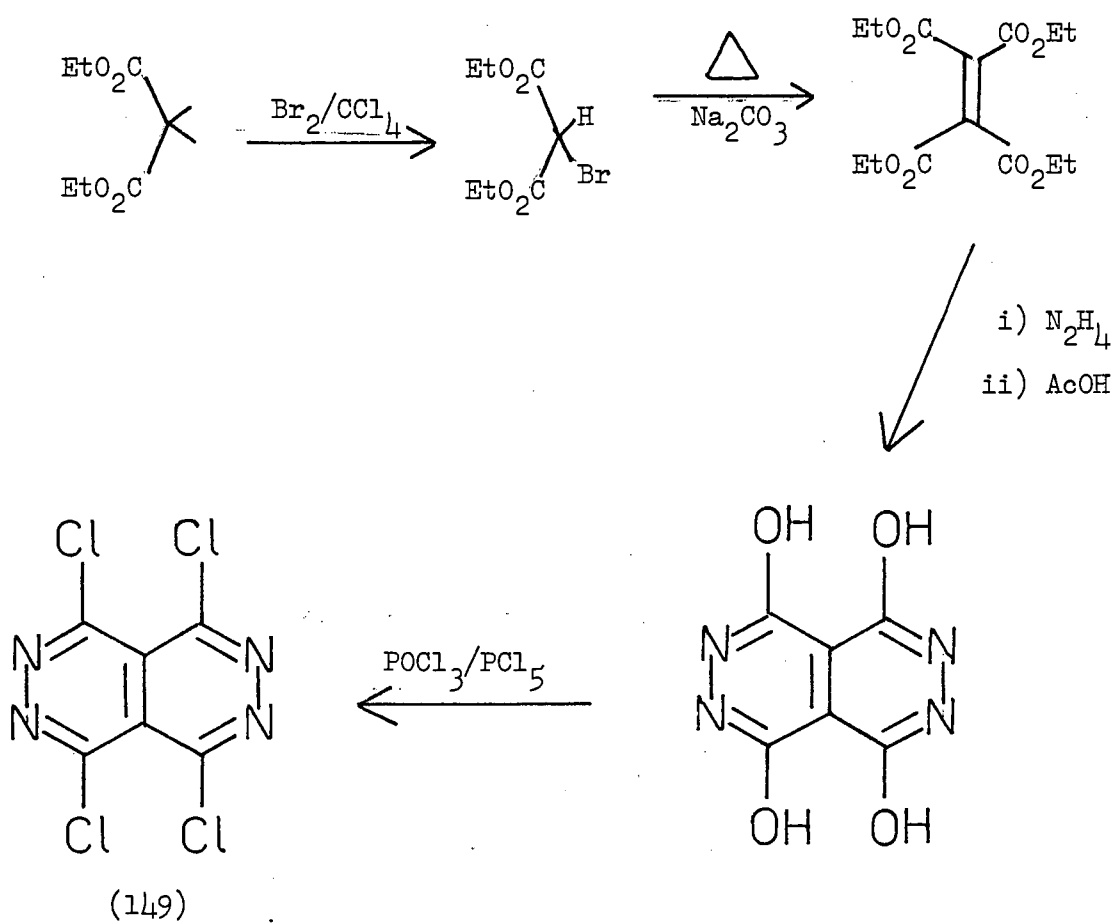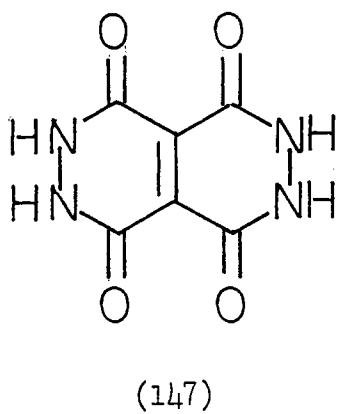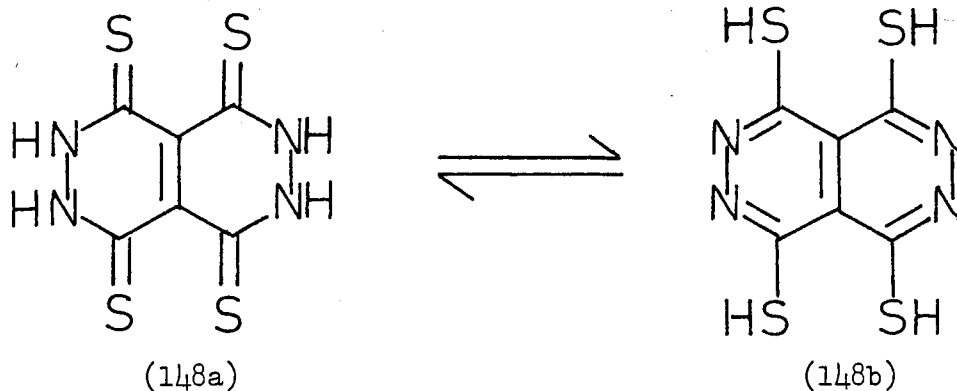
Steven[18] attempted to synthesise 1,2,5,6-tetrathia-3,4,7,8-tetra-azacyclopent[fg]acenaphthylene (146) by reaction of the known octahydropyridazino[4,5-d]pyridazine-1,4,5,8-tetrone (147) with phosphorus pentasulphide. It was expected that this reaction would give the tetrathione (148a), the thiol tautomer (148b) of which would have been readily oxidisable to (146). Unfortunately, however, no thionated product was isolated.

Adembri[95] in 1972, reported the synthesis of 1,4,5,8-tetra-(ethylthio)pyridazino[4,5-d]pyridazine (150) by reaction of the 1,4,5,8-tetrachloro derivative (149) with sodium ethanethiolate in refluxing ethanol. The starting material, compound (149), was synthesised from diethyl malonate by the reactions illustrated in Scheme 12.

(149)　　　　　　　　　　　　(150)
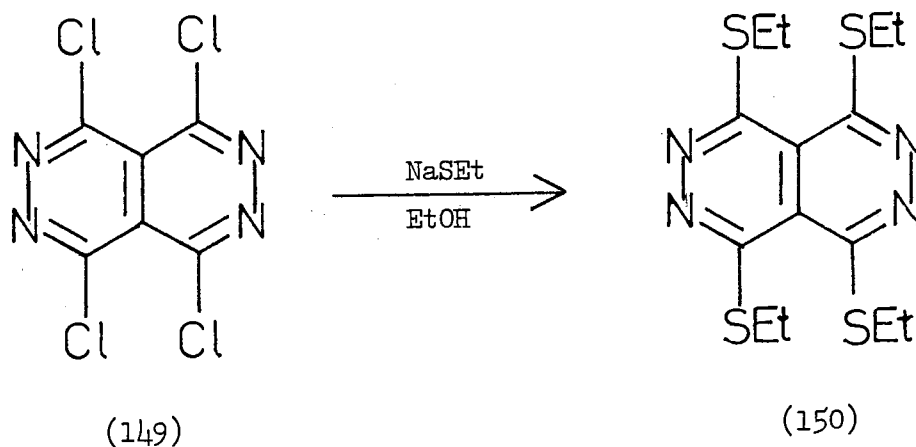
It was proposed, therefore, to synthesise compound (148) by reaction of tetrachloropyridazinopyridazine (149) with sodium hydrogen sulphide and to oxidise it (if oxidation did not occur spontaneously) to the bis-disulphide (146).

The reaction of compound (149) with sodium hydrogen sulphide in refluxing ethanol gave a brown product, the mass spectrum of which showed a parent ion at $^m/e$ 288 [compound (146) requires $^m/e$ 256] and further prominent peaks at $^m/e$ 256,226,192,156,112 and 100. Accurate mass measurements established that the ions of $^m/e$ 288,256,226 and 156 had the compositions $C_6N_4S_5$, $C_6N_4S_4$, $C_6H_2N_4S_3$ and C_5S_3, respectively. No other accurate mass measurements were made but it seems likely that the peaks at $^m/e$ 192,112 and 100 correspond to $C_6N_4S_2$, C_4S_2 and C_3S_2, respectively. Thus all the major peaks, with the exception of $^m/e$ 226, which was probably due to an impurity, are explicable in terms of a parent ion $C_6N_4S_5^+$ and its fragments. It is possible that part of the peak at $^m/e$ 256 was due to the presence of the expected product (146) in the sample but, since this peak was much less intense than $^m/e$ 288, it is unlikely that significant amounts of this compound were present.

Unfortunately, the brown product was virtually insoluble in solvents other than hot dimethylformamide. Attempts to recrystallise it from this solvent or to purify it by vacuum sublimation led to decomposition. Elemental analysis (C,H,N) of the crude solid gave results which, though far from satisfactory, were sufficiently close to those expected for $C_6N_4S_5$ to indicate strongly that this was the major constituent of the product.

An attempt to obtain the tetrathione (148a) by treatment of the tetrone (147) with phosphorus pentasulphide in boiling pyridine gave a brown solid (B) which was very similar to the product (A) obtained
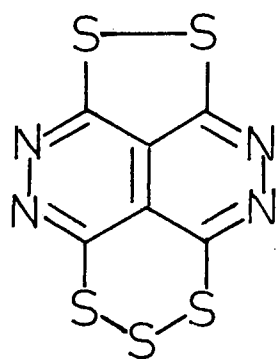
(151)
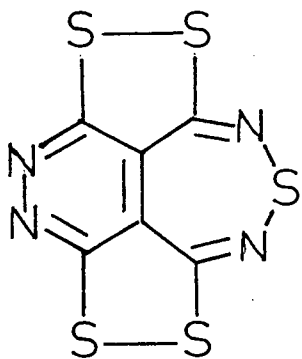
(152)
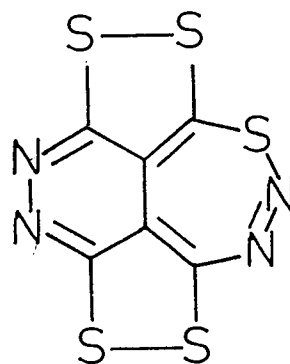
(153)
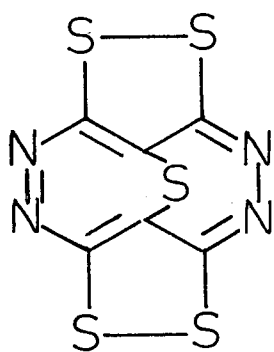
(154a)
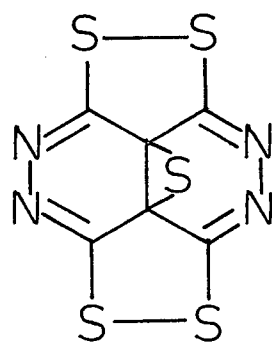
(154b)

from the tetrachloro compound and sodium hydrogen sulphide. The mass spectrum of solid (B) showed a parent ion at $^m/e$ 288 and further prominent peaks at $^m/e$ 226,156,112 and 100; the peak at $^m/e$ 256 was also present though it was less intense than the corresponding peak from product (A). Each of the two mass spectra showed a number of minor peaks that were absent or very weak in the other. It may be concluded, therefore that the two products (A) and (B) contained the same major component ($^m/e$ 288) but differed in the nature or relative importance of the minor components.

The structure of the product $C_6N_4S_5$ remains unknown but various possibilities should be considered and, assuming that no major rearrangement of the C-N skeleton has occurred, these may be grouped into three main types derived from the tetrathiotetra-azacyclopentacenaphthylene (146) in the following ways: (i) by insertion of a sulphur atom into one of the S-S bonds [structure(151)], (ii) by insertion of a sulphur atom into one of the pyridazine rings [structures(152)-(154a)] and (iii) by co-ordination of a sulphur atom to a sulphur or nitrogen lone pair (i.e. structures containing $\overset{+}{N} - \overset{-}{S}$ or $\overset{+}{S} - \overset{-}{S}$ units). In addition, each of the structures of type (ii) might be written in a valence-tautomeric form containing an episulphide ring [e.g.(154b)]. Structures of type (iii) are considered to be unlikely since N-sulphides and S-sulphides appear to be known only as transient intermediates which readily lose sulphur.

A spectroscopic analysis of the product $C_6N_4S_5$ failed to provide evidence to prove or disprove any of the previously illustrated structures (151-154). The insolubility of the product prevented a ^{13}C n.m.r. study and an X-ray crystallographic study was not possible since a pure sample of the product could not be isolated.
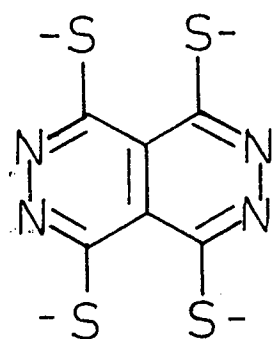
(155)
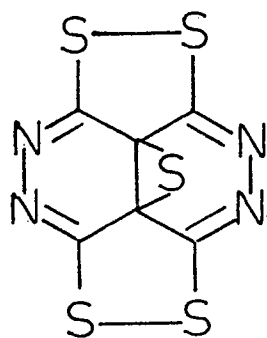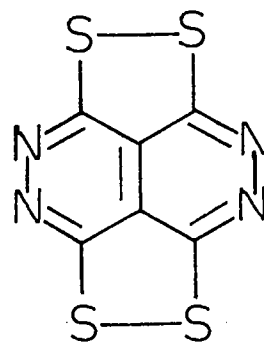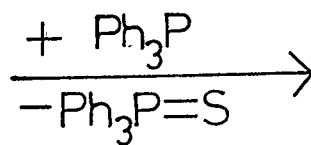
(154)   (146)

Since conventional analytical techniques failed to characterise the_∧known product, $^m/e$ 288, a limited number of attempts were made to chemically degrade the solid into a more soluble and hence character-isable compound.

If the solid had structure (151) treatment with alkaline sodium dithionite would be expected to reduce the disulphide bonds, giving the tetrasodium thiolate salt (155), and free sulphide ion. Acidi-fication of the solution should then yield the 1,4,5,8-tetramercapto-pyridazinopyridazine(148b) or the bis-disulphide (146) if spontaneous oxidation of (148b) occurred.

The reduction was attempted three times, and in two reactions starting material was recovered quantitatively. The third reaction gave a dark coloured solid of $^m/e$ 226 (28%) which was thought to be the previously observed contaminant, $C_6H_2N_4S_3$. No other product was isolated from this reaction. These experiments indicate that the penta-sulphide is probably not the dithio-trithio compound (151).

The removal of sulphur from organic molecules by treatment with triphenylphosphine is a well established synthetic method which is applicable in a variety of situations[96]. All of the three possible types of structures considered for $C_6N_4S_5$ might be expected to lose one sulphur atom in this way, thus yielding the required tetrathio- compound (146). In practice, however, the reaction was not straightforward. The brown solid reacted with one mole equivalent of triphenylphosphine, under nitrogen, to yield triphenylphosphine sulphide, which was extract-able with chloroform, and a brown residue which was apparently polymeric, being insoluble in common organic solvents and insufficiently volatile for the measurement of a mass spectrum.

An attempt to purify the unknown solid ($^m/e$ 288) by vacuum sublimation also led to decomposition. The dark brown sublimate and residue were insoluble and involatile solids. No infra-red or mass spectra could be obtained and elemental analyses indicated that decomposition had occurred.

Section two.   The Synthesis of 4-Thioaroyl-1,2-dithiole-3-

thiones and Related Compounds

Teste[32] and Leaver[31] reported the synthesis of a series of 4-thioaroyl-1,2-dithiole-3-thiones (37) by thionation of the corresponding 4-aroylcompounds (38). Compounds (37) were studied to see if they exhibited single bond - no bond resonance but no evidence for this was found. Leaver[31] et al. concluded, on the bases of chemical evidence and ^{1}H n.m.r. spectra, that isomeric thioacyl compounds (37; $R^1=R^2$) were interconvertible but that the tautomeric equilibrium was not rapidly established on the n.m.r. time-scale. They further reported that thionation occurred only with purified phosphorus pentasulphide and that compound (37) was isolated in very low yields.

In all reported compounds of type (37) R^1 and R^2 are aryl and it seemed possible that the low yields were due to the high reactivity of the thioketonic grouping at C-4. Accordingly the synthesis of (37; $R^1=R^2=NH_2$) was attempted, in the hope that the presence of a thioamido group would lead to greater stability and higher yields. Starting materials for proposed syntheses of compound (37; $R^1=R^2=NH_2$) were obtained from amide and nitrile derivatives of malonic acid by two routes: (i) by reaction with carbon disulphide and sulphur and (ii) by reaction with 2-methylthio-1,3-dithiolanylium salts.

$$CH_2 \quad NCCONH_2 \quad (156) \xrightarrow[\text{NaOCH}_3]{\text{CS}_2\text{-S}} \quad (38g)$$
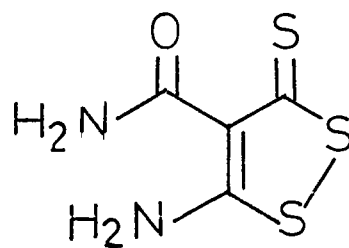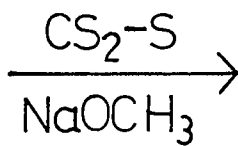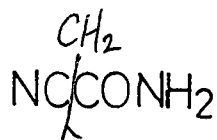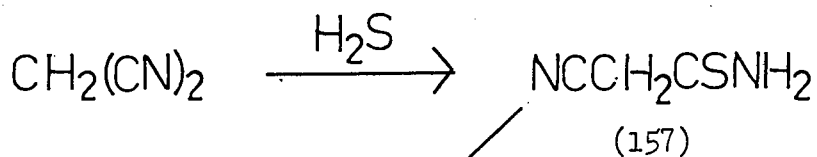
$$CH_2(CN)_2 \xrightarrow{H_2S} NCCH_2CSNH_2 \quad (157)$$
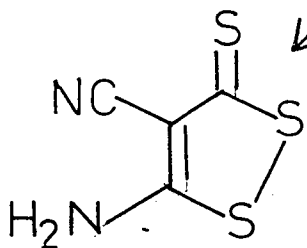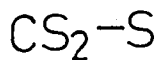
(158)
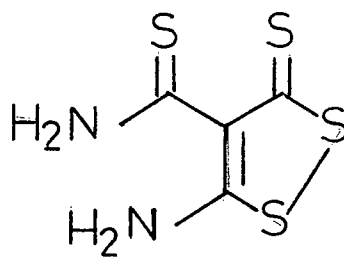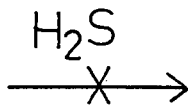
(37)

(i) The Reaction of Malonic Acid Derivatives with Carbon
     Disulphide and Sulphur

Gewald[97], in 1966 reported the synthesis of 5-amino-4-carbox-
amido-1,2-dithiole-3-thione (38g) from the reaction of cyanoacetamide
(156), carbon disulphide and sulphur in the presence of sodium methoxide.
This reaction was repeated and the amidodithiolethione (38) was treated
with phosphorus pentasulphide in boiling xylene and with phosphorus
pentasulphide and bromine[98] in 1,2-dichloroethane. Surprisingly no
thionation occurred in either case and starting material was recovered
quantitatively. Reaction of compound (38g) with phosphorus pentasulphide
in pyridine gave a red-brown gum from which a small amount of solid was
isolated on trituration. Attempts to purify the product failed, pro-
ducing a maroon gum. The mass spectrum of the solid showed a parent
ion at ^{m}/e 240 with fragment ion peaks at ^{m}/e 216,184,176,154 and 112.
The parent ion is 32 mass units higher than expected, and elemental
analysis gave values close to those required for $C_4H_4N_2S_5$ or $C_4H_4N_2O_2S_4$
i.e. the expected product plus one sulphur, or two oxygen, atoms.
Since the product was only isolated in small yield no work was carried
out to establish the structure.

Since compound (37g) could not be obtained by thionation of the
carboxamidodithiolethione (38g) an attempt was made to obtain it
directly from cyanothioacetamide (157) carbon disulphide and sulphur
using Gewald's procedure. Perhaps not surprisingly, however, the
thioamide was not obtained but 5-amino-4-cyano-1,2-dithiole-3-thione
(158) was isolated instead. Presumably the elemental sulphur, instead
of providing an additional sulphur atom for the formation of (37),
acted merely as an oxidant, converting the intermediate dithiolate
anion (159) into the dithiolethione (158).

$$\text{CH}_2\text{—C}(=\text{S})\text{NH}_2,\ \text{CN} \xrightarrow[-\text{H+}]{\text{base}} \left[\overset{-}{\text{CH}}\text{—C}(=\text{S})\text{NH}_2,\ \text{CN} \longleftrightarrow \text{CH}=\text{C}(\text{S}-)\text{NH}_2,\ \text{CN} \right]$$

$$\downarrow \text{CS}_2/\text{base}$$

(158) $\xleftarrow{\ S_8\ }$ (159)
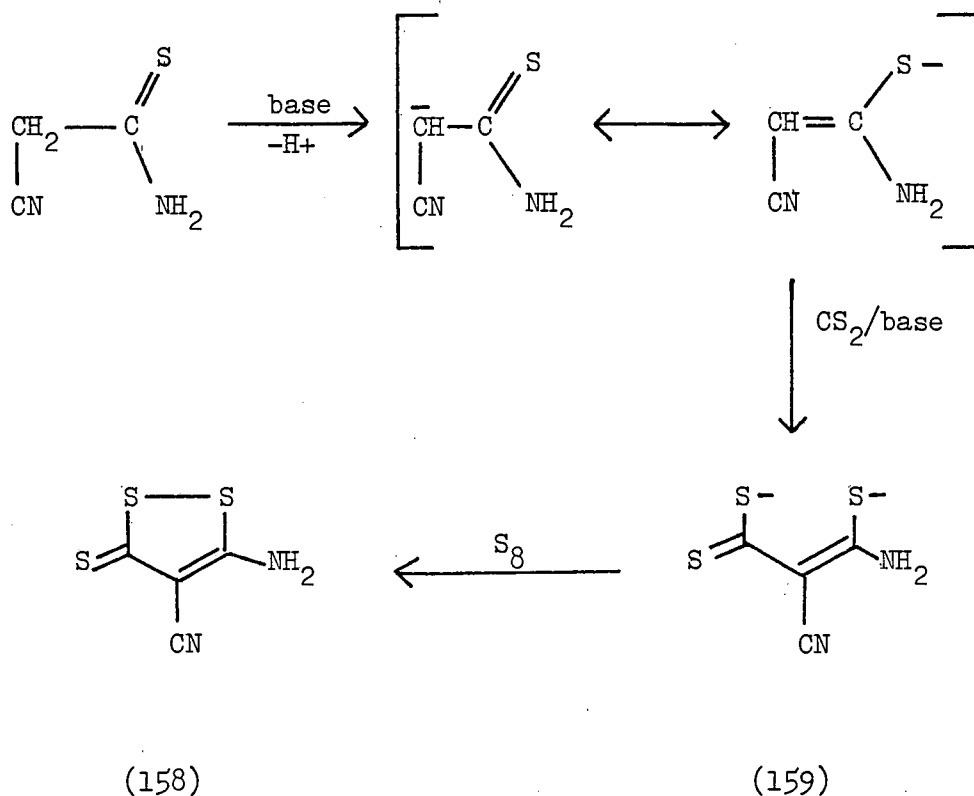
This result suggested that a similar reaction with dithiomalon-
amide in place of cyanothioacetamide might yield the required compound.
In practice, however, no reaction occurred and dithiomalonamide was
recovered. The failure of the reaction in this case can perhaps be
attributed to extensive delocalisation of charge on to the sulphur
atoms or the dithiomalonamide anion, thus reducing the nucleophilicity
of the central carbon.

$$\xrightarrow{-\text{H}^+}$$
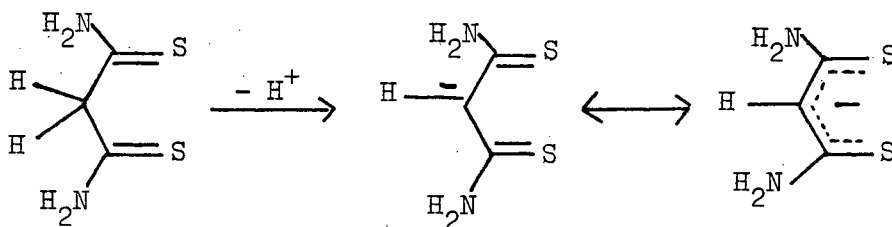
The conversion of nitrile groups into thioamides has been extensively studied, and a further approach to the synthesis of (37g) appeared possible by the hydrothionation of compound (158).

$$R-C\equiv N \xrightarrow{H_2S} R-\underset{NH_2}{\overset{S}{\underset{\|}{C}}}$$
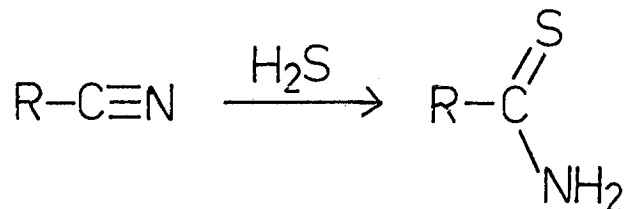
In practise, however, neither the procedure of Schmidt[99] (direct addition of hydrogen sulphide in the presence of α-picoline and 2-dimethylaminoethanol) nor that of Schicke[100] and of Oae[101] (reaction with O,O-diethyl dithiophosphate in the presence of water) yielded any characterisable product.

(ii) The Reaction of 2-Methylthio-1,3-dithiolanylium methosulphate
       with Derivatives of Malonic Acid

A second approach to compound (37g), based on Davidson's attempted synthesis of compounds (40-42), involved reaction of the salt (43) with malonic acid derivatives.

Reaction of the methosulphate (43) with malonamide gave a yellow microcrystalline solid identified as 1,3-dithiolan-2-ylidene malonamide (160). α-(1,3-Dithiolanylidene)ketones are known[34] to react with phosphorus pentasulphide to give 1,2-dithiole-3-thiones, a molecule of ethylene being eliminated. Unfortunately, however, treatment of the malonamide derivative (160) with phosphorus pentasulphide in xylene, or pyridine, did not yield the dithiomalonamide derivative (161) or compound (37g), the di-amide (160) being recovered almost quantitatively. A more direct synthesis of compound (161) was not possible since dithiomalonamide did not react with the salt (43).

Scheme 13

$$R-C{\equiv}N \;+\; (EtO)_2P-SH$$
$$\overset{\|}{\underset{S}{}}$$

$$\downarrow$$

$$\left[\begin{array}{c} R-C{=}NH \\[4pt] | \\ S\,P(OEt)_2 \\ \| \\ S \end{array} \right]$$

$$\downarrow H_2O$$

$$R-\overset{\displaystyle S}{\underset{\displaystyle \diagdown NH_2}{C}} \;+\; (EtO)_2P-OH$$
$$\overset{\|}{\underset{S}{}}$$
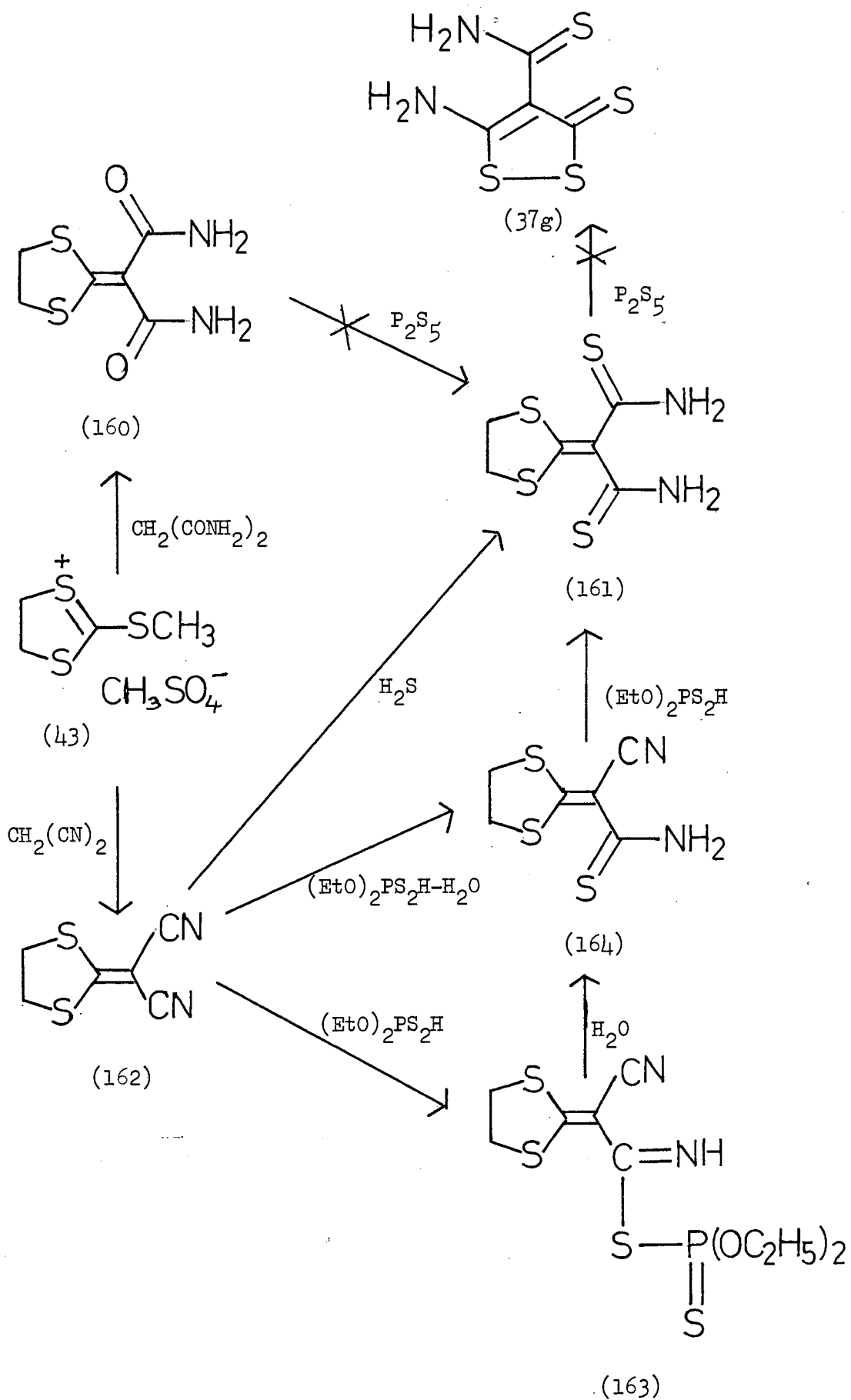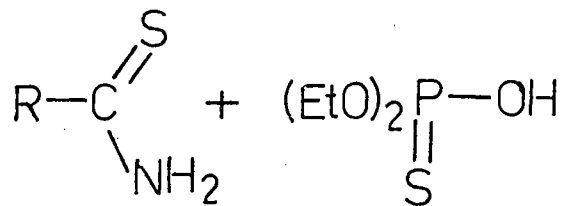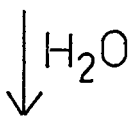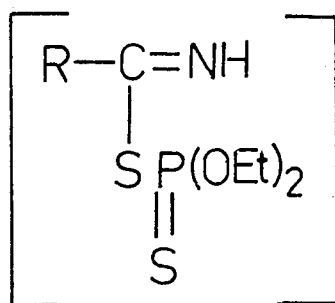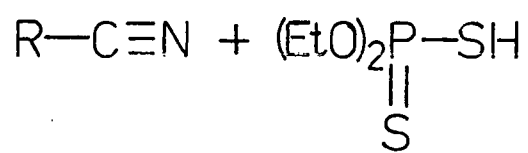
Scheme 14

The synthesis of thioamides by treatment of nitriles with hydrogen sulphide was mentioned earlier; however, hydrogen sulphide did not react with the nitrile groups in 1,3-dithiolan-2-ylidene malononitrile (162). Reaction of (162) with 0,0-diethyl dithiophosphate gave an orange solid (163). The infra-red spectrum of this product showed absorptions at 3340 and 2200 cm^{-1}, assigned to N-H and C≡N stretching modes, and the mass spectrum showed a parent ion peak at ^{m}/e 354. These results indicated that the $_\wedge$iminophosphate ester *PRODUCT WAS THE* (163). The structure was established conclusively by elemental analysis and 'H n.m.r. spectroscopy, which showed four well resolved resonances in agreement with the proposed structure. Compound (163) is an analogue of the proposed intermediate in Oae's[101] mechanism (Scheme 14) for the hydrothionation of nitriles by 0,0-diethyl dithiophosphate. The hydrothionation was repeated using an excess of phosphate ester in the presence of water and 1,3-dithiolan-2-ylidene cyanothioacetamide (164) was isolated, i.e. hydrothionation of only one nitrile group had taken place. Prolonged reaction of (164) and the phosphate ester failed to effect hydrothionation of the second nitrile group. The cyanothioacetamide (164) was also isolated from hydrolysis of the dithiophosphate (163), thus giving further proof that Oae's mechanism, for hydrothionation of nitriles, is correct.

The reactions of 2-methylthio-1,3-dithiolanylium methosulphate are illustrated in Scheme 13.

The octathiadicyclopenta[cd,ij]-s-indacene (165) may conveniently be discussed within this section since canonical structures (165a) and (165c) can be drawn that contain two 4-thioacyl-1,2-dithiole-3-thione moeities. The compound is composed entirely of carbon and sulphur atoms and will henceforth be referred to as C_8S_8. It was thought that
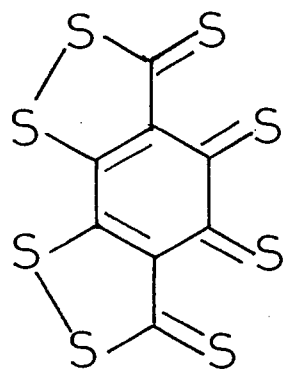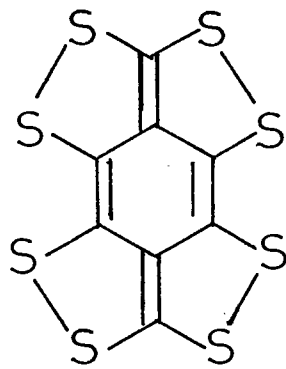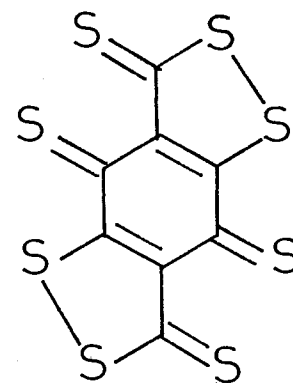
(165a)   (165b)   (165c)

compound (165) would be likely to form an electrically-conducting

charge-transfer complex with tetracyanoquinodimethane,TCNQ (166).
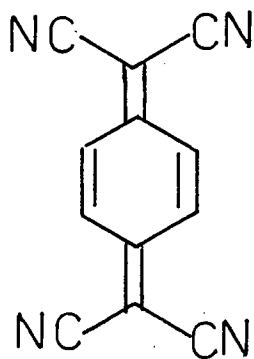
(166)
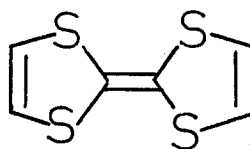
(167)

Since the early 1970's there has been a great deal of interest in

the synthesis and properties, particularly in the electrical conductivity,

of charge-transfer complexes containing dithiole derivatives as charge-

donor components[102-104]. One of the most important requirements for

high conductivity in a charge-transfer complex is the formation of

separate donor and acceptor "stacks" in the crystal lattice, so that

there is little or no energy barrier to the transfer of electrons from

site to site within a stack. Such electron-transfers involve exchange

of oxidation states, neutral molecule and radical-ion, between two

adjacent molecules. The classic example of an "organic metal" is the

tetrathiofulvalene,TTF (167) - tetracyanoquinodimethane,TCNQ (166)

charge-transfer complex. The complex crystallises in parallel uniform

stacks (103) and exhibits a room temperature conductivity of $10^3 \text{ohm}^{-1} \text{cm}^{-1}$.

It was expected that compound (165) would be readily oxidisable to

a radical-cation and that its complex with TCNQ, providing it had the

required type of crystal lattice, would possess interesting electrical

properties.
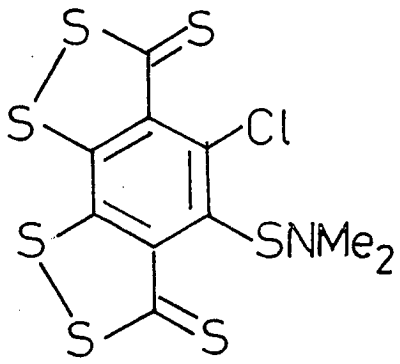
(169)
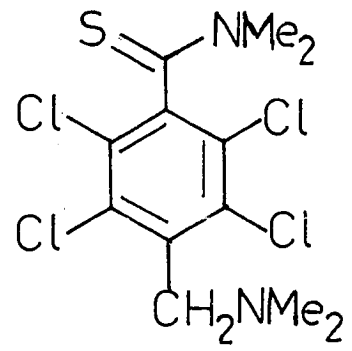
(170)
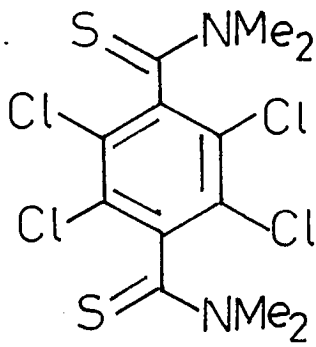
(171)
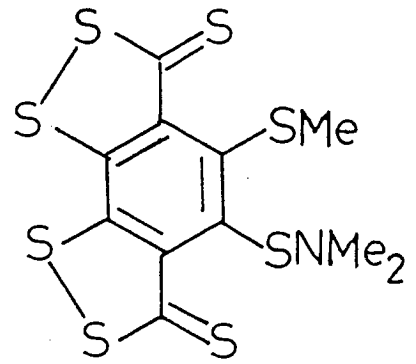
(172)

Steven[18] attempted to synthesise C_8S_8 by the sulphurisation of hexachloro-p-xylene (168) in dimethyl formamide but obtained a mixture from which four compounds were isolated. Mass spectroscopy suggested that the products were probably compounds (169-172), and demonstrated that solvent participation in the reaction had occurred. The formation of compounds (169-172) encouraged the belief that a synthesis of C_8S_8 by sulphurisation of compound (168) would be possible provided a suitable inert solvent could be found.

(168)   (165)
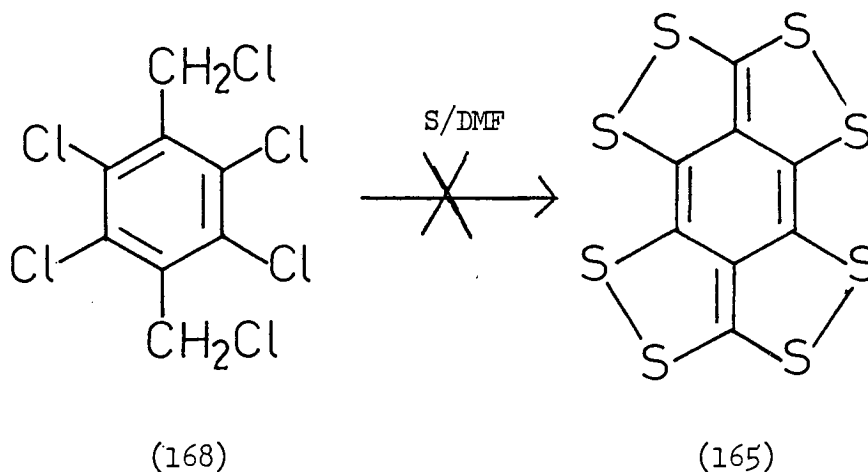
Accordingly, sulphurisation of compound (168) was attempted in sulpholane at 150°C but a black intractable and involatile solid was isolated. A similar product was obtained when the sulphurisation was carried out in refluxing N-methylpyrrolidine-2-one.

Reaction of compound (168) with elemental sulphur in sodium methoxide-methanol (a modification of Becke's[94] dithiobenzoic acid synthesis - see earlier) gave a bright red solid. The mass spectrum indicated that a possible product was 2,3,5,6-tetrachloro-4-methyl dithiobenzoic acid (173), contaminated with various di- and tri- chloro-compounds.

Table 1 Mass spectrum of C_8S_8

Ion ($^m/e$)	Abundance (%)	Probable composition
352	70	$C_8S_8^+$
320	8	$C_8S_7^+$
308	8	$C_7S_7^+$
288	12	$C_8S_6^+$
276	18	$C_7S_6^+$ (a)
192	8	$C_8S_3^+$
176	8	$C_8S_8^{2+}$ (b)
160	5	$C_8S_7^{2+}$ (b)$[+C_8S_2^+?]$
148	8	$C_7S_2^+$
144	5	$C_8S_6^{2+}$ (b)$[+C_4S_3^+?]$
136	10	$C_6S_2^+$
124	15	$C_5S_2^+$
112	25	$C_4S_2^+$
100	25	$C_3S_2^+$
88	10	$C_2S_2^+$
82	10	– ?
80	10	C_4S^+
76	25	CS_2^+
64	100	S_2^+
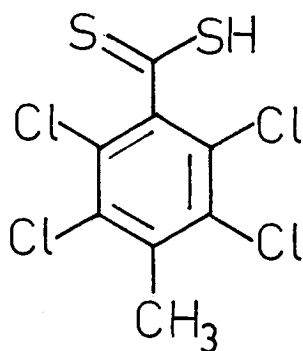
(173)

It was thought that a higher reaction temperature and/or a stronger base might cause further sulphurisation, so the reaction was repeated using sodium 2-methoxyethoxide and with sodium $\underline{t}$-butoxide, in the respective alcohols. No sulphurisation occurred under these conditions, starting materials being recovered, but, by using sodium 1-propoxide in propan-1-ol, a dark maroon solid was isolated after 18 hours reflux. The mass spectrum of the solid showed parent ion peaks at $^{m}/e$ 352 (M+) and 176 (M^{2+}) and seventeen fragment ion peaks with abundances $\geqslant$ 5% of base peak (Table 1). All except one of these peaks can be accounted for in terms of the molecular formula C_8S_8, though their modes of formation are not known. An exact mass measurement confirmed the molecular formula as C_8S_8 (error <1ppm) but attempts to recrystallise the product failed, owing to poor solubility in organic solvents. However, an elemental analysis of the crude product gave results which, though far from satisfactory, were reasonably close to those expected for C_8S_8.

All ions of $\geqslant$ 5% of S_2^+ are listed in table 1, however, there are also two strong peaks at 38 and 36 (1:3) which indicate HCl. This is probably a residue from the washing since no other chlorine-containing ions seem to be present.

(a)   A metastable ion peak at m/e 216.5 reveals the transition

$$C_8S_8^+ \longrightarrow C_7S_6^+ + CS_2$$

(b)   Peaks at 176.5, 160.5 and 144.5 due to doubly-charged ions containing one ^{13}C atom provide evidence for these assignments.

Attempts to repeat this synthesis of C_8S_8 (165) failed and no further investigation of the compound was possible. Mass spectroscopy indicated that a variety of products had been formed but no attempt was made to separate them. Exact mass measurements were not carried out but some possible structures based on observed m/e values are shown opposite and these suggest that more severe conditions might be required.

$\alpha,\alpha,\alpha^1,\alpha^1-2,3,5,6$-Octachloro-$\underline{p}$-xylene (174) was also investigated as an alternative starting material for C_8S_8. Reaction with sulphur in sodium 1-propoxide-propan-1-ol gave a dark product, the mass spectrum of which showed a parent ion at m/e 414, but there was no evidence for the formation of C_8S_8. Some of the possible products that correspond to observed m/e values could be intermediates in the formation of C_8S_8, but, as Steven[18] reported, solvent and/or alkoxide had participated in their formation. The formation of the thioester groups presumably occurred by reaction of the mono-or di-, chloromethyl group with alkoxide followed by oxidation of the methylene group by sulphur. This was analogous to the formation of (171) reported by Steven[18].

(174)

$C_{11}H_7Cl_3OS_4$ (388)

$C_{11}H_8Cl_2OS_5$ (386)
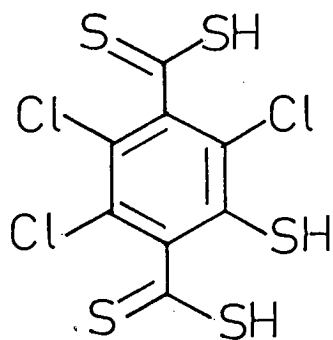
$C_8H_3Cl_3S_5$ (364)
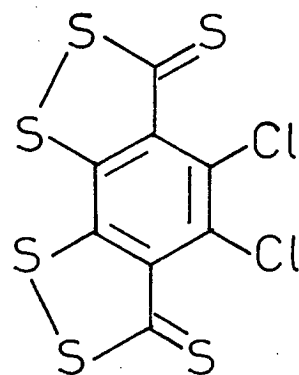
$C_8Cl_2S_6$ (358)
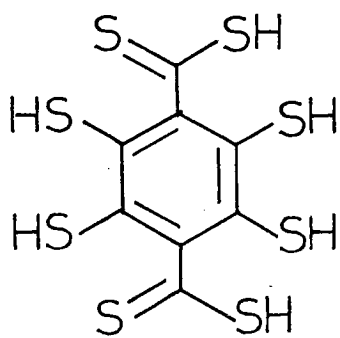
$C_8H_6S_8$ (358)
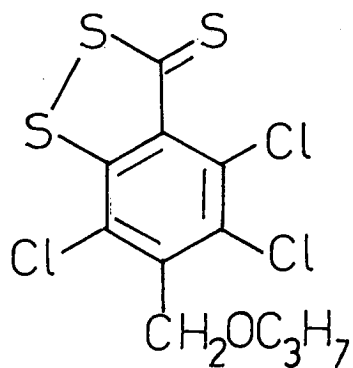
$C_{11}H_9Cl_3OS_3$ (356)
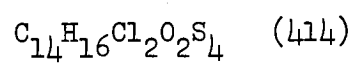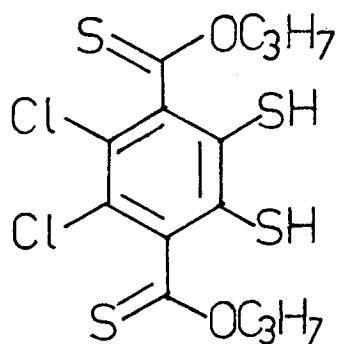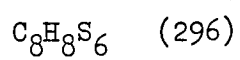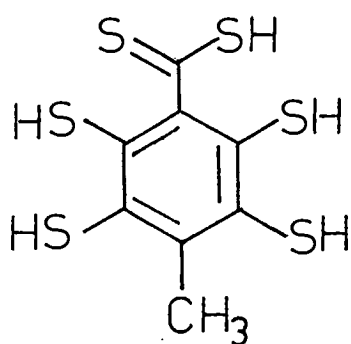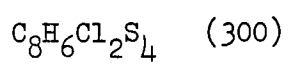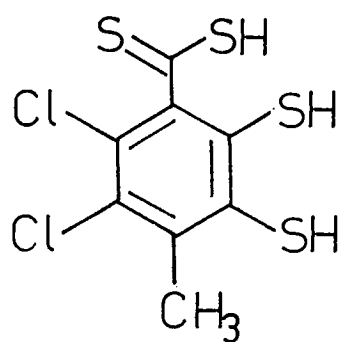
S SH

Cl SH

Cl SH

CH$_3$

$C_8H_6Cl_2S_4$ (300)

S SH

HS SH

HS SH

CH$_3$

$C_8H_8S_6$ (296)

S OC$_3$H$_7$

Cl SH

Cl SH

S OC$_3$H$_7$

$C_{14}H_{16}Cl_2O_2S_4$ (414)

Section three.   The Synthesis and Reactions of Complexes

containing Cyclopalladated Nitrogen and

Sulphur Donor Ligands

Notes

1. This section describes an investigation of the potential of

certain stable organopalladium complexes as intermediates in

heterocyclic synthesis. Since interest in the complexes was

centred on their use in synthesis, stereochemical studies were

not carried out unless otherwise stated, and the way in which

their formulae are depicted is purely arbitrary.

2. The complexes can be represented in two different canonical

forms exemplified below: (a) the commonly used structure

containing a carbon–palladium single bond and a single N–Pd or

S–Pd bond in which the heteroatom contributes two electrons,

and (b) a "carbene-complex" structure containing a carbon-

palladium double bond and a single N–Pd or S–Pd bond in which

the heteroatom contributes one electron. No attempt has been

made to establish the actual bonding around the palladium atom,

but it is thought that most of the complexes are closer to

canonical structure (a) than to canonical structure (b).
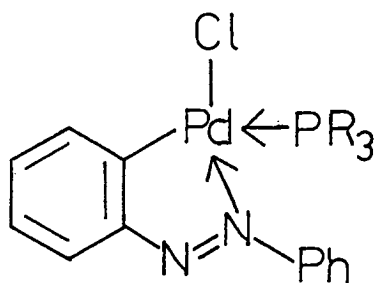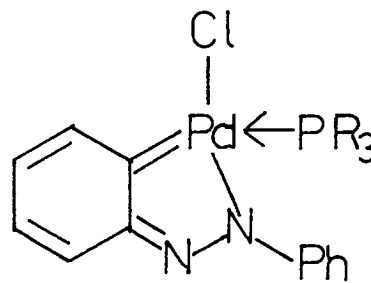
(a)   (b)
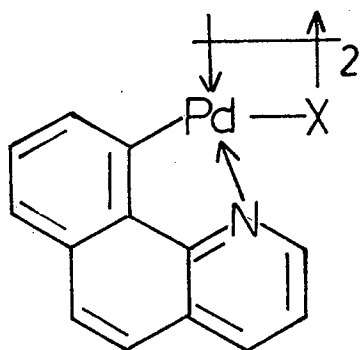
(175)

a: X = Cl

b: X = OCOCH$_3$
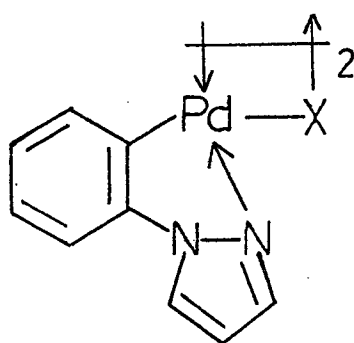
(176)

a: X = Cl

b: X = OCOCH$_3$
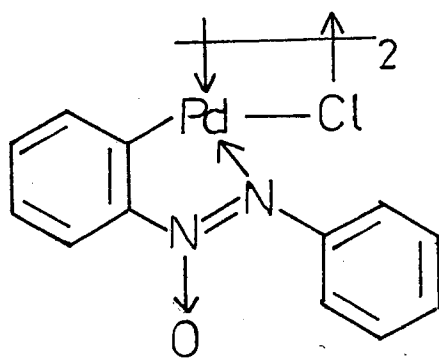
(59a)

(i)   The Synthesis of Acetate- and Chloride-Bridged

dimeric Cyclopalladated Complexes of Benzo[h]quinoline,

1-Phenylpyrazole and Azoxybenzene

Numerous nitrogen donor ligands are reported to undergo cyclo-
palladation on treatment with palladium acetate and/or sodium tetra-
chloropalladate (see introduction). The ortho-palladated chloride-
bridged complexes of benzo[h]quinoline (175a), 1-phenyl pyrazole (176a)
and azoxybenzene (59a) have been synthesised, and characterised, by
Lewis[49], Bruce[56] and Petridis[44], respectively.

In agreement with the unpublished work of Hay and Leaver, the
benzo[h]quinoline-palladium acetate complex (175b) was isolated in high
yield from the reaction of benzo[h]quinoline and palladium acetate in
refluxing acetic acid. A yellow complex was obtained after purification
and a comparison of spectroscopic data showed identity with the previously
obtained sample.

Reaction of 1-Phenyl pyrazole with palladium acetate under identical
conditions gave a fawn coloured product. Attempts to recrystallise the
complex (176b) failed and, at temperatures above 120°C decomposition
occurred with precipitation of metallic palladium. The ^{1}H n.m.r. spectrum
of the complex showed a singlet at δ 2.3 (integral 3 units) due to the
acetate ligands and three signals in the aromatic region (integral 7
units) in agreement with the proposed structure. The resonance at lowest
field, δ 7.4(d,1H) was assigned to H-3 of the pyrazole ring. The mass
spectrum showed peaks at ^{m}/e 392, 308 and 249, the second of which was
assigned to the monomeric cyclopalladated acetate complex (or dimer^{2+})
and the peak at ^{m}/e 249 to the fragment ion (177), providing further
evidence of orthopalladation. The peak at ^{m}/e 392 was tentatively

$$\left[\begin{array}{c} \text{(structure)} \end{array} \right]^{+}$$
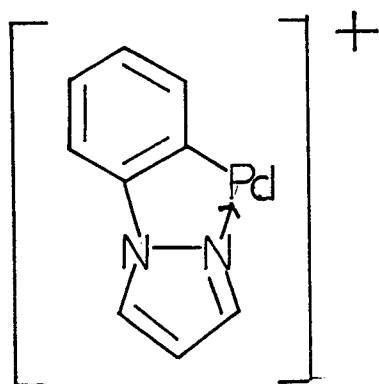
(177)
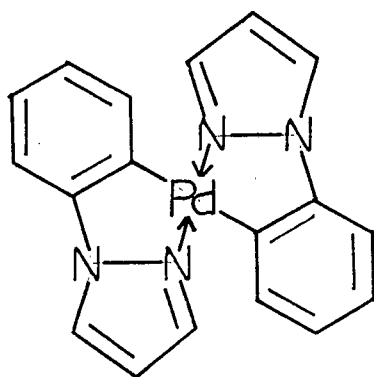
(178)

assigned to bis[2-(1-pyrazolyl)phenyl]palladium(II) (178) thought to be formed by a reorganisation of the bridged complex in the mass spectrometer. (This reaction and other anomalous mass spectroscopic reactions will be discussed later.) Elemental analysis of the crude pyrazole complex (176b) gave values consistent with the proposed structure.

Di-μ-chlorobis[2-phenylazoxy)phenyl]dipalladium(II), (59a) was synthesised by the method discussed earlier and spectroscopic data were consistent with those reported by Balch and Petridis[44].

(ii)   The Synthesis of Chloride-Bridged Cyclopalladated Complexes of 4,4'-Dimethoxythiobenzophenone, Xanthenethione and Thioxanthenethione

Davis[41] had demonstrated the potential of cyclopalladated complexes as intermediates in heterocyclic synthesis with the synthesis of 1,2-benzisothiazolo[2,3-a]pyridinium perchlorate (130) from di-μ-acetatobis[2-(2-pyridyl)phenyl]dipalladium(II), (69b).

i) Et$_4$NSCSNMe$_2$

ii) (SCN)$_2$

iii) Br$_2$

(69b)   (130)
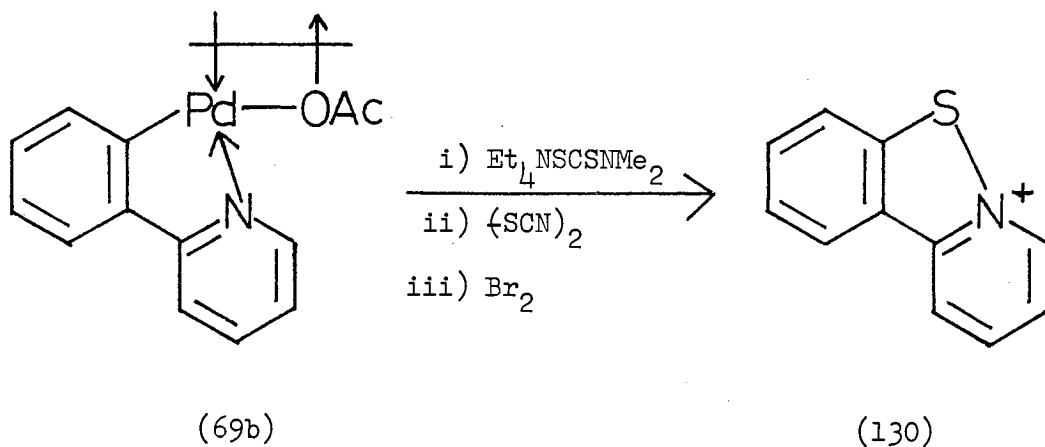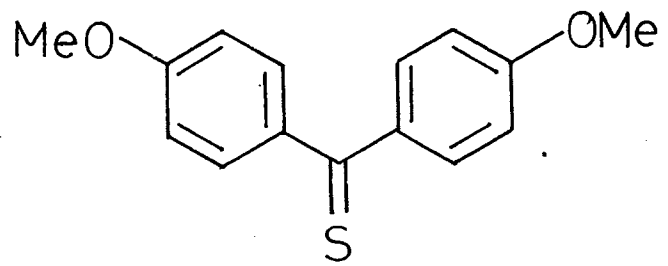
(50b)
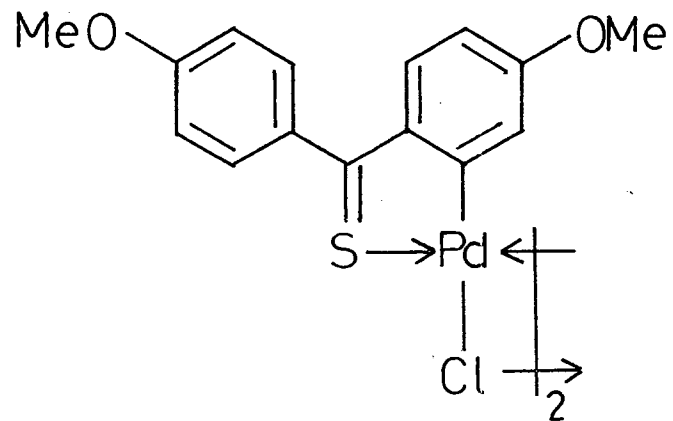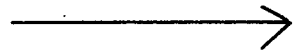
(51b)
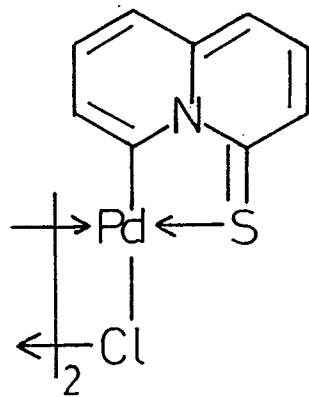
(53)

It was thought that Davis's procedure could be extended to provide a synthesis of 1,2-dithiolium salts via the <u>cyclo</u>palladation of suitable thiones. Prior to this study the only reported <u>cyclo</u>palladation complexes containing sulphur donor ligands were the complexes of thiobenzophenones (51b) and quinolizine-4-thione (53) discussed in the introduction.

To extend the study of thiones as donor ligands for cyclopalladation, xanthene-9-thione (179a) was treated with palladium acetate in refluxing acetic acid. The only products isolated were palladium sulphide and xanthen-9-one. At ambient temperature, the reaction gave a small amount of a red-brown product but again the main products were palladium sulphide and xanthen-9-one (>96%). No attempt was made to identify the solid. The results are analogous to those of Alper [40] who reported the desulphurisation of 4,4'-dimethoxythiobenzophenone (50b) by sodium tetrachloropalladate in refluxing methanol.

The thiobenzophenone complex (51b) was synthesised by the method of Alper [40] and, using the same procedure, xanthene-9-thione (179a) and thioxanthene-9-thione (179b) were converted into the chloride-bridged complexes (180a) and (180b).

(179)

a: X = O

b: X = S

Na$_2$PdCl$_4$ / CH$_3$OH

(180)

a: X = O

b: X = S
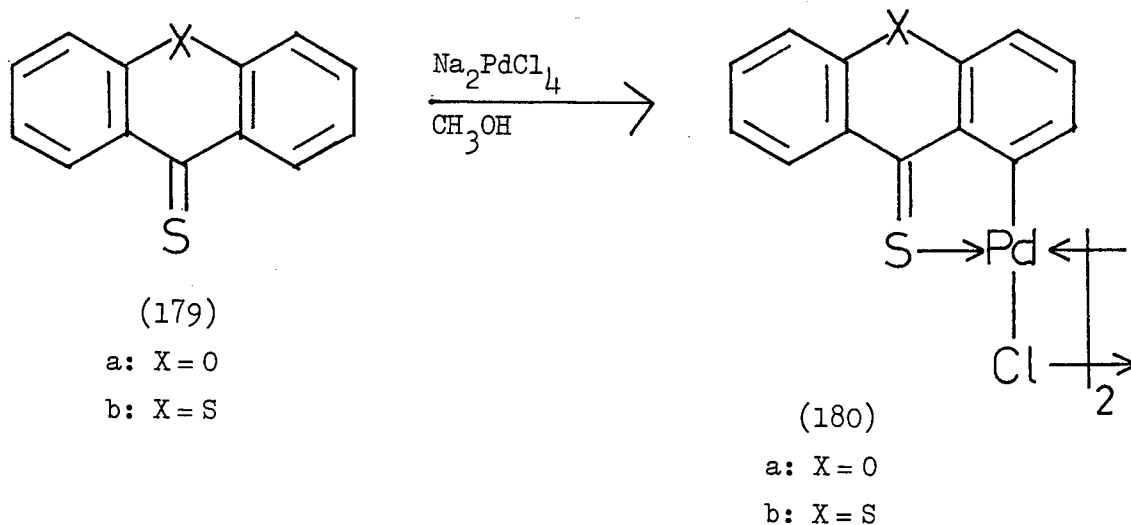
The structures of complexes (180) could not be established directly since, like previously described chloride-bridged dimers, the complexes were involatile and insoluble in organic solvents. The structures, and proof of cyclopalladation were established indirectly by converting the complexes (180) into the more soluble phosphine complexes [see discussion (iv)].

(iii)   Synthesis of Dimeric Chloride-bridged Complexes of Thioamides and Thiolactams

Davis[41] reported that reaction of quinolizine-4-thione with sodium tetrachloropalladate gave a russet-brown solid believed to be the cyclopalladated complex (53). Conclusive structural investigations and studies of the reactions of the complex were not carried out since Davis was unable to repeat the preparation.

Quinolizine-4-thione differs from other ligands which have been reported to undergo cyclopalladation in being a cyclic thioamide (i.e. a thiolactam). Since palladation of quinolizine-4-thione appeared to be less straightforward than the corresponding reactions of other nitrogen and sulphur donor ligands, several other thioamides and thio-lactams were studied as potential substrates for cyclopalladation. The reaction of quinolizine-4-thione and sodium tetrachloropalladate in methanol gave an orange complex, similar to that described by Davis[41], and elemental analysis indicated that it was the cyclopalladated complex (53) rather than the complex (181) of the type L_2PdCl_2.
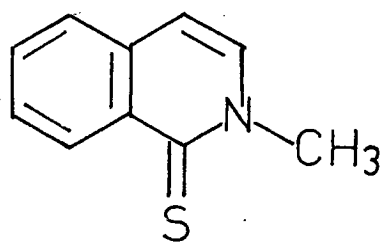
(182)
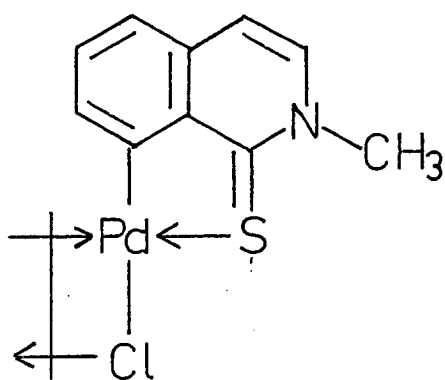
(183)
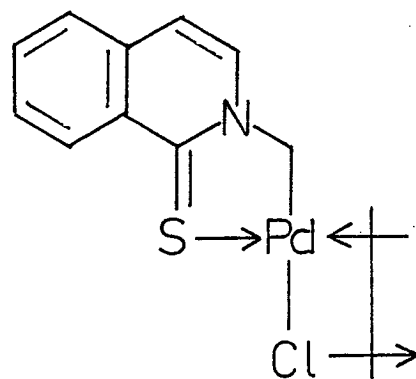
(184)
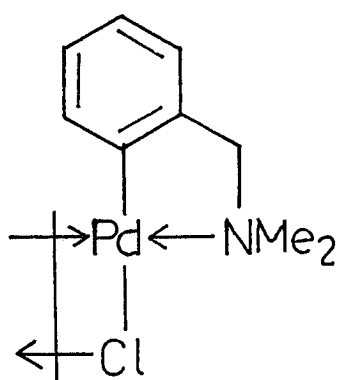
(57)
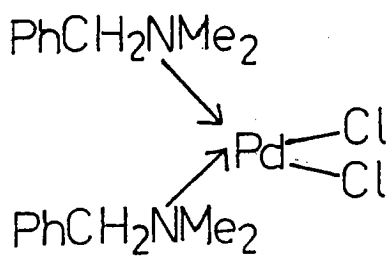
(186)
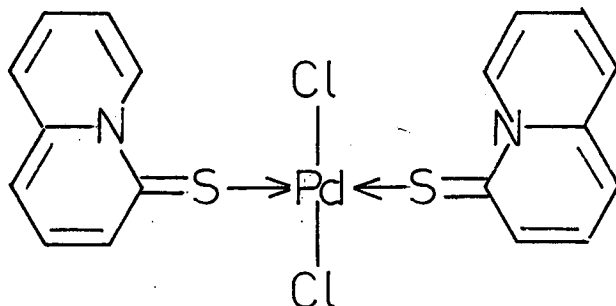
(181)

N-Methylisoquinoline-1-thione (182), which can also be regarded as a thiolactam, reacted with sodium tetrachloropalladate to give an orange-brown solid. Elemental analysis gave values indicating that the product was a cyclopalladated chloride-bridged complex, for which there are two possible isomeric structures (183) and (184). Compound (183) would be the expected product from palladation of the isoquinoline nucleus, whereas complex (184) would be the product from reaction of palladium with the N-methyl group.

The formation of compound (184) would be analogous to the reaction of 8-methylquinoline (185) and sodium tetrachloropalladate reported by Hartwell[57] and by Nomoyama[60].

(185)
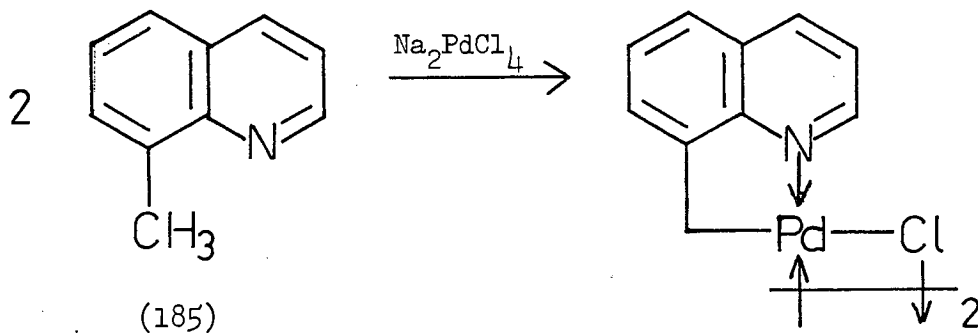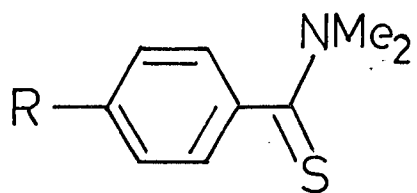
(187)

a: R = H
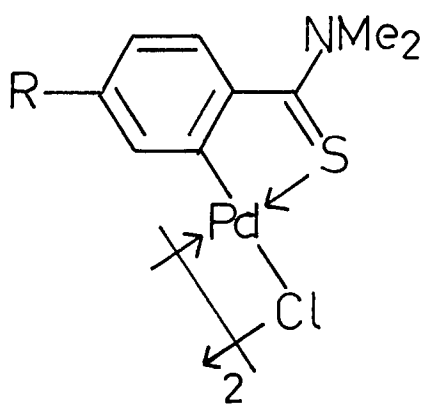
b: R = Me

(188)

a: R = H

b: R = Me
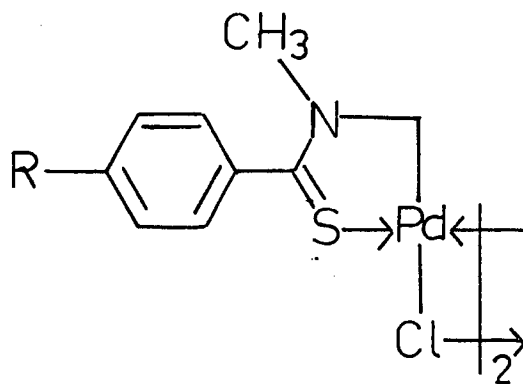
(189)

a: R = H

b: R = Me

There is no precedent, however, for the palladation of an N-methyl group and the formation of compound (184) was thought unlikely. As will be described later, structure (185) was in fact established by a study of the complexes obtained by bridge-splitting with sodium N,N-dimethyldithiocarbamate and with triethylphosphine.

A comparison of the reactions of the thiolactams (53) and (182) with that of a thioamide was carried out by using N,N-dimethylthio-benzamide (187a). Elemental analysis of the brown complex obtained by reaction of compound (187a) with sodium tetrachloropalladate, indicated that the product was a cyclopalladated complex. Cyclopalladation of (187a), as with the isoquinoline thione (182), can give rise to two possible isomeric complexes (188a) and (189a). Owing to low solubility and involatility, a spectroscopic study of the complex was limited and it was necessary once again to use bridge-splitting reagents to obtain structural information.

p-Methyl-N,N-dimethylthiobenzamide (187b) was also treated with sodium tetrachloropalladate as it was thought that the presence of a p-methyl group might result in a more soluble complex (188b) and/or (189b), and might also help to differentiate between the two possible structures if a ^{1}H n.m.r. spectrum could be obtained. The reaction gave a brown solid but, although slightly more soluble than (188a) or (189a), the complex could not be studied by n.m.r. Conclusive proof of the structure was obtained by a study of the derived triethylphosphine complex (see later).

Further work on metal displacement from the cyclopalladated complexes of thioamides and thiolactams (to be discussed later) demonstrated that these complexes did not react as expected and, to obtain more data on

this type of system, N-methylquinoline-4-thione (190), a vinylogous
thioamide and an isomer of compound (182), was treated with sodium
tetrachloropalladate. The resulting orange complex showed the character-
istic properties of chloride-bridged dimers but the elemental analysis
was not consistent with the expected structure (191).

(190)

(191)

fig. (iv)

$$\begin{pmatrix} C \\ \diagdown \\ X \end{pmatrix} \equiv \text{ organic ligand where X is a donor atom}$$
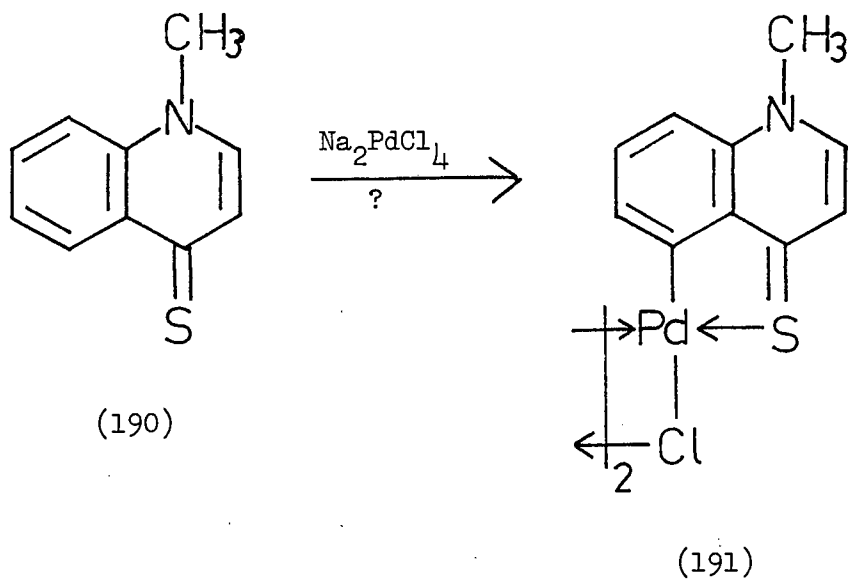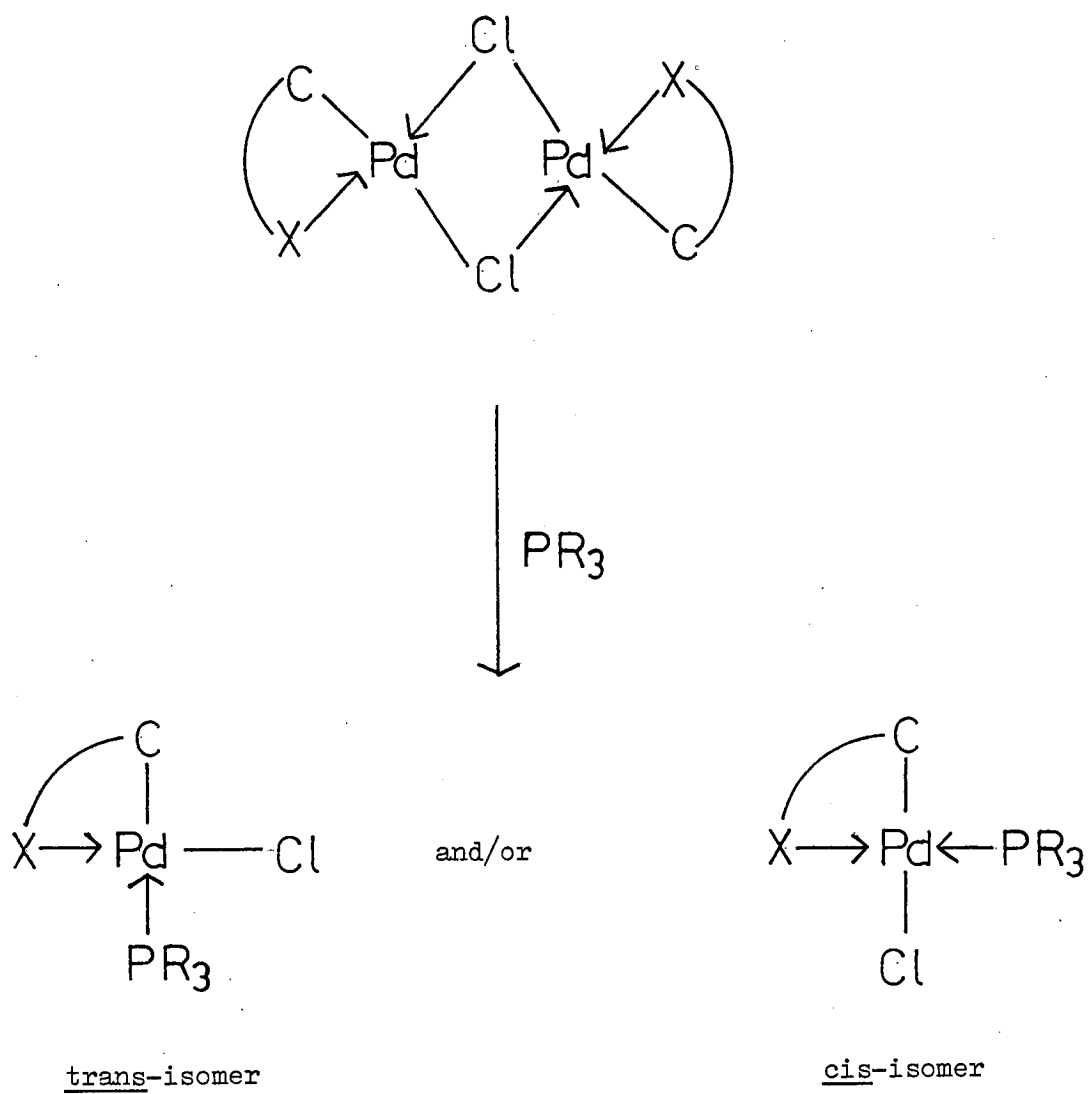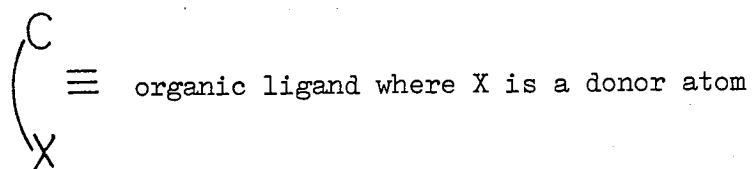
(iv)   Conversion of Dimeric Chloride-bridged Complexes

into Monomeric Phosphine Complexes

Notes

1. In the reactions of cyclopalladated chloride-bridged dimers

with organophosphines, the process of bridge-splitting could

yield either or both of two stereoisomeric complexes which will

be designated cis and trans. In this context the terms cis

and trans refer to the position of the phosphine group relative

to the carbon-palladium σ-bond. The terms are illustrated in

figure (iv).

Crociani et al.[105] have shown by means of infra-red studies,

that orthometallated complexes of azobenzene (azb) and of

N,N-dimethylbenzylamine may exist in either cis- or trans-

forms. The complex $Pd(azb)(C_5H_5N)Cl$, in particular, shows

evidence for the presence of both stereoisomers.

2. In this section one mole equivalent of the cyclopallated dimer

was treated with two mole equivalents of triethylphosphine

unless otherwise stated.

(180)

a: X = 0

b: X = S

PEt₃

(192a)

X = 0

X = S

(192b)

X = 0
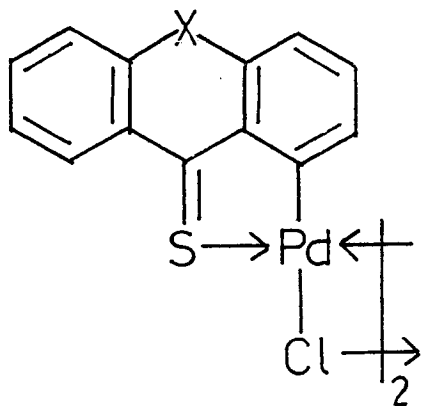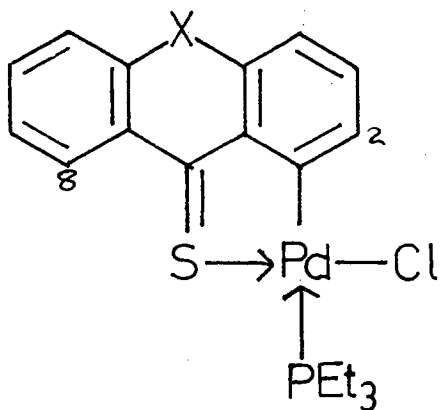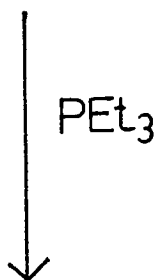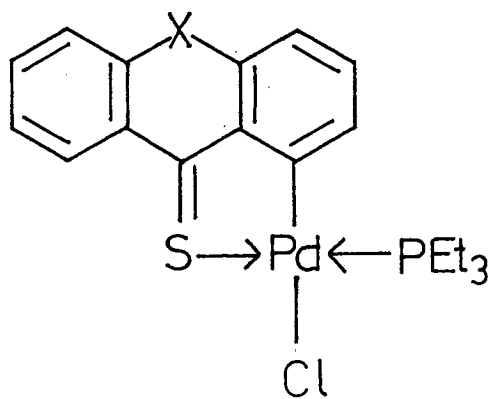
X = S

Since the cyclopalladated chloride-bridged complexes described

in the previous sections were exceedingly insoluble solids, no n.m.r.

spectra could be obtained to establish conclusively that cyclo-

palladation had occurred. The use of "bridge-splitting" reagents,

such as organophosphines, is a well-established technique for the

investigation of such insoluble dimers and it has been discussed fully

in the introduction. The resulting monomeric chloro(phosphine)complexes

are usually quite soluble and can be readily characterised spectro-

scopically.

The reaction of the xanthenethione complex (180a) with triethyl-

phosphine gave one product, a reddish-brown crystalline solid. The

complex was characterised by analytical and spectroscopic methods and

identified as the monomeric triethylphosphine complex (192; X=0).

The ^{1}H n.m.r. spectrum of complex (192;X=0) showed aliphatic and

aromatic proton resonances in the required intensity ratio but the

aromatic region of the spectrum was complex and consisted of two multi-

plets at δ 8.3-8.6 and δ 7.1-7.9 in the intensity ratio 3:11. Since

there are only seven aromatic protons in structure (192), each of these

multiplets must represent a non-integral number of protons (1.5 and 5.5)

and it was necessary to assume the presence of two stereoisomers, one

of which gave two proton resonances at low field and the other only one.

Under high resolution, the low-field multiplet showed a pattern of

peaks that was not inconsistent with this hypothesis; it comprised

two doublets of doublets, attributed to H-8(ortho- and meta- coupled)

in both stereoisomers, and a presumed triplet, the lowest field line

of which was obscured by the highest field doublet. This triplet was

attributed to H-2 in the trans-isomer (192a;X=0) and equality of P-H

and H-H(ortho) coupling constants was assumed in order to account for

the multiplicity of the signal. Nonoyama and Yamasaki[106] observed a very similar triplet in the spectrum of the ortho-metallated rhodium complex (193) and they attributed it to H-9 of the benzoquinoline ligand in which C-10 is trans to phosphorus; the H-9 signal of the other benzoquinoline ligand was a doublet, P-H coupling being absent when C-10 was cis to phosphorus.

(193)
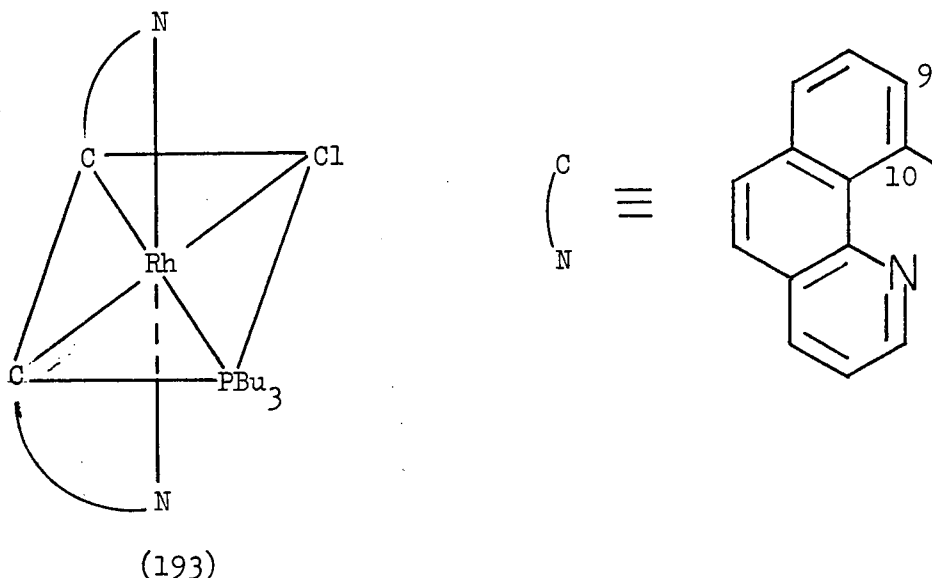
If this interpretation of the spectrum of complex (192a;X=0) is correct, the H-2 signal of the cis-isomer (192b;X=0) must form part of the high-field multiplet (δ 7.1-7.9) and this is probably due to the absence of a deshielding effect from the Pd-Cl bond.

Independent evidence for the presence of two stereoisomers of compound (192;X=0) was obtained from the ^{31}P n.m.r. spectrum which showed two resonances, at 24.4 and 12.2 p.p.m. The intensity ratio of these signals was 1:2 for a freshly prepared solution, changing to 1:1 after 5 minutes and finally to 1:0.8 after 45 minutes. This suggests that there are two stereoisomers which can interconvert fairly easily and that their relative stabilities are not the same in solution as in the crystalline state.

The mass spectrum of complex (192;X=O) gave no useful structural evidence since no palladium-containing fragments were observed, and the only molecular ions observed arose from products of an anomalous spectrometric reaction that will be discussed later.

The reaction of the thioxanthenethione complex (180b) with tri-ethylphosphine gave a purple solid that was identified as the cyclo-palladated complex (192;X=S). Its ^{1}H n.m.r. spectrum resembled that of the complex (192;X=O) but the low-field part of the aromatic proton region was clearly split into a doublet at δ 9.0 and a triplet at δ 8.8. By analogy with complex (192;X=O) these two resonances were assigned to H-8 (of both stereoisomers) and to H-2 (of the trans-isomer), respectively. The ^{31}P n.m.r. spectrum showed two resonances at 22.7 and 11.9 p.p.m., the intensity ratio being 1:5 for a freshly made solution, changing to 1:3 after 30 minutes. No further isomerisation occurred after this time. Thus the thioxanthenethione complex (192;X=S) differed slightly from the oxygen analogue; with X=S a limited amount of isomerisation occurred in solution whereas with X=O, isomerisation was more extensive and the predominant isomer was not the same in the fresh solution (and presumably in the solid) as in the final solution.

The ^{13}C n.m.r. noise-decoupled spectrum of complex (192;X=S) contained twenty-four clearly visible lines of which nineteen were due to the aromatic carbons of the thioxanthenethione ligand and five to the triethylphosphine group. The five lines of the phosphine group comprised a group of three and a group of two assigned to the CH$_2$ and CH$_3$ groups, respectively, the observed splitting being attributable to the presence of cis and trans isomers and to carbon-phosphorus coupling. Of the nineteen aromatic resonances, two low-field signals at 178.0 and 170.8 p.p.m. were assigned to the thiocarbonyl carbon atoms of isomers (192a;X=S) and (192b;X=S).
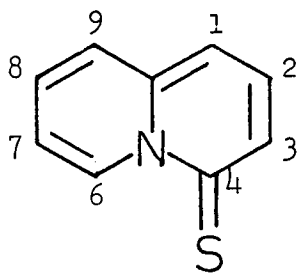
(52)
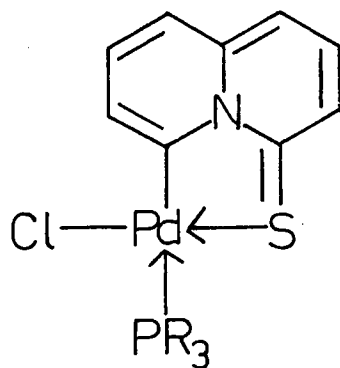
(195)

a: R = Et

b: R = Ph

The thiocarbonyl carbon (C-9) resonates at 210.6 p.p.m. in thioxanthene-thione (179b) and had thus been moved 30 - 40 p.p.m. upfield as a result of complexing with palladium. The mass spectrum of complex (192;X=S) was inconclusive, showing weak fragments with a palladium isotope pattern at $^m/e$ 458 and 412. The peak at $^m/e$ 458 was tentatively assigned to structure (194) i.e. the expected parent ion minus C_2H_4.

(194)
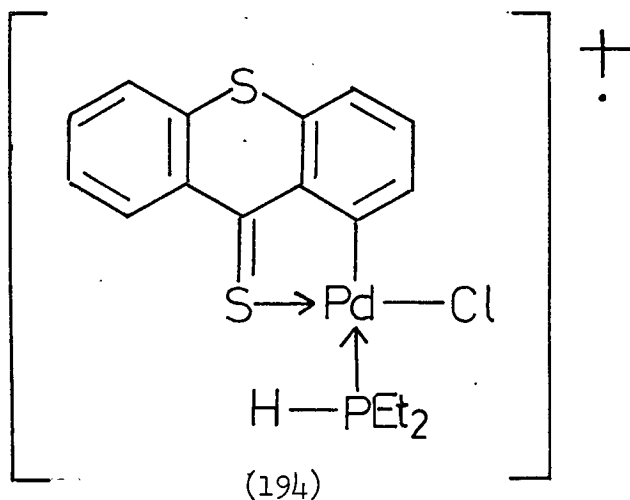
Davis[41] reported that the reaction of triethylphosphine with the quinolizine-4-thione complex (53) produced two yellow solids that were separable by chromatography but spectroscopically identical. He proposed that the solids were the cis- and trans- isomers of the phosphine complex (195a). This reaction was repeated and two yellow solids identical with Davis's were isolated and then recombined. As reported by Davis the ^{1}H n.m.r. spectrum was consistent with structure (195); it showed a resonance at δ 8.9, downfield of the remaining aromatic protons, assigned to H-7 but there was no resonance attributable to H-6 which, in the parent thione, occurs at δ 10.3.
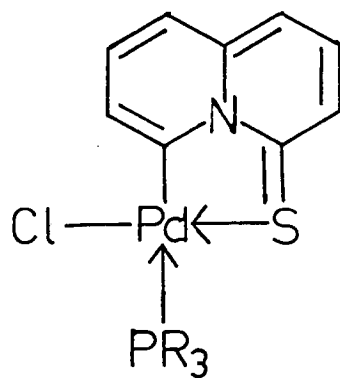
(195)
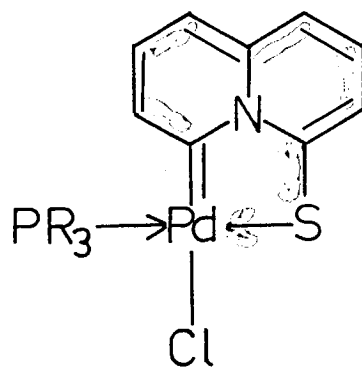
a: R = Et

b: R = Ph

(196)

a: R = Et

b: R = Ph

1	11	3422.4	171.11
2	15	2877.4	143.86
3	57	2682.5	134.12
4	115	2642.3	132.11
5	108	2609.5	130.47
6	129	2585.6	129.27
7	130	2529.8	126.48
8	112	2373.9	118.69
9	105	2271.5	113.57
10	90	1574.7	78.73
11	94	1542.6	77.13
12	89	1510.6	75.53
13	106	0.0	0.00
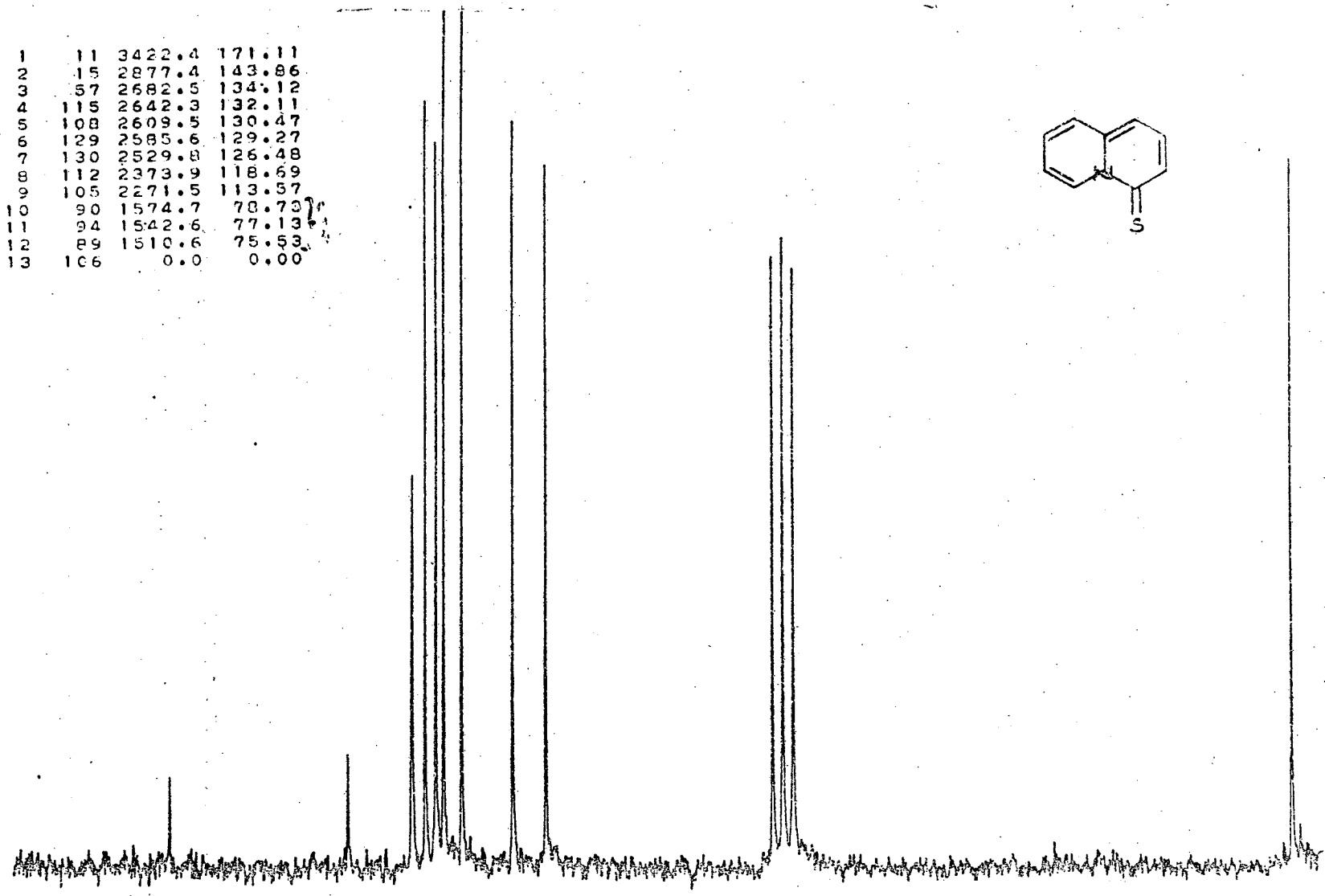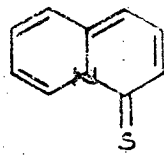
SPECTRUM 1

SPECTRUM 2
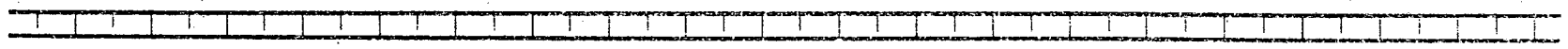
1	10	3677.8	183.88
2	8	3519.2	175.95
3	7	3272.1	163.60
4	3	3254.6	162.73
5	14	2890.8	144.93
6	82	2628.7	131.43
7	22	2622.4	131.11
8	3	2618.6	130.92
9	35	2438.5	121.92
10	32	2416.9	120.84
11	26	2373.5	118.67
12	3	1613.1	80.65
13	982	1582.3	79.11
14	48	1566.4	78.31
15	943	1550.4	77.52
16	55	1534.5	76.72
17	1000	1518.5	75.92
18	17	1502.0	75.09
19	22	1488.9	74.44
20	6	1483.8	74.19
21	84	311.6	15.58
22	3	307.1	15.35
23	84	287.5	14.37
24	23	277.1	13.85
25	6	263.7	13.18
26	144	164.1	8.20
27	431-	0.0-	0.00
28	7-	25.4-	1.27
29	4-	29.8-	1.49
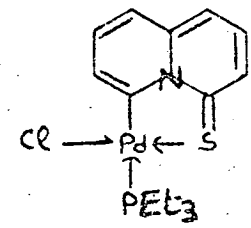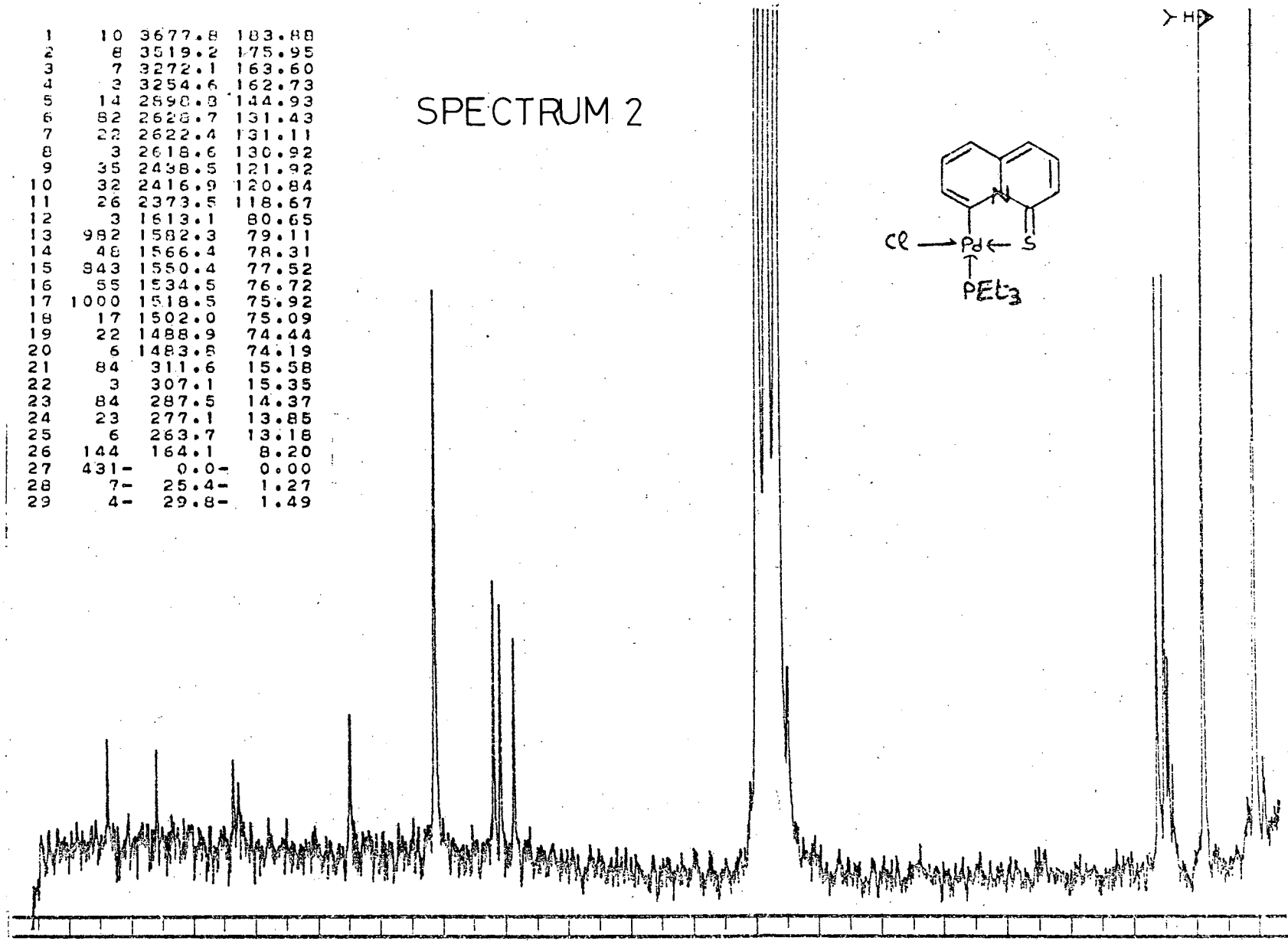
To obtain conclusive proof that palladation of quinolizine-4-thione had occurred at C-6, the ^{13}C n.m.r. spectrum of the phosphine complex (195a) was compared with that of the parent thione (52). Compound (52) contains nine carbon atoms of which two are quaternary (C-4 and C-9a) whereas in complex (195a) the quinolizine nucleus contains three quaternary carbon atoms (C-4, C-6 and C-9a). The two spectra are reproduced opposite.

Spectrum 1, of quinolizine-4-thione, contains nine lines and the two quaternary carbons resonate at 171.1 p.p.m. (C-4) and 143.9 p.p.m. (C-9a). The remaining seven tertiary carbon atoms resonate between 134 and 113 p.p.m. but no attempt was made to assign the lines in this region.

Spectrum 2, of the complex (195a) contains twelve lines though each stereoisomer has eleven distinguishable carbon atoms. The aromatic portion of the spectrum contains nine lines, and the remaining three can be assigned to the phosphine group. The phosphine CH_3 signal was a singlet and the phosphine CH_2 signal was a doublet due to phosphorus-carbon coupling (J_{p-c} 24 Hz). A spectrum with single-frequency off-resonance proton decoupling (SFORD) established that five of the aromatic resonances were due to quaternary carbon atoms, and the remainder were due to methine (=CH-) carbons. The spectrum is in agreement with Davis's suggestion that the complex is a mixture of the two stereoisomers, and since the quaternary carbon resonance at 144.9 p.p.m. was approximately twice the intensity of the other quaternary signals it was assigned to C-9a in both isomers. Of the three quaternary resonances, C-9a is the one least likely to be affected by changes in configuration around the palladium atom. Two closely spaced signals at 163.6 and 162.7 p.p.m. were assigned to the thiocarbonyl carbon atoms (C-4), while the high

frequency resonances, at 183.9 and 175.9 p.p.m. were assigned to C-6 of the two isomers. The high resonance frequency of C-6 compared with the values of 145 - 165 p.p.m. reported by Garber et al.[107] for other cyclometallated complexes, may be attributed to a high contribution from the "carbene-type" canonical structure (196), since carbene carbon atoms in metal complexes are reported[108] to be deshielded. The possibility of contributions from a "carbene-structure" would be greater for the complex of quinolizine-4-thione than for previously discussed examples since the canonical structures (195) and (196) are likely to be more similar in energy.

Conclusive proof that the complex was a mixture of cis- and trans- isomers was obtained from the ^{31}P n.m.r. spectrum, which showed two peaks at 17.9 and 14.6 p.p.m. The signal intensities, initially in the ratio 1:2, again varied with time indicating that the complexes were equilibrating in solution as for compounds (192;X=O) and (192;X=S).

The triphenylphosphine-quinolizinethione complex (195b) was synthesised by a similar procedure and spectroscopic and analytical data were consistent with the proposed structure. The ^{1}H n.m.r. spectrum resembled that of complex (195a), showing a low-field doublet of doublets assigned to H-7, and the absence of a signal for H-6 at $\delta 10.3$. In contrast to the triethylphosphine complex (195a), the triphenyl compound (195b) was not separable into two bands by chromatography and its ^{31}P n.m.r. spectrum showed only one resonance at 19.7 p.p.m., assigned to the trans-stereoisomer (195b). This is thought to be due to the steric constraints of the system forcing the bulky triphenyl- phosphine group to take a trans configuration, so avoiding a repulsive interaction with H-7.

A yellow solid was isolated from the reaction of triethylphosphine
with the chloride-bridged N-methylisoquinoline-1-thione complex (183)
and/or (184), but elemental analysis and spectroscopic evidence were
only partially in agreement with the expected structure (197).

(197)
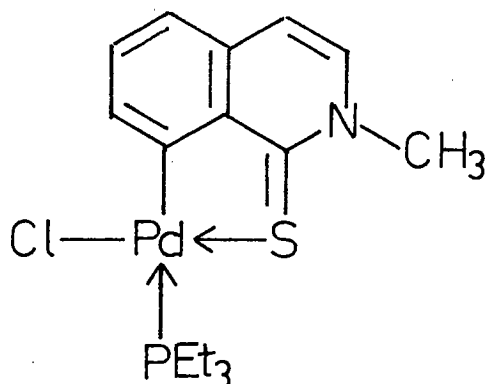
The aromatic region of the ^{1}H n.m.r. spectrum showed a one-proton
doublet at δ 7.0(J=7 Hz) attributed to H-4, a multiplet at δ 7.2 - 7.7,
within which the H-3 doublet was distinguishable at δ 7.5, and a triplet
at δ 8.6. The triplet was equivalent in intensity to ca. 0.5H, being
similar in this respect, and in chemical shift, to the low-field triplets
in the spectra of the xanthenethione and thioxanthenethione complexes
(192). This suggested the presence of two stereoisomers and the N-Me
signal was also consistent with the presence of two isomers, being
split into two almost equal lines at δ 4.0 and 4.1. These features,
together with the absence of a signal due to H-8 (δ 9.1 in the parent
thione) provided strong evidence in support of palladation at C-8 and
could have been taken as confirmation of structure (197) had it not
been for a 38% excess of integrated intensity in the ^{1}H resonances of
the phosphine ligand. This anomaly together with the unsatisfactory
analytical results, leaves the structure of the complex in doubt.

(200)

(199)

(198)

a: R = H
b: R = Me
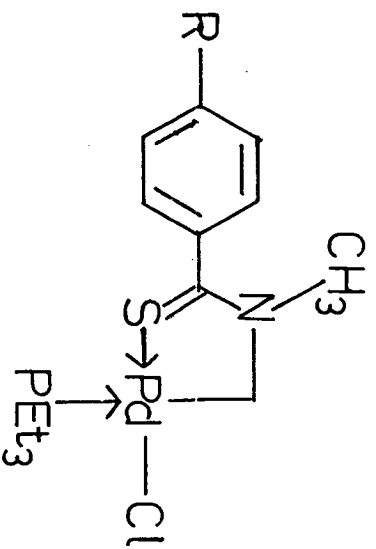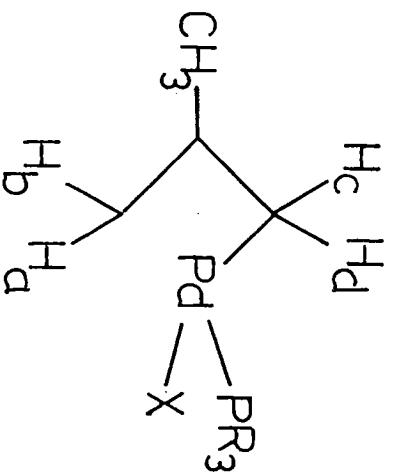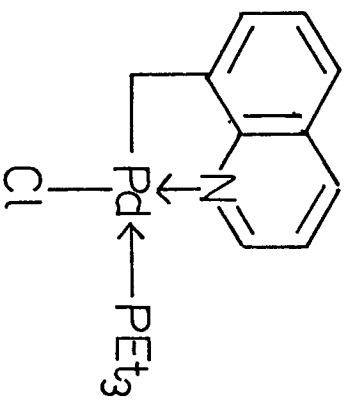
		Hz	
1'	7	3994.7	194.73
2	9	2744.6	137.23
3	39	2609.2	130.45
4	8	2580.6	129.03
5	61	2573.8	128.68
6	73	2537.2	126.86
7	115	1573.8	78.68
8	8	1566.5	78.32
9	10	1552.1	77.60
10	114	1541.9	77.09
11	8	1520.2	76.01
12	100	1509.9	75.49
13	16	1113.5	55.67
14	15	1109.0	55.45
15	27	911.4	45.56
16	55	301.5	15.07
17	60	275.4	13.77
18	99	162.9	8.14
19	120	0.0	0.00

SPECTRUM 3
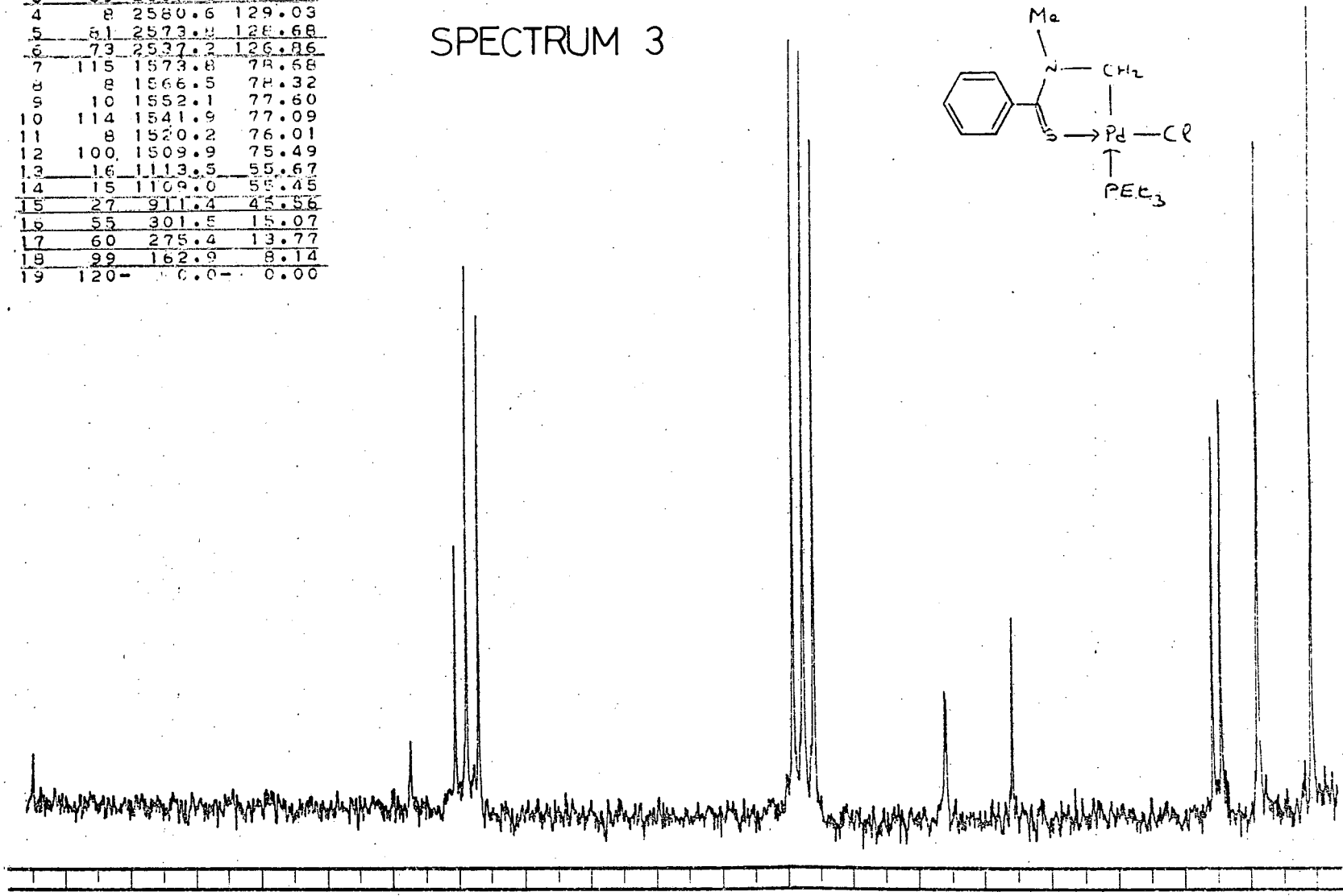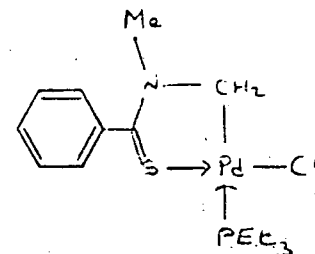
Treatment of the chloride-bridged N,N-dimethylthiobenzamide complex (188a) and/or (189a) with triethylphosphine gave only one product identified as chloro-(N-methyl-N-thiobenzoylaminomethyl)tri-ethylphosphine palladium(II), (198a). The ^{1}H n.m.r. spectrum contained a multiplet at δ 7.2 - 7.5 (5H), assigned to the phenyl group and tri-ethylphosphine resonances at δ 1.8 and 1.2. The remaining signals were a doublet at δ 4.2 (2H, J_{PH}=3 Hz) and a singlet at δ 3.2 (3H) assigned to the N-CH$_2$Pd and N-CH$_3$ groups respectively. Support for these proton assignments were found in studies of palladium-phosphine complexes by Hartwell (57) and by Powell et al.[109].

Hartwell[57] and his co-workers reported the synthesis and characterisation of the cyclopalladated triethylphosphine complex (199) of 8-methylquinoline. They assigned a doublet at δ 3.1 (J_{P-H} 4 Hz) to the CH$_2$—Pd group, and suggested that the signal was a doublet as a result of coupling between the methylene protons and phosphorus _via_ palladium. They also suggested that the phosphine group must be _trans_ to the methylene group on the basis of a comparison with complexes of type (200). Powell and Shaw[109] reported that in type (200) complexes substantial coupling (6 - 10 Hz) was observed between phosphorus and protons H$_a$ and H$_b$ (i.e. trans) but that no coupling was observed between phosphorus and protons H$_c$ and H$_d$.

Conclusive proof of the proposed structure (198a) was obtained from a study of ^{13}C n.m.r. noise-decoupled and off-resonance spectra. The noise-decoupled spectrum (spectrum 3) contained ten lines in agreement with the proposed structure shown below with an arbitrary numbering scheme.
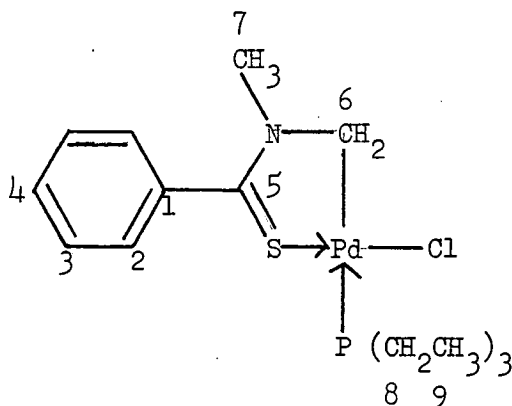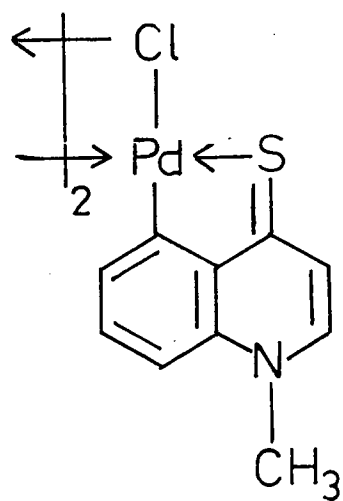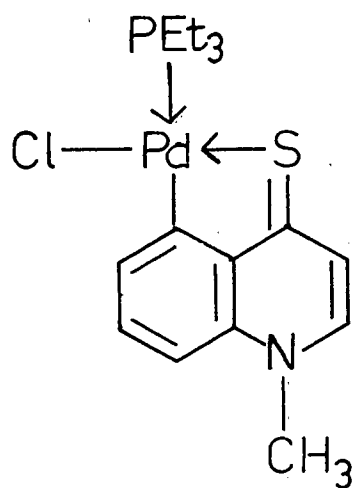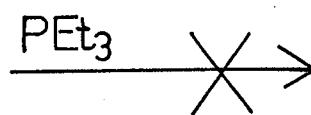
(191)   (201)

The quaternary carbon atoms C-1 and C-5 were observed at 137.2 and 194.7 p.p.m. respectively and signals at 130.5, 128.7 and 126.9 p.p.m. (observed as doublets under off-resonance conditions) were assigned to carbon atoms 4, 2 and 3 respectively. The N-CH$_3$ signal (C-7) was at 45.6 p.p.m. and the N-CH$_2$ signal (C-6) at 55.5 p.p.m., the latter being a doublet owing to carbon-phosphorus coupling (J$_{C-P}$= 4.5 Hz) and being split into a triplet of doublets under off-resonance conditions. The ethyl carbon atoms (C-8,9) resonated at 14 and 8 p.p.m., the C-8 signal at 14 p.p.m. being a doublet as a result of coupling with phosphorus. (This was confirmed by the SFORD spectrum.)

Elemental analysis was in agreement with the proposed structure but mass spectrometric evidence was inconclusive as a result of the complex undergoing an anamalous mass spectrometric reaction.

Complex (198b) was obtained by a similar method, and elemental analysis and spectroscopic evidence were in agreement with the proposed structure.

The formation of complexes (198a) and (198b) is the first reported metallation of an N-methyl group and the products are the first cyclo-metallated complexes that contain a thioamide as the donor ligand.

The reaction of triethylphosphine with the presumed chloride-bridged N-methylquinoline-4-thione complex (191) gave an orange solid, spectroscopic and elemental analysis of which were not in agreement with the expected structure (201). The ^{1}H n.m.r. spectrum contained five very broad resonances while a mass spectrum showed a parent ion at $^m/e$ 412. Elemental analysis gave values that did not help to identify the product and the actual structure of the complex remains unknown.
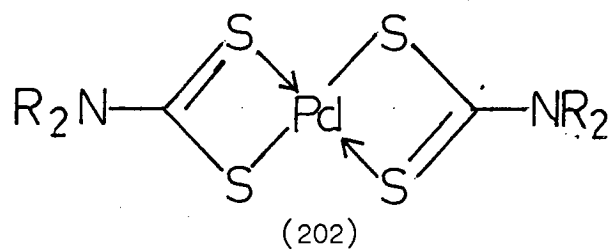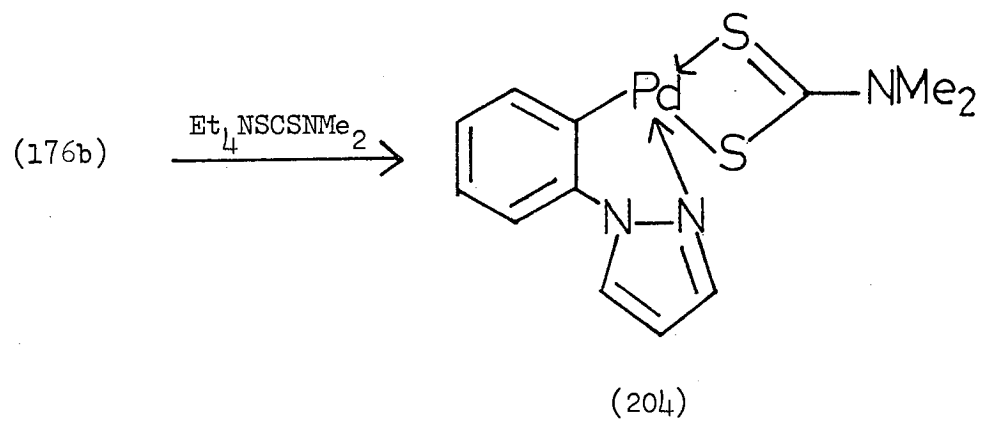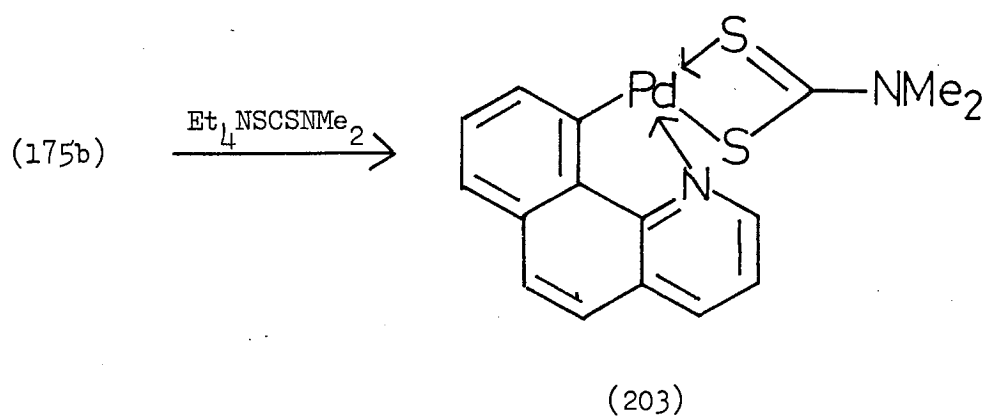
(202)

a: R = Me

b: R = Et

(175b) $\xrightarrow{\text{Et}_4\text{NSCSNMe}_2}$

(203)

(176b) $\xrightarrow{\text{Et}_4\text{NSCSNMe}_2}$

(204)

(v)   Conversion of Dimeric Chloride-bridged Complexes into

Monomeric Dithiocarbamato-Complexes

Davis[(41)] reported that attempts to synthesise monomeric cyclo-palladated N,N-diethyldithiocarbamato-complexes by reaction of the chloride-bridged dimers with sodium N,N-diethyldithiocarbamate in acetone gave inseparable mixtures of the desired dithiocarbamato-complexes and bis(N,N-diethyldithiocarbamato)palladium (202b). A satisfactory route to the required complexes was found in the reaction of the soluble acetato-complexes with tetraethylammonium N,N-diethyl-dithiocarbamate in dichloromethane. This method was therefore used to prepare the orthopalladated N,N-dimethyldithiocarbamato-complexes (203) and (204) of benzo[h]quinoline and 1-phenylpyrazole and these were easily characterised spectroscopically and by elemental analysis.

Davis briefly reported that 2-(2-pyridyl)phenyl(N,N-dimethyl-dithiocarbamato)palladium(II), (205), was also isolated in a low yield from the reaction of the corresponding chloride-bridged dimer (69) with sodium dimethyldithiocarbamate in dimethylformamide.

(69)   (205)

(206)

(207)

(208)
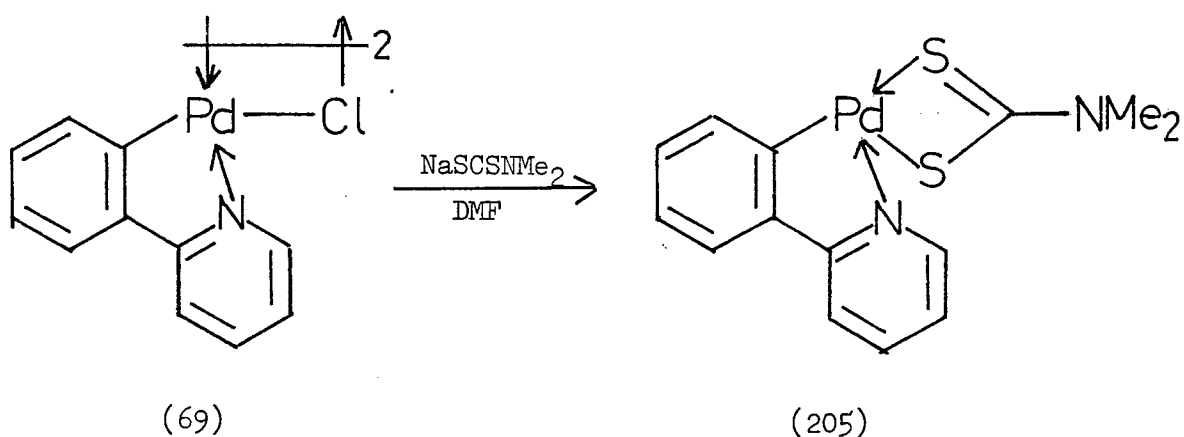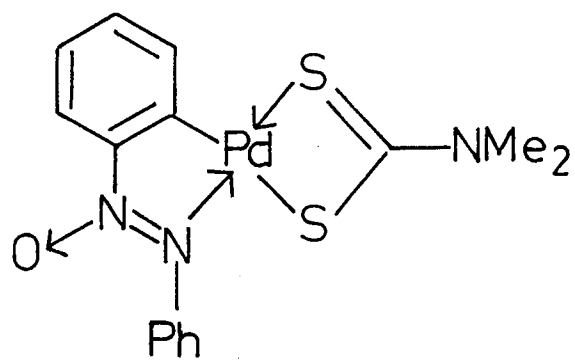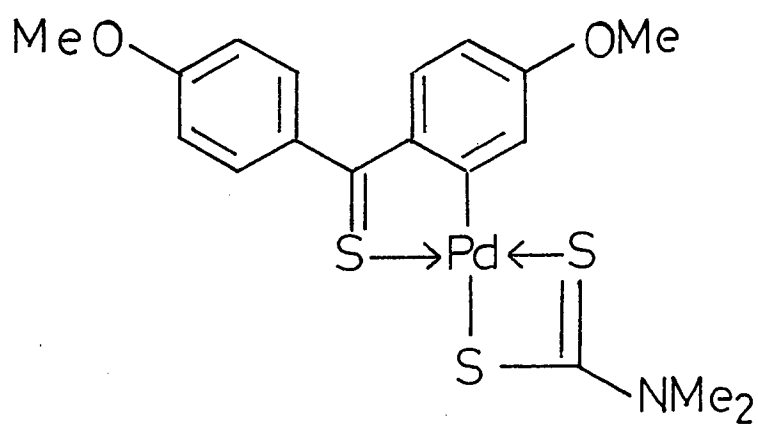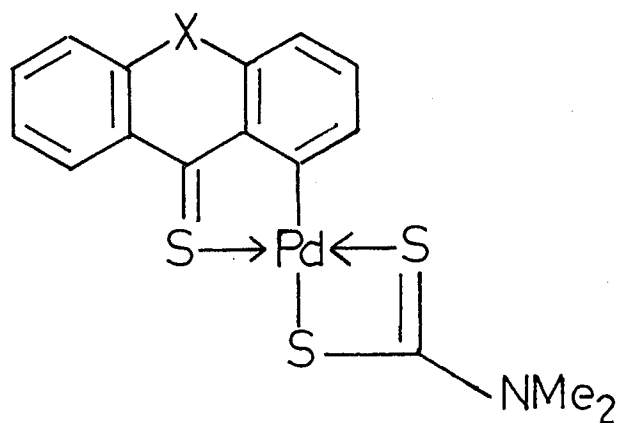
a: X = 0
b: X = S

It was thought worthwhile to re-investigate this reaction since it would obviate the need to convert the chloride-dimers to the more soluble acetato-complexes or to synthesise palladium acetate. These reaction conditions were used first in the reaction of the chloride-bridged azoxybenzene complex (50b) with sodium dimethyldithiocarbamate and, by using dry dimethylformamide and a non-aqueous work-up, a good yield of the required complex (206) was obtained. Mass spectroscopy showed the expected parent ion at $^m/e$ 423 and fragment ions consistent with the proposed structure. The ^1H n.m.r. spectrum was well-resolved and showed a complex multiplet at δ 7.1 - 7.8 with two singlets at δ 3.4 and 3.3, demonstrating the non-equivalence of the two N-methyl groups.

Similar exchange reactions of complexes (51b), (180a) and (180b) gave the dimethyldithiocarbamato-complexes of 4,4'-dimethoxythiobenzophenone (207), xanthenethione (208a) and thioxanthenethione (208b) in yields of 52-66%. The mass spectra of complexes (207), (208a) and (208b) showed the expected parent ion peaks and elemental analyses were consistent with the proposed structures. Only complex (207) however was sufficiently soluble to obtain a ^1H n.m.r. spectrum. The aromatic region of the spectrum contained four well resolved resonances δ 7.6 (2H,d,<u>ortho</u>-coupled), 7.3(1H,d,<u>ortho</u>-coupled), 6.9(2H,d,<u>ortho</u>-coupled and 1H,d,<u>meta</u>-coupled) and 6.5(1H,dd,<u>ortho</u>- and meta-coupled). These signals were assigned to H-2' and 6',H-6, H-3'5' and 3, and to H-5 respectively.

S→Pd←S

Me₂N

S

(209)

N—Me

S→Pd←S

Me₂N

S
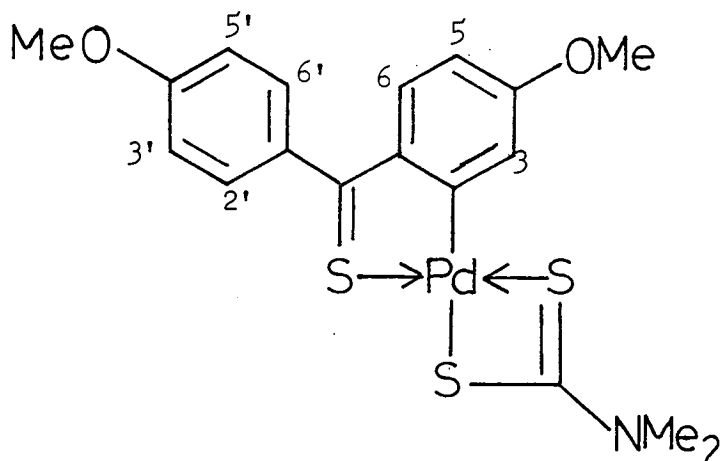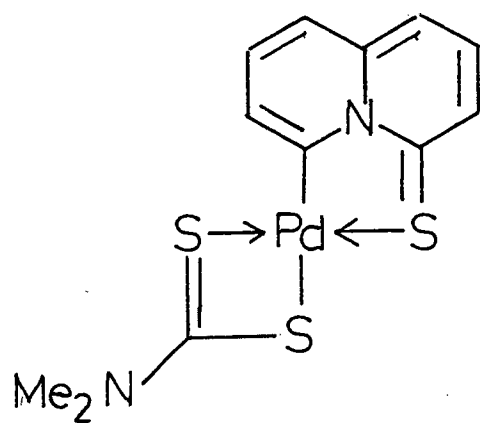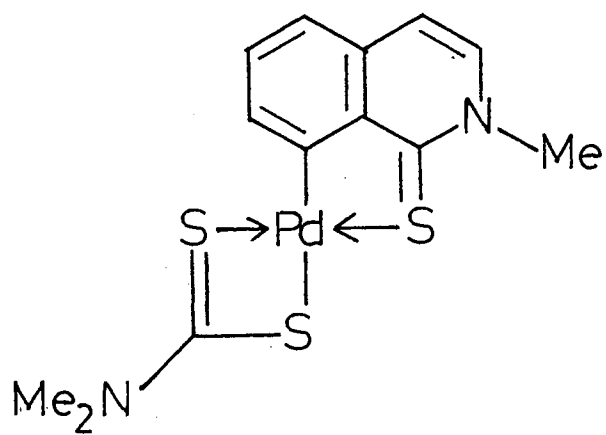
(210)

Attempts to dissolve the complexes (208a) and (208b) in warm dimethyl sulphoxide led to the formation of a yellow solid thought to be bis(dimethyldithiocarbamato)palladium(II), (202a). Consequently, no n.m.r. spectra could be obtained but there is little doubt that the complexes are correctly represented by formula (208).

Reaction of the quinolizine-4-thione complex (53) with sodium dimethyldithiocarbamate gave an orange solid that was sparingly soluble in dichloromethane and chloroform. The mass spectrum of the complex showed a parent ion peak at $^m/e$ 386 and fragment ion peaks consistent with the structure (209). Elemental analysis was also in agreement with structure (209) but, owing to the very low solubility, no n.m.r. spectra could be obtained. However, in view of the evidence for the structure of the phosphine complex (194), there can be little doubt that the dithiocarbamato-complex is correctly represented by formula (209).

Treatment of the chloride-bridged N-methylisoquinoline-1-thione complex (182) and/or (184) with sodium N,N-dimethyldithiocarbamate gave a yellow solid that was readily identified by elemental analysis and spectroscopy as (1-thioxo-N-methylisoquinoline-8-yl)(N,N-dimethyldithiocarbamato)palladium(II), (210). The aromatic portion of its ^{1}H n.m.r. spectrum consisted of three resolved signals; doublets at δ 7.9 and 7.3(J=7 Hz) assigned to H-4 and H-3 respectively, and a broad multiplet at δ 7.5 assigned to H-5,6 and 7. Three singlets at δ 4.1, 3.3 and 3.2 were assigned to the N-methyl groups of the isoquinoline and dithio-carbamate groups. The absence of a signal due to H-8(δ 9.1 in the parent thione) was further proof that palladation had taken place at the 8-position of the isoquinoline nucleus. Mass spectrometry gave the expected parent ion at $^m/e$ 400 and a fragment ion at $^m/e$ 280 (M^+-Me_2NCS_2), in agreement with the proposed structure.
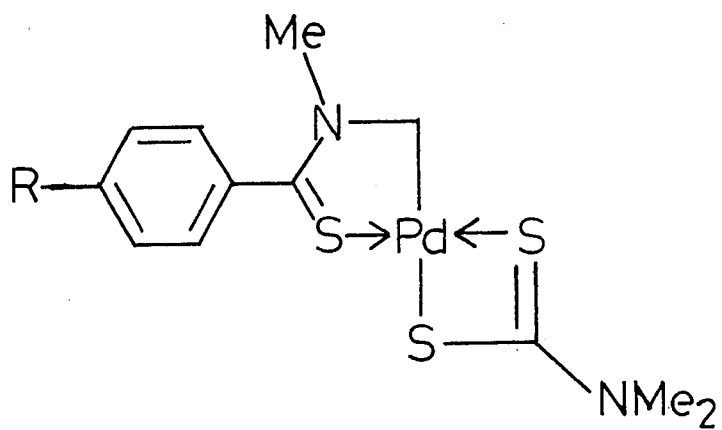
(211)

a: R = H

b: R = Me
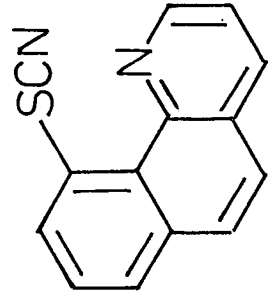
(212)
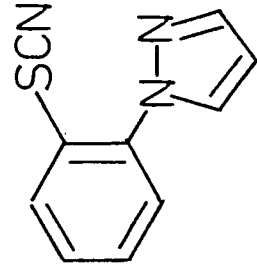
(213)
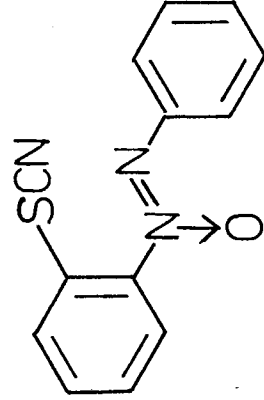
(214)

Reaction of sodium N,N-dimethyldithiocarbamate with the chloride-bridged complex derived from N,N-dimethylthiobenzamide gave a yellow solid from which the expected analytical and mass spectrometric (M^+ 390) data were obtained. The ^{1}H n.m.r. spectrum of the complex was unexpectedly deficient in N-Me resonances (two singlets present at δ 3.2 and 3.3; ca. 6H) but was otherwise consistent with the structure (211a), showing a singlet at δ 4.5 (ca. 2H; N-CH$_2$-Pd) and a multiplet at δ 7.3 - 7.6 (ca. 5H; C$_6$H$_5$). A similar dithiocarbamato-complex (211b) was obtained from the chloride-bridged dimer derived from N,N-dimethylthio-p-toluamide.

(vi)   Reactions of Cyclopalladated Complexes containing

Dithiocarbamate Ligands with Bromine and with Thiocyanogen

For cyclopalladated complexes to be of use in heterocyclic synthesis the palladium atom must be easily replaced by a suitable non-metallic atom or group. Davis[41] reported that treatment of dithio-carbamato-complexes containing cyclopalladated ligands with bromine or thiocyanogen (a pseudo-halogen) gave high yields of the depalladated halogeno- or thiocyanato- ligands. The efficiency of the reaction was attributed to the presence of the dithiocarbamato-ligand which remained firmly bonded to palladium so preventing repalladation of the liberated ligand. The present study was carried out to investigate the generality of this process and to discover any possible limitations on its use in synthesis.

To begin the investigation, the dithiocarbamato-complexes (203), (204) and (206), containing N-donor ligands, were treated with thio-cyanogen and the thiocyanato-compounds (212) - (214) were isolated. All of these gave mass spectra consistent with the expected structures but only compound (212) was obtained analytically pure.

(215)   (216)

The ^{1}H n.m.r. spectrum of (212) showed three well structured

multiplets in the aromatic region, one of which was at significantly

lower field, δ 8.9, than the others. In view of the complexity of

splitting and overlap of resonances, no attempt was made to assign

the signals other than the doublet of doublets at δ 8.9 which was

assigned to H-2, i.e. the proton ortho- to the nitrogen atom.
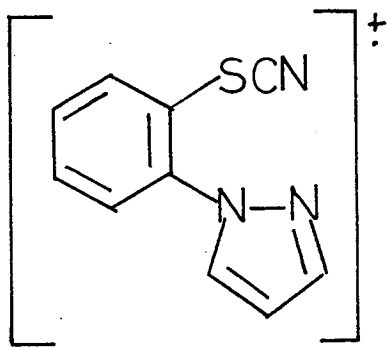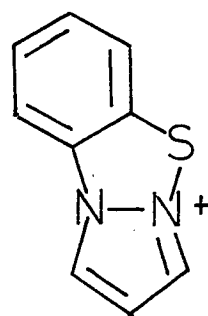
The mass spectrum of the pyrazole derivative (213) showed strong

peaks at m/e 201 and 175 consistent with the parent ion (215) and the

pyrazolobenzothiazolium cation (216) respectively. The ^{1}H n.m.r.

spectrum of the compound showed one resonance (1H, triplet) at higher

field, δ 6.5, than the other aromatic signals which were closely grouped

into two multiplets (3H each) at δ 7.8 and 7.5. The triplet at high

field was assigned to H-3 of the pyrazole ring but, in view of the

complexity of the two multiplets, no further assignment was attempted.

The infra-red spectrum gave a sharp absorption at 2140 cm^{-1} interpreted

as a nitrile (S-C≡N) stretching band.

2-Thiocyanatoazoxybenzene (214) was a yellow solid that appeared

to decompose on recrystallisation or chromatography. Its infra-red

spectrum showed a band at 2150 cm^{-1}, confirming the presence of the

thiocyanato-group, and its mass spectrum showed the expected strong

parent ion at m/e 255. There was no fragment ion corresponding to loss

of CN, as in previous cases, but strong peaks at m/e 208 (M$^+$-HCN) and

226 (M$^+$-29) were observed. The ^{1}H n.m.r. spectrum of the compound

showed two very complex multiplets (integration ratio of 4:5) that

could not be interpreted.

Having prepared these aromatic thiocyanato-compounds it was hoped

that Davis's synthesis of a fused isothiazolium salt (130) via organo-

palladium complexes could be extended to related systems. The iso-

ArC=CH—CH=$\overset{+}{N}$Me$_2$ $\xrightarrow{\text{(i)}}$ ArC=CH—CH=$\overset{+}{N}$Me$_2$

| |

Cl   SeCN   ClO$_4^-$

ClO$_4^-$

$\Big\downarrow$ (ii)

$\xleftarrow{\text{(iii)}}$ ArC=CH—CH=NAr$'$

Ar — (ring: Se, N—Ar$'$) |

                                                    SeCN

ClO$_4^-$

(217)

(218)
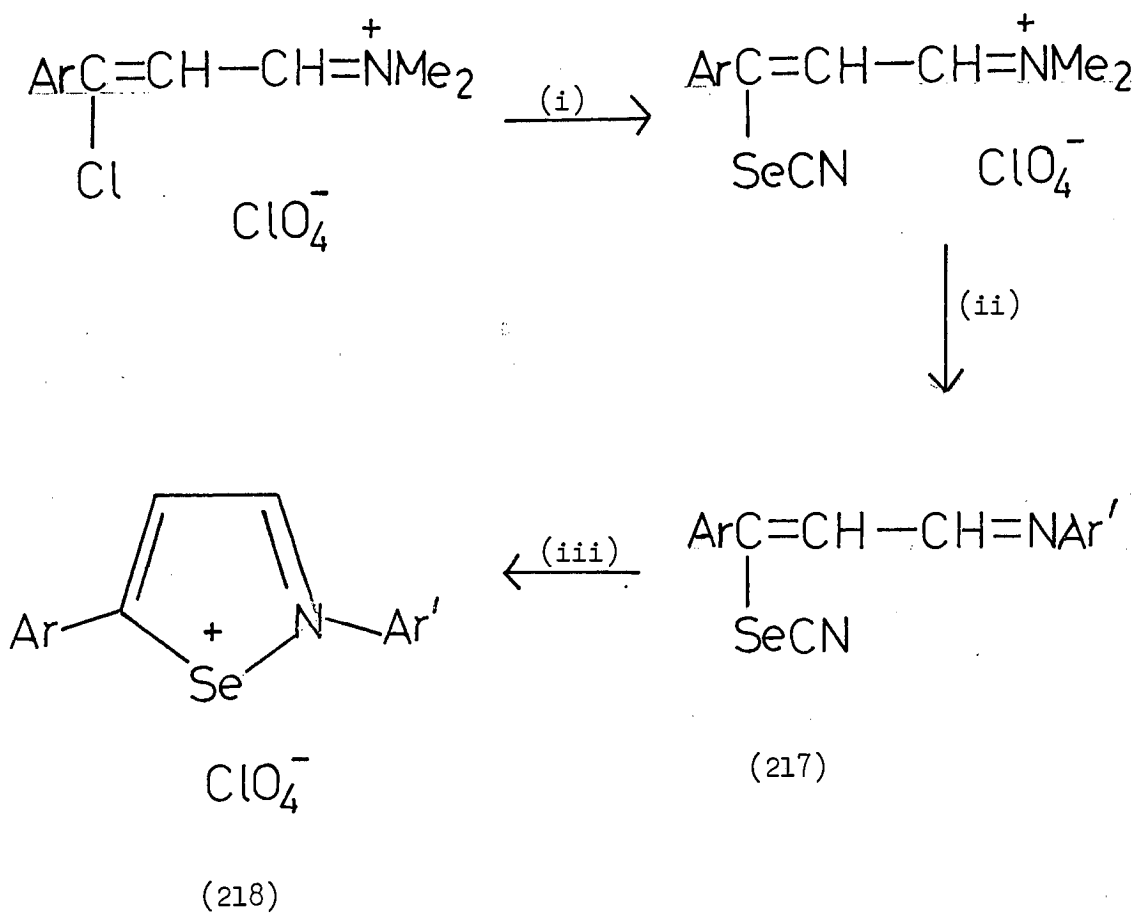
Scheme 15

(i)   NaSeCN/DMF
(ii)   Ar$'$NH$_2$
(iii)   HClO$_4$

thiazolium salt (130) was synthesised by the action of bromine on 2-(2-thiocyanatophenyl)pyridine but it was thought desirable to find another method for the cyclisation since some of the aromatic nuclei (e.g. 1-phenylpyrazole) were likely to be susceptible to attack by bromine. A report by Liebscher and Hartmann[110] on the synthesis of selenazolium salts (218) by acid induced cyclisation of the selen-acyanatoimines (217), Scheme 15, pointed the way to a possible method for the cyclisation of compound (212) and related thiocyanates.

Reaction of 10-thiocyanatobenzo[h]quinoline (212) with perchloric acid gave a white solid, that was identified as the novel fused iso-thiazolium salt (219).

(212)   (219)
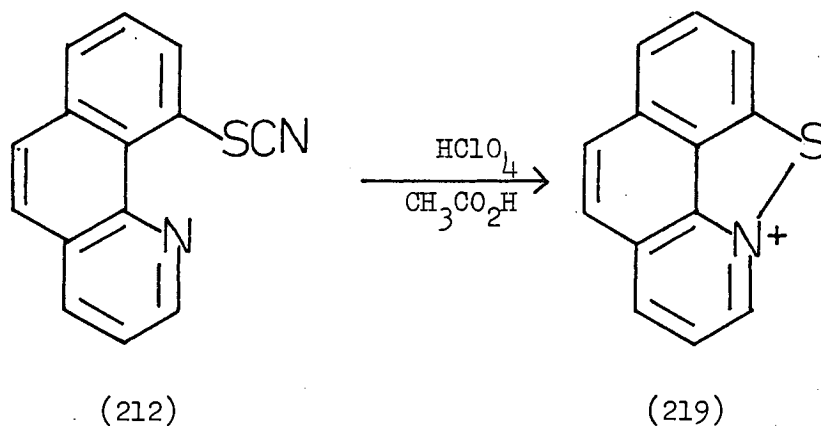
The ^{1}H n.m.r. spectrum of the perchlorate was well resolved and, as expected, the resonances had shifted downfield from those of benzo-[h]quinoline. There were two multiplets at δ 9.6 and 8.1 - 8.8 which integrated in the ratio 1:7. The low-field signal, a doublet of doublets, was assigned to H-2 but, owing to the complexity of the other multiplets, no further assignments were possible.
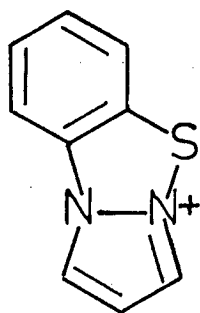
(220)
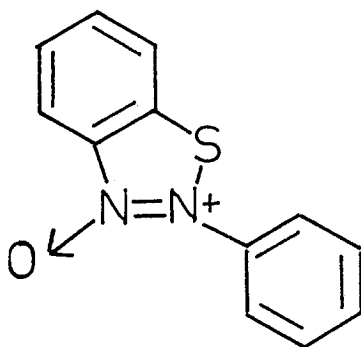
(221)

Attempts to cyclise 1-(2-thiocyanatophenyl)pyrazole (213) by reaction with perchloric acid failed, compound (213) being recovered quantitatively, and boron trifluoride, a Lewis acid, gave the same result. Treatment of (213) with bromine (Davis's original procedure) was equally ineffective, yielding multicomponent gums from which no solid product could be isolated. It was thought that the most probable reaction of (213) with bromine was bromination of the pyrazole ring at the 4-position which is relatively electron-rich. The failure to isolate the salt (220) from these reactions was disappointing but the synthesis of compound (213) was itself a further illustration of the use of organopalladium complexes in synthesis.

The reaction of 2-thiocyanatoazoxybenzene (214) with acid was viewed with interest since a possible product of cyclisation would be the N-oxidothiadiazolium salt (221), an unusual and novel system. A chocolate-brown solid was isolated from the reaction of compound (214) with perchloric acid and its infra-red spectrum, though poorly resolved, showed the characteristic broad absorption of 1100 cm^{-1} due to the perchlorate ion. Elemental analysis indicated that the product had retained the whole of the SCN grouping and further that the solid was a di-perchlorate salt. The ^{1}H n.m.r. spectrum in trifluoroacetic acid showed four multiplets at δ 9.0, 8.8, 8.3 and 7.9 which integrated in the ratio 1:1:4:3. It is difficult to envisage any reasonable structure based on this evidence but the di-cation (222) might perhaps be suggested as the least unlikely possibility.

(214)

+ H⁺ →

(222)

HClO₄
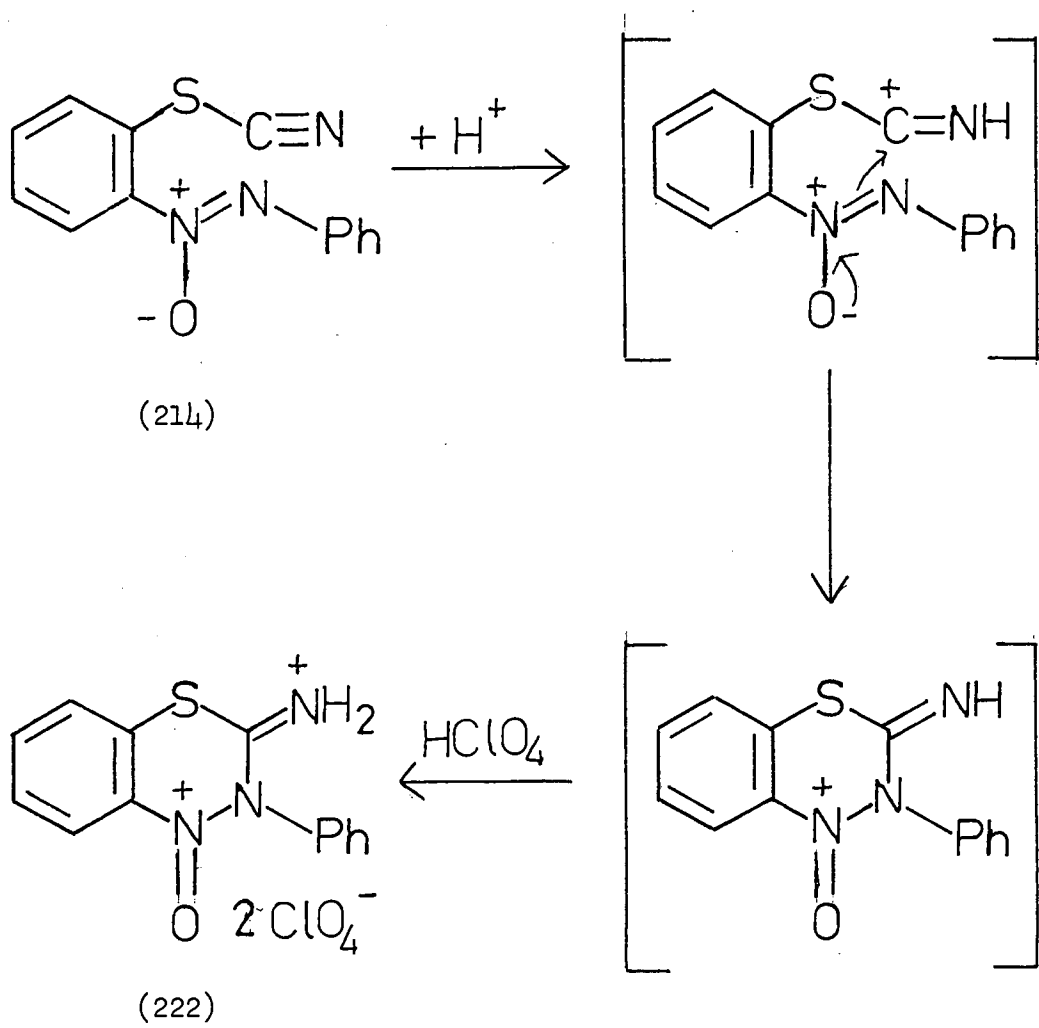
Scheme 16

(224)

(225)

a: X = 0
b: X = S

(222a)   (222b)
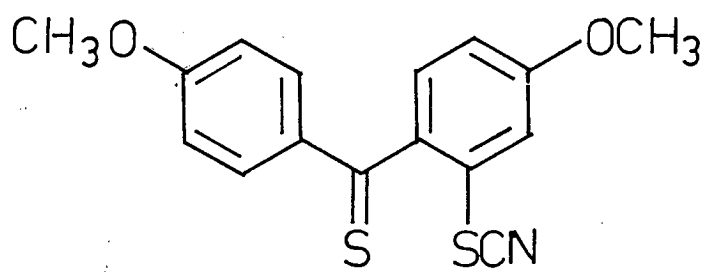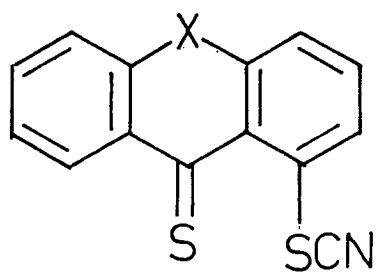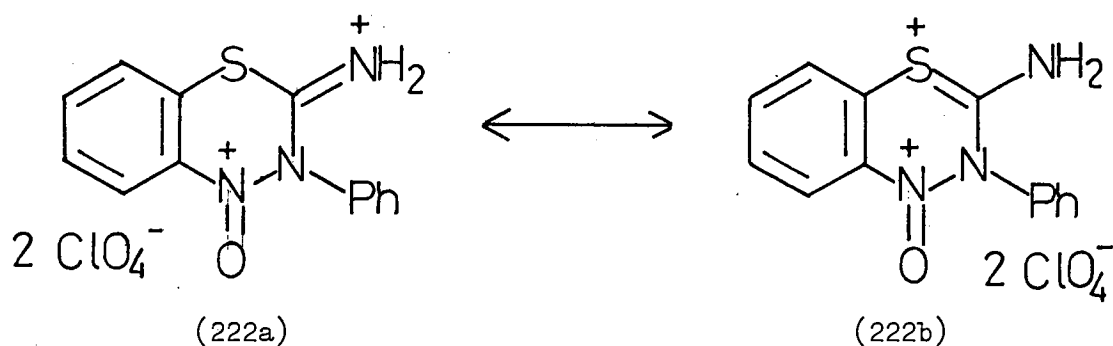
Structure (222) would be a novel heterocyclic system possibly formed by protonation of the nitrile and cyclisation _via_ attack on the azo-group by the nitrilium ion (Scheme 16).

A small sample of the diperchlorate was dissolved in aqueous sodium hydroxide and the resulting solution was extracted with chloroform.   Evaporation of the chloroform gave a very pale yellow solid, the mass spectrum of which showed weak peaks at $^m/e$ 213 and 77 tentatively assigned to the benzothiadiazolium (223) and the phenyl ion, respectively.

(223)
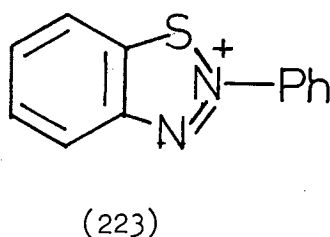
The next part of the investigation of the synthetic utility of cyclopalladated complexes was concerned with the reactions of complexes containing S-donor ligands.   The dithiocarbamato-complexes (207), (208a) and (208b), containing cyclopalladated 4,4'-dimethoxythiobenzophenone, xanthenethione and thioxanthenethione ligands, were treated with thiocyanogen.   Again, however, the products (224), (225a) and (225b) could not be purified since recrystallisation or chromatography appeared to cause decomposition.

$$CH_3O \quad \text{(structure with positions 5', 6', 3', 2', 4, 5, 7 and } OCH_3, \ S\text{—}S^+, \ ClO_4^-)$$
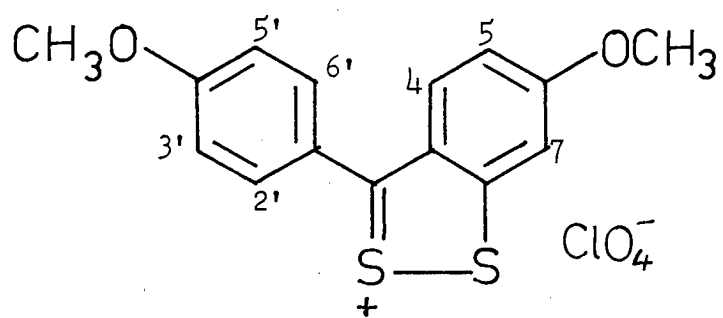
(227)

The infra-red and mass spectra of the product from complex (207) were consistent with those expected for 4,4'-dimethoxy-2-thiocyanato-thiobenzophenone (224). The infra-red spectrum contained sharp nitrile stretching bands at 2120 and 2095 cm^{-1} and the mass spectrum showed strong peaks at $^{m}/e$ 315 and 289 corresponding to the parent ion and the 1,2-dithiolium cation (226) respectively.

(226)
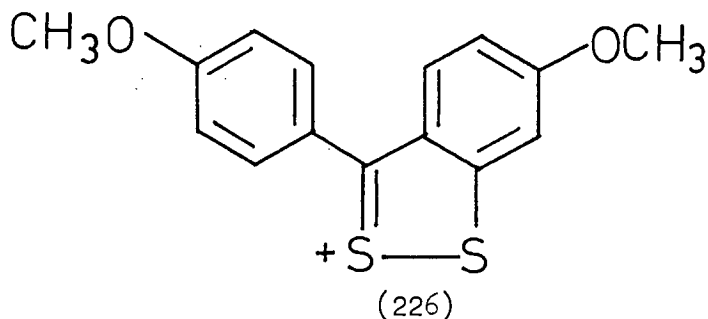
The crude thiocyanatothiobenzophenone (224) was treated with perchloric acid to yield an orange crystalline solid identified as the previously unknown 3-p-anisyl-6-methoxybenzo-1,2-dithiolium perchlorate (227). The ^{1}H n.m.r. spectrum of the salt was resolved into five groups of peaks, the aromatic region containing four of these at δ 8.4(1H,d), 7.9(3H,m), 7.5(1H,dd) and 7.3(2H,d). The doublet at δ 8.4 was assigned to H-4, the multiplet to H-7,2' and 6', the doublet of doublets to H-5 and the remaining doublet at δ 7.3 to H-3' and 5'. The non-equivalence of the methoxy groups was shown by two closely spaced singlets at δ 4.2 and 4.0.

This is the first reported synthesis of a 1,2-dithiolium salt *via* organopalladium intermediates, and is an extension of the use of such complexes in heterocyclic synthesis.

The mass spectra of the fused thiocyanato-derivatives (225a) and (225b) showed the expected parent ion peaks and fragment ions due to loss of NC - (228). Exact mass measurements for the parent ion (225a) confirmed the proposed structure.

(125)

(229)

a: X = O
b: X = S

(228)
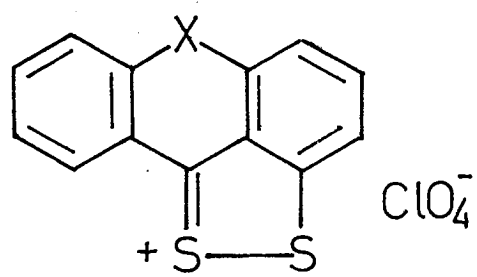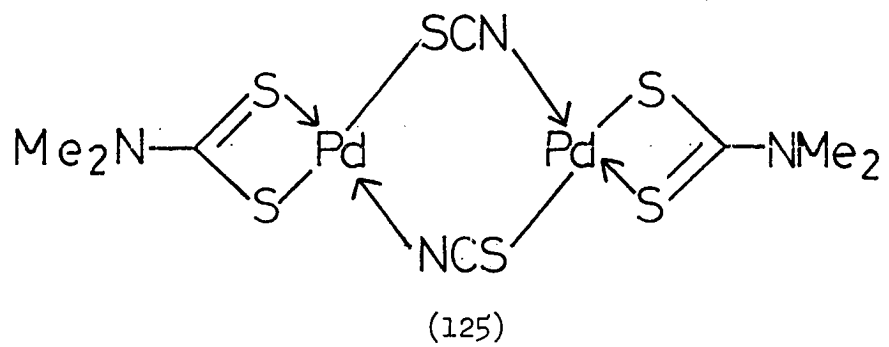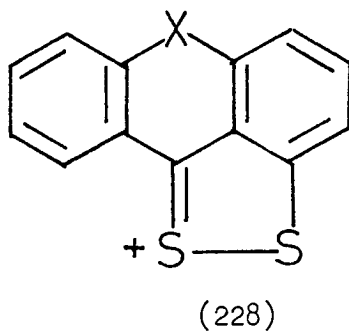
Treatment of 1-thiocyanatoxanthene-9-thione (225a) with perchloric acid yielded a bright red solid, elemental analysis of which showed the presence of nitrogen (ca. 1%), even after repeated recrystallisation from glacial acetic acid. Mass spectrometry indicated that the nitrogen contaminant was bis(N,N-dimethyldithiocarbamato)palladium(II) and/or the thiocyanato-bridged complex (125) which had co-precipitated with the sparingly soluble thiocyanatoxanthenethione (225a) during the reaction of the dithiocarbamate complex (208a) with thiocyanogen. Since compound (225a) could not be purified (see earlier), elimination of the nitrogen contaminant could only be accomplished by treatment of complex (208a) with thiocyanogen in an exceedingly dilute solution. Treatment of the uncontaminated thiocyanatoxanthenethione with perchloric acid then gave a pure sample of the xantheno-1,2-dithiolium perchlorate (229a).

An impure sample of the dithiolium salt (229b) was isolated as a purple-blue solid by ring closure of the thiocyanatothioxanthene-thione (225b) but, like its oxygen analogue (229a), this was contaminated with nitrogen-containing compounds that could not be removed by recrystal-lisation. Attempts to obtain a pure sample by the previously described dilution method were ineffective in this case.

(52)

Na$_2$PdCl$_4$ / MeOH

NaSCSNMe$_2$/DMF

Br$_2$

Me$_2$N

Cu(?)

HN=C(R)NH$_2$

(231)

(230)
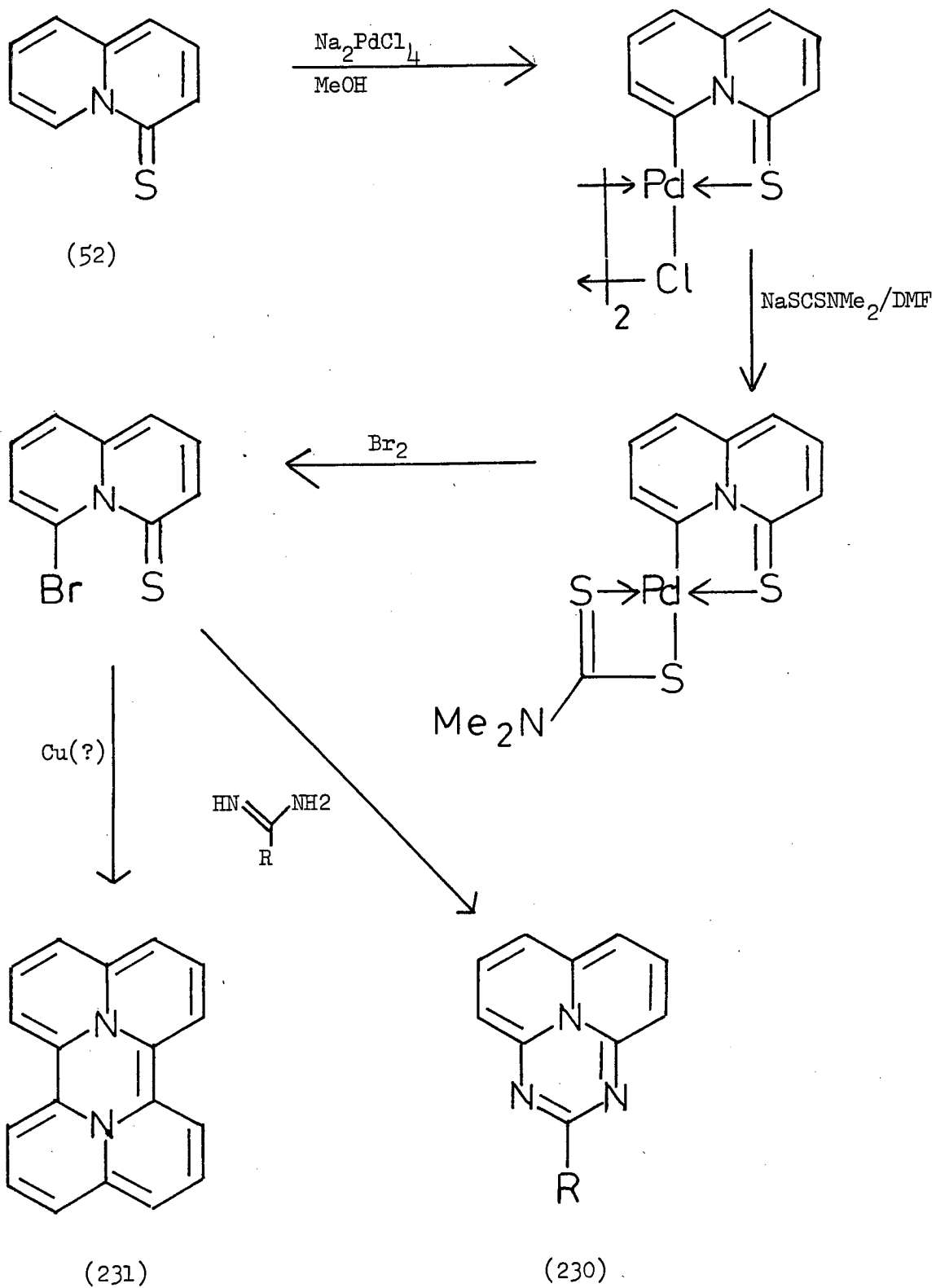
Scheme 17

When this investigation into the synthetic utility of cyclo-palladation was started, the preparation of a 6-substituted quinolizine-4-thione was regarded as one of the most important objectives. With the successful preparation of 6-palladated quinolizine-4-thione complexes, the first part of this objective had been achieved and it only remained to replace the palladium atom by some other atom or group. A 6-halogenoquinolizine-4-thione would be particularly valuable as a synthetic intermediate in the cyclazine field since, by reaction with an amidine, it might be converted into a 1,3-diazacycl[3,3,3]azine (230) and, by dehalogenative and desulphurative coupling, into the pyrazinodi-quinolizine (231) which possesses an 18 π electron molecular periphery. A potential sequence of reactions is outlined in Scheme 17 and various other possibilities may be easily envisaged. No 6-functionalised quinolizin-4-ones or -4-thiones, other than two 6-hydroxy-compounds, are known at the present time and conventional routes to such compounds do not appear promising.

Addition of bromine to a dilute solution of the quinolizine complex (209) in dichloromethane gave a deep maroon solution which persisted for ten minutes, after which the colour became progressively lighter and a red-purple precipitate was formed. The precipitate was identified as di-μ-bromobis(N,N-dimethyldithiocarbamato)dipalladium(II), (125b). A second solid (yellow), isolated from the solution, was identified by spectroscopy and its melting point, as quinolizine-4-thione (52). No evidence of a bromo-quinolizinethione was found. Similar colour changes were observed and quinolizine-4-thione was again obtained, together with the complex (125) when the quinolizine complex (209) was treated with thiocyanogen.
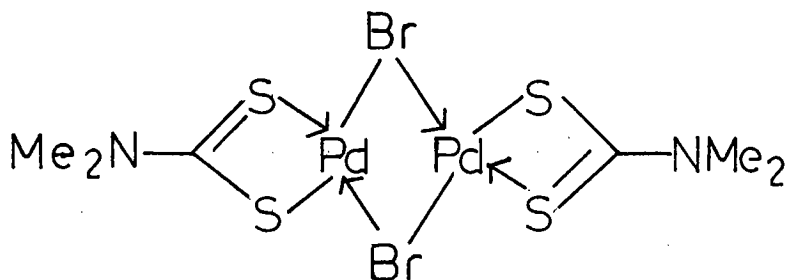
(125b)

These reactions of the quinolizine complex (209) were surprising
since it appeared from the colour changes, that addition of bromine,
or thiocyanogen, to a solution of the complex resulted in the form-
ation of the assumed Pd(IV) intermediate (232). Decomposition of
(232) however, to the bridged complex (125a) or (125b) was accompanied
by replacement of the palladium by hydrogen rather than by bromine
or thiocyanate.
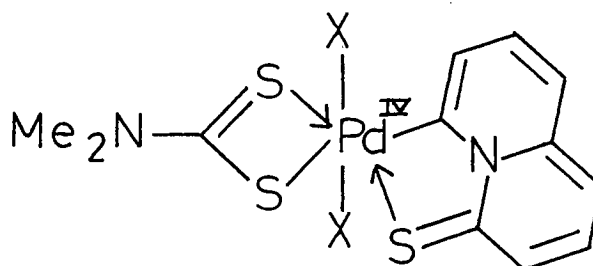
(232)

a: X = Br

b: X = SCN

A possible reason for this unexpected result is that the electron
donating thioamide group (of quinolizine-4-thione) stabilises the
electron-deficient palladium(IV) atom thus affording increased stability
to the intermediate compared with the intermediates of previously
discussed reactions. Certainly, the dark colour observed during the
reaction was longer lived than in previous cases, and it is known
from the work of others (111) that thioamide ligands (in the form of
dithiocarbamate) are capable of stabilising the higher oxidation
states of palladium and of nickel. Owing to the increased stability,

the intermediate might then decompose via a homolytic process instead
of by the rapid reductive elimination that is believed to occur in
other cases. This could yield a 4-thioxoquinolizin-6-yl radical
that would abstract a hydrogen atom from chloroform (the reaction
solvent) giving the observed product.

To test this suggestion, the complex (209) was treated with thio-
cyanogen in 1,1,2-trichloro-1,2,2-trifluoroethane ("Arklone"), a
relatively inert solvent that does not contain hydrogen. As in
chloroform, a deep maroon colour was initially produced and this
slowly lightened with the formation of complex (125a). Evaporation
of the filtrate gave an orange solid that showed strong infra-red
absorptions at 2100 and 1550 cm^{-1} attributed to thiocyanato- and
dithiocarbamato- groups while the mass spectrum showed peaks at
^{m}/e 255, 224, 192, 175 and 160 (cf quinolizinethione, ^{m}/e = 161). A
^{1}H n.m.r. spectrum could not be obtained owning to the low solubility
of the solid. All attempts to purify the product failed and no
structure can be suggested that would agree with the spectroscopic
and analytical data.

Two further attempts were made to synthesise a 6-substituted
quinolizine-4-thione from the dithiocarbamato-complex (209). With
iodine in dichloromethane no reaction occurred, even under reflux
conditions, and the complex was recovered quantitatively. The complex
was also recovered after treatment with N-bromosuccinimide in chloro-
form, though the reagent was reduced to succinimide.

A final attempt was made to synthesise 6-bromoquinolizine-4-thione
by treating the easily soluble triphenylphosphine complex (195b) with
bromine in Arklone. Addition of bromine to the solution caused

immediate precipitation of a red-brown solid which was extremely
involatile and insoluble in common organic solvents. Owing to the
involatility and insolubility no n.m.r. or mass spectra could be
obtained and the infra-red spectrum showed no strong peaks other
than the aromatic C-H bending bands. No products remained in the
Arklone. The formation of an insoluble and involatile product was
similar to the reaction of thiocyanogen with complex (209) in Arklone.

From these limited reactions of cyclopalladated quinolizine
complexes it appears that they are often complex and solvent dependent.
Reactions in chloroform or dichloromethane gave quinolizine-4-thione
(i.e. replacement of palladium by hydrogen) while reactions in Arklone
gave insoluble (and in one case involatile) products of undetermined
structure. In no case was a simple 6-substituted product isolated.

In view of the complexity of the reactions of cyclopalladated
quinolizine complexes attention was turned to the dithiocarbamato-
complexes of cyclopalladated N-methylisoquinoline-1-thione (210) and
N,N-dimethylthiobenzamide (211a). It was hoped that more information
would be obtained that might help to clarify the behaviour of complexes
containing cyclopalladated thioamide ligands.

Treatment of these complexes with thiocyanogen in chloroform
gave dark coloured solutions which gradually lightened with precipi-
tation of the bridged palladium complex (125a). The only other
products isolated were N-methylisoquinoline-1-thione (182), contam-
inated with a trace of N-methylisoquinolin-1-one, and N,N-dimethylthio-
benzamide (187a). These reactions are thus analogous to that of the
quinolizine complex (209) with thiocyanogen in chloroform. As a
group, however, the thioamide complexes (209 - 211) differ from the

(233)

a: X = H
b: X = Cl

(234)

i) NaSCSNMe$_2$

ii) (SCN)$_2$

(235)
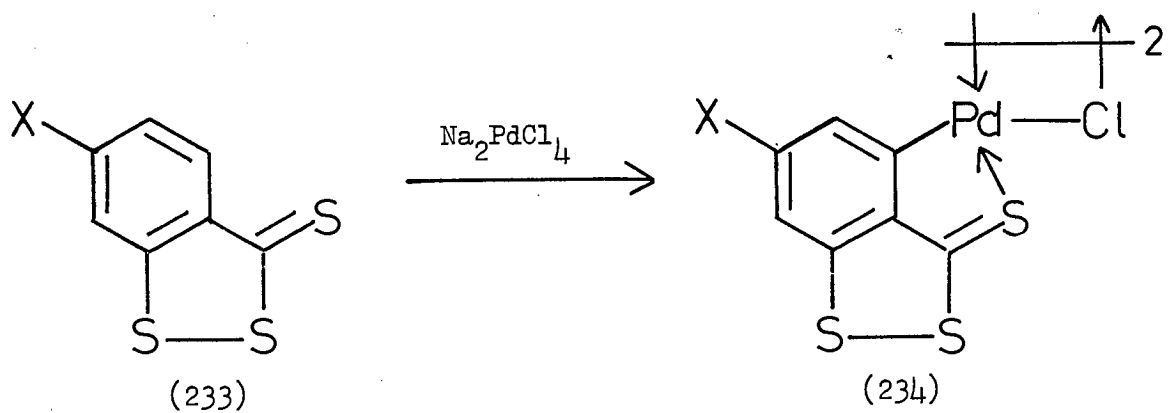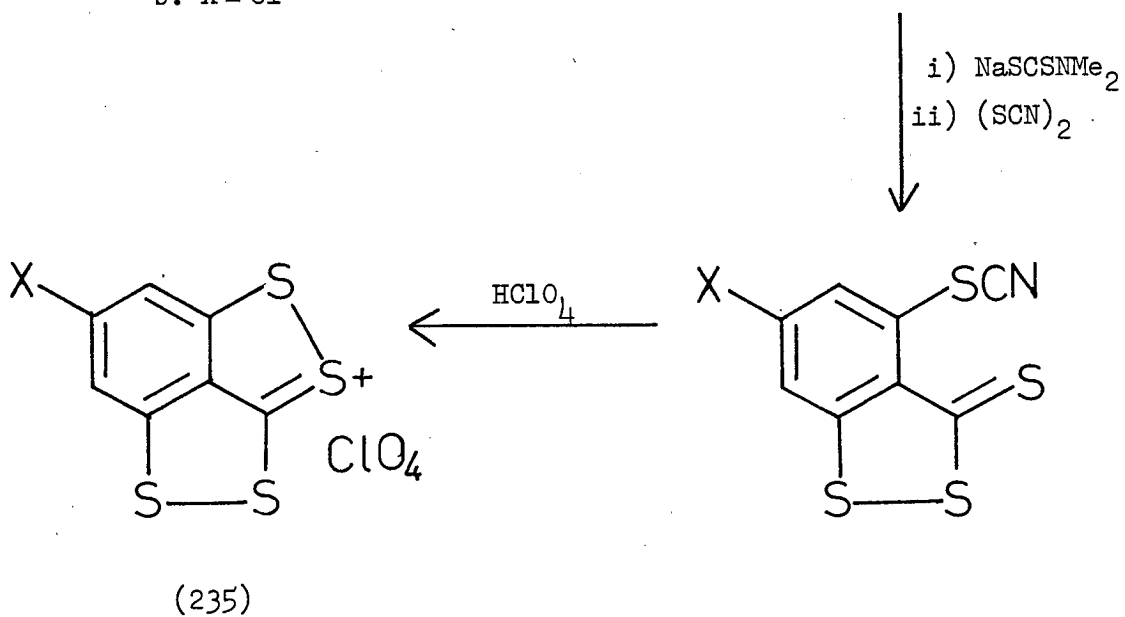
Scheme 18

cyclopalladated complexes discussed previously. It is thought that the electron-donating ability of the thioamide nitrogen atom gives enhanced stability to the palladium(IV) intermediates thus preventing, in some way, the normal reductive elimination process.

Treatment of the dithiocarbamato-complex of N-methylisoquinoline-1-thione (210) with bromine, in chloroform, produced a deep maroon solution but, no precipitate of the bromine bridged complex (125b) was formed. Evaporation of the solution to dryness gave a maroon solid of undetermined structure that was only sparingly soluble in organic solvents.

(vii)   The Synthesis and Reactions of Palladium Complexes
         derived from 1,2-Dithiole-3-thiones

In Sections 1 and 2 the synthesis and reactions of various ring-fused thiathiophthens and 1,2-dithioles, were discussed. Subsequent experience in the synthesis of heterocycles via cyclopalladated complexes suggested that an opportunity might exist to extend this study by synthesising benzo(de,d'e')1,2-dithiolo-1,2-dithiolium perchlorate (235a) from 4,5-benzo-1,2-dithiole-3-thiones (233a). The proposed synthesis is illustrated in Scheme 18.

Reaction of the thione (233a) with sodium tetrachloropalladate gave a russet solid which, like previously discussed chloride-bridged complexes, was highly involatile and insoluble in common organic solvents. Elemental analysis was consistent with the structure (234a) but spectroscopic evidence of structure was lacking. To determine whether cyclopalladation had occurred, the complex was treated with triethylphosphine to split the chloride bridges. However, unlike

(236a)

X = H,Cl

(236b)

X = H,Cl
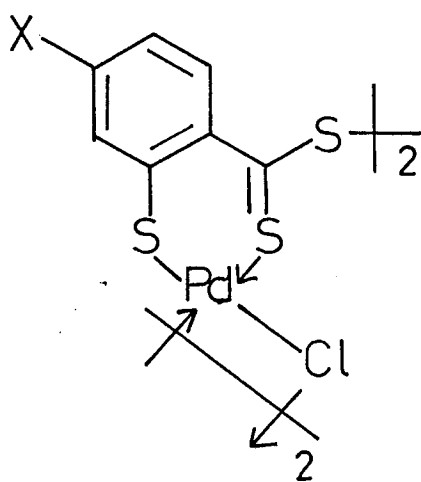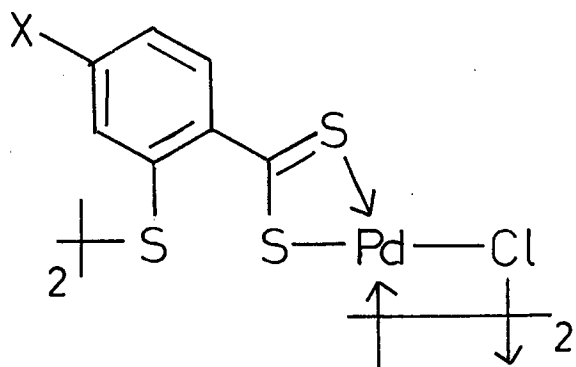
previously reported phosphine complexes, the product was only slightly soluble in common organic solvents and no [1]H n.m.r. spectrum could be obtained. Mass spectroscopic evidence was inconclusive, since no palladium-containing ions were observed, but the spectrum showed peaks [m]/e 240 and 184 (benzodithiolethione). Elemental analysis of the pure complex gave values consistent with the suggested orthopal-lated complex. It was thought that larger alkyl groups on the phosphine might lead to a more soluble complex but reaction of the chloride-bridged complex with tri-n-butylphosphine gave only a very small yield of solid, the major product being a dark coloured gum. Elemental analysis of the solid did not support the expected structure.

An orange solid was isolated by reaction of the chloride-bridged complex with sodium diethyldithiocarbamate and elemental analysis gave values consistent with the expected cyclopalladated dithio-carbamato-complex. Evidence from mass spectroscopy was again incon-clusive owing to the product undergoing an anomalous mass spectrometric reaction (see later). The [1]H n.m.r. spectrum which, because of low solubility, was obtained by the Pulsed Fourier Transform method, showed well resolved resonances in the aromatic proton region that closely resembled the spectrum of 4,5-benzo-1,2-dithiole-3-thione (233a). Integration suggested that four aromatic protons were present and thus the n.m.r. evidence led to the conclusion that cyclopalladation had not taken place.

The analytical results for these complexes, and the n.m.r. observations for the dithiocarbamato-complex point to two possible isomeric structures (236a) and (236b) for the original chloride-bridged complex. Both structures (236a) and (236b) are polymeric,

2

(233)

$\xrightarrow{\text{PdCl}_4{}^{2-}}$

2

$-\text{Cl}^-$

2

Cl—S

(239)

[H]

$\frac{1}{2}$S

(236)

Scheme 19
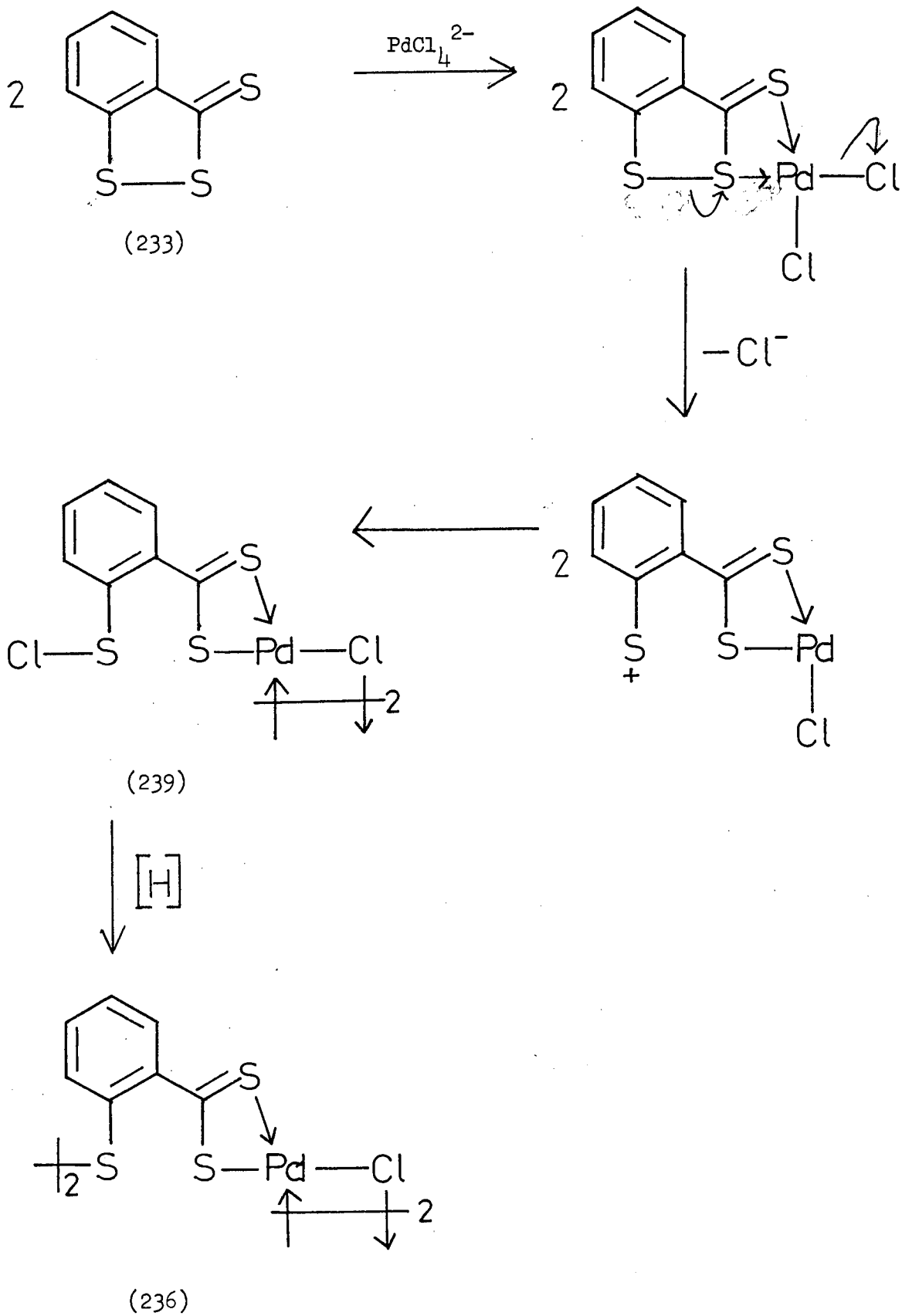
thus accounting for the very low solubility. Their formation would involve cleavage of the dithiole sulphur- sulphur bond. Structure (236a) is thought to be the more likely since, in view of the high affinity of palladium for sulphur, the initial step in the formation of the complex could well be the co-ordination of both the thione-sulphur and S-2 of the dithiole ring to palladium. The subsequent cleavage of the disulphide bond and the reformation of such a bond, intermolecularly, involves a reductive process that is not easily accounted for (n disulphide bonds are replaced by $n/2$ such bonds). If no reduction occurred, the expected product of dithiole ring-cleavage would be the sulfenyl chloride (239) and conversion of this into the disulphide (236) could be the reductive step (Scheme 19).

Since complex (236) is isolated in yields of 85 - 90%, the formation of the disulphide cannot be the result of hydrolysis to a sulphenic acid followed by disproportionation. (3R-SOH $\longrightarrow$ R-S-S-R+R-SO$_2$H+H$_2$O). The only other possibility is that the solvent, methanol acts as a reducing agent, being itself oxidised to formaldehyde.

Assuming the structure (236a) to be correct for the initial chloride-bridged complex, structures (237) and (238) will represent the derived triethylphosphine and dithiocarbamato-complexes, respectively. The "dimeric" character of these structures accounts well for the low solubility of the complexes.

In seeking conclusive evidence for the suggested structures for complexes (236) - (238), attempts were made to synthesise a soluble dithiocarbamato-dimer (238) so that an osmometric molecular weight determination could be carried out. Complexes (238a-d) were

(233)

X = H,Cl

Na$_2$PdCl$_4$

(236)

NaSCSNR$_2$

PR$_3$

(238)
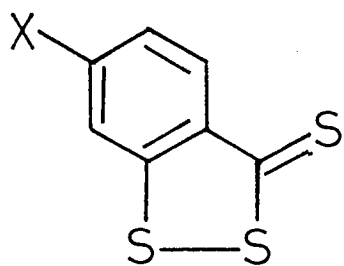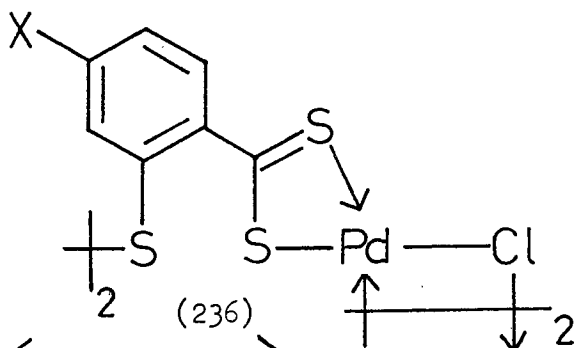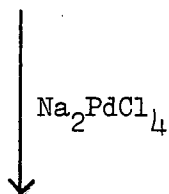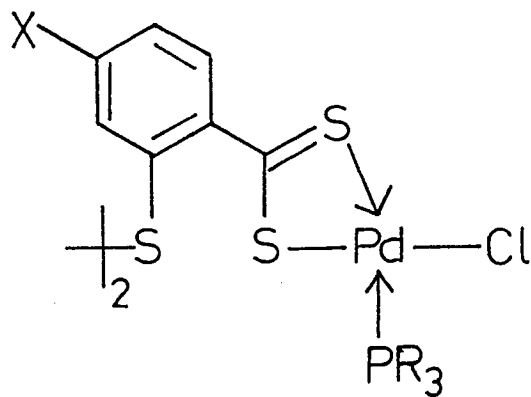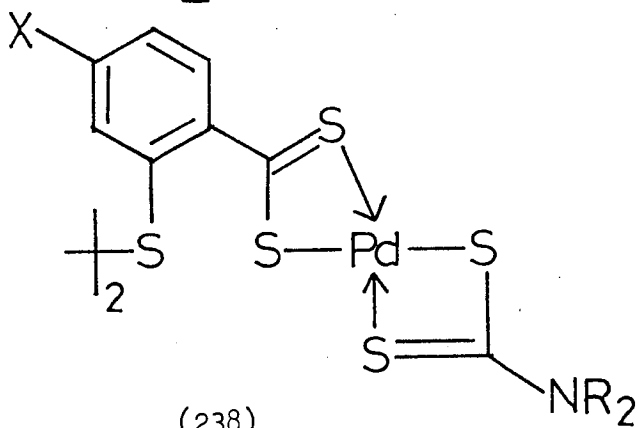
R = a: CH$_3$

b: CH$_3$CH$_2$

c: CH$_3$CH$_2$CH$_2$CH$_2$

d:

X = H,Cl

(237)

R = Et, nBu

Scheme 20
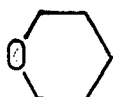
synthesised but (238a) and (238b) did not have the required solubility for the determination to be attempted and the di-n-butyldithiocarbamato-complex (238c;X=H) was a gum that could not be isolated analytically pure, though its ^{1}H n.m.r. spectrum was in agreement with the proposed structure. Attempts to isolate the morpholinodithiocarbamato-complex (238d;X=H) analytically pure failed owing to the low solubility of the complex in common solvents.

To obtain conclusive proof that the benzo-1,2-dithiole-3-thione system does not undergo cyclopalladation, 6-chloro-4,5-benzo-1,2-dithiole-3-thione (233b) was used in place of the parent compound. If cyclopalladation occurred, the ^{1}H n.m.r. spectrum of e.g. the dithiocarbamato-complex would show two meta-coupled doublets; if complex (236b) were formed, however, the spectrum would contain one ortho-coupled doublet, one meta-coupled doublet and one ortho- and meta-coupled doublet of doublets. The required dithiocarbamato-complex derived from the thione (233b) was obtained by the general procedure (Scheme 20) and its ^{1}H n.m.r. spectrum showed the features appropriate to the structure (238b;X=Cl). Mass spectroscopy showed peaks at ^{m}/e 218 (233b) and 402 (202b) while a weak palladium containing fragment ion at ^{m}/e 443 was tentatively assigned to the "half-molecule" minus one ethyl group, conveniently represented as (240).

(240)

(241)

1) Na$_2$PdCl$_4$
2) NaSCSNMe$_2$

(242)

(243)

1) Na$_2$PdCl$_4$
2) NaSCSNEt$_2$
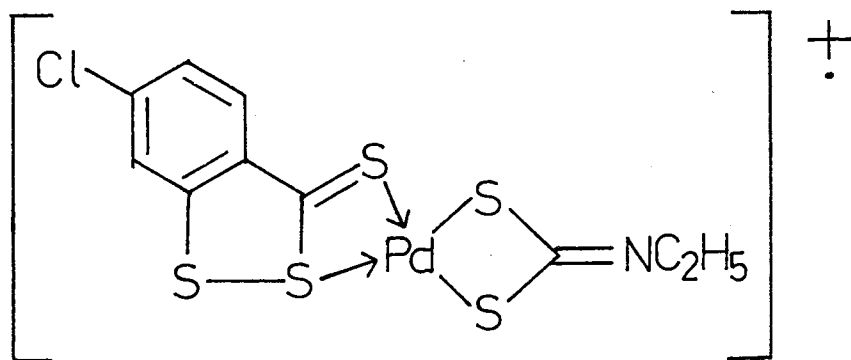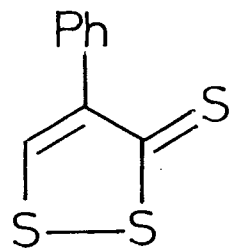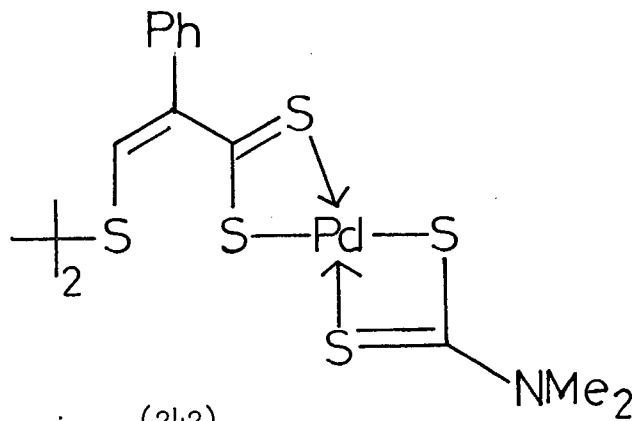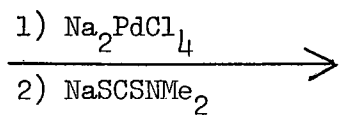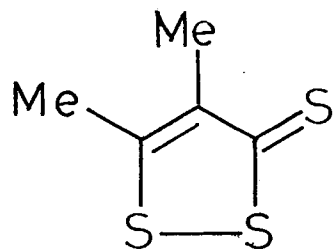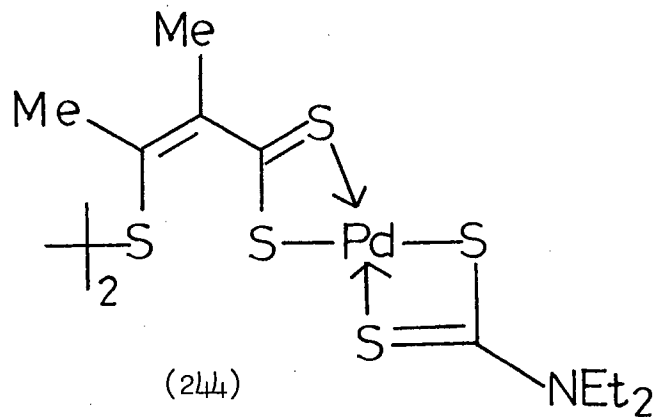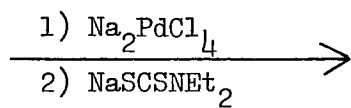
(244)

In further attempts to obtain a complex that was suitably crystalline, for X-ray analysis, and/or soluble in common organic solvents, for a molecular weight determination by osmometry, 4-phenyl-1,2-dithiole-3-thione (241) and 4,5-dimethyl-1,2-dithiole-3-thione (243) were treated with sodium tetrachloropalladate and the resulting chloride-bridged complexes were converted into the corresponding dithiocarbamato-complexes (242) and (244). Unfortunately, neither complex had suitable physical characteristics, to enable any structural determinations to be carried out. Complex (242) had only a limited solubility; a pure sample could not be isolated but the mass spectrum of the crude complex showed a peak at $^m/e$ 436 tentatively assigned to a M^{2+} ion or to the fragment ion (245).

(245)
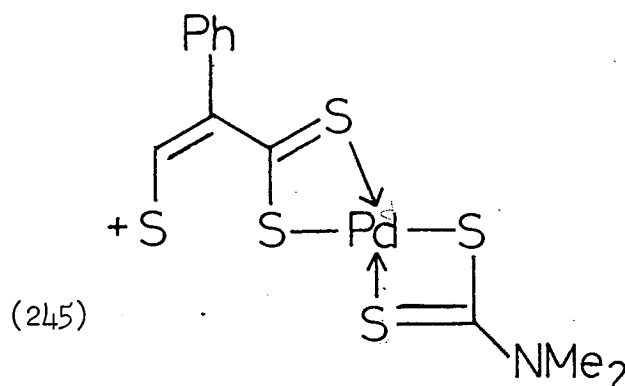
Complex (244) was a dark maroon gum that was not isolated in a pure form even after repeated chromatography. The ^{1}H n.m.r. spectrum (60 MHz)was consistent with the proposed structure, containing four well resolved signals - two singlets at δ 2.5 and 2.2 (methyl groups), a quartet at δ 3.7 and a triplet at δ 1.3 (N-ethyl groups).

(viii)   <u>Anomalous Mass Spectrometric Reactions of Cyclo-
             palladated Complexes</u>

A study of the mass spectra of the <u>cyclopalladated</u> complexes
revealed the presence of some unexpected ion-peaks. The peaks could
only be explained by assuming that the original complex had undergone
a bimolecular reaction in the mass spectrometer, since nuclear magnetic
resonance and elemental analysis had shown the complexes to be pure.
Bruce[39] has recently reported that certain cyclometallated molybdenum
and ruthenium complexes undergo similar reactions.

For the purpose of this discussion, an anomalous mass spectro-
metric reaction can be defined as a bimolecular reaction of a complex,
or compound, that occurs as a result of electron-impact during the
measurement of a mass spectrum. Since the vapour pressure of a sample
in the mass spectrometer is extremely low ($<10^{-5}$ torr), the possibility
that bimolecular processes occur in the vapour can be excluded. It
must be assumed, therefore, that the observed reactions occur in the
solid sample when it is introduced into the electron beam. The possi-
bility that the reactions are purely thermal processes cannot be
entirely excluded although, in the case of one complex (208a), this
was shown to be unlikely since no products corresponding to the
observed ion peaks were produced when the complex was heated in an
evacuated sublimation apparatus. Although some of the reactions have
been referred to in earlier sections, the present discussion will be
limited to the mass spectroscopic reactions of cyclopalladated dithio-
carbamato-complexes. Since the reactions were dependent on the nature
of the cyclopalladated ligand, examples of each type will be discussed.

(247)

(246)

(248)

(249)

Cleavage
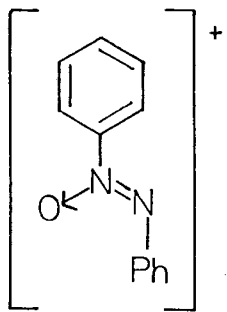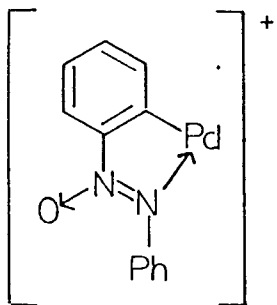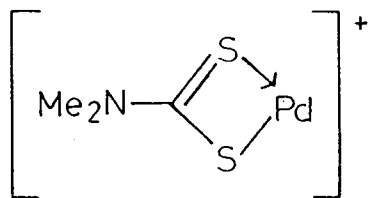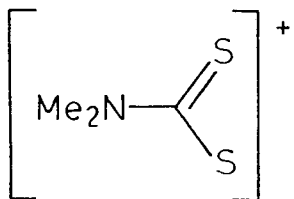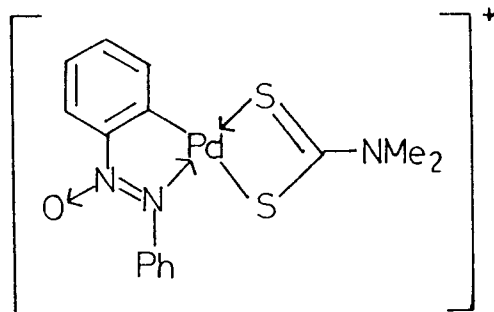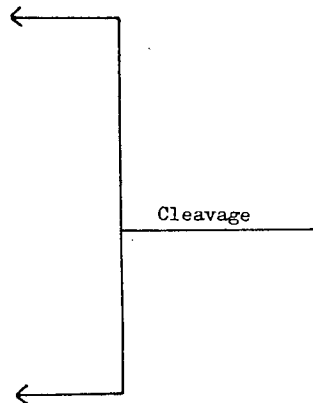
(206)

disproportionation
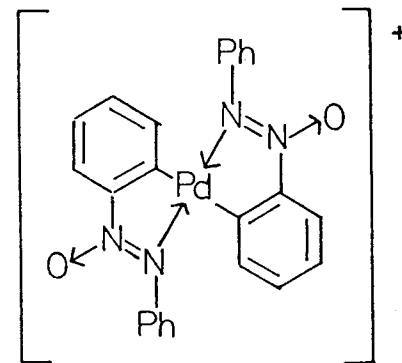
(250)
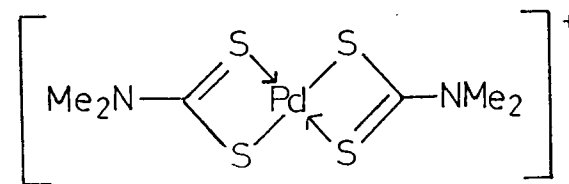
(251)

(a)   Complexes containing nitrogen donor ligands or thioamide

ligands.

example (i):   2-(Phenylazoxy)phenyl(N,N-

dimethyldithiocarbamato)palladium(II), (206).

The mass spectrum of complex (206) showed the expected parent

ion at ^{m}/e 423 with other palladium-containing ions at ^{m}/e 500, 346,

303 and 226 and palladium-free ions at ^{m}/e 197 and 120.   The peaks

at ^{m}/e 303, 226, 197 and 120 may be represented as (246), (248), (247)

and (249) respectively, and are products of normal mass spectrometric

cleavage.   The peaks at ^{m}/e 500 and 346, on the other hand, are evi-

dently due to the ions (250) and (251) which are products of dispro-

portionation of the original complex.   Such ions can only be formed

by a bimolecular process and it seems likely that this is electron

impact-induced within the solid sample.   These reactions are illustrated

in Scheme 21.

example (ii):   4-Thioxoquinolizin-6-YL(N,N-

dimethyldithiocarbamato)palladium(II), (209).

The mass spectrum of complex (209) showed the expected parent

ion at ^{m}/e 386 with strong palladium-containing ions at ^{m}/e 426 and

346 attributed to the disproportionation products (252) and (251),

respectively.

(252)

(255)

(254)

(253)

mass
spectrometer

(208a)

NMe₂
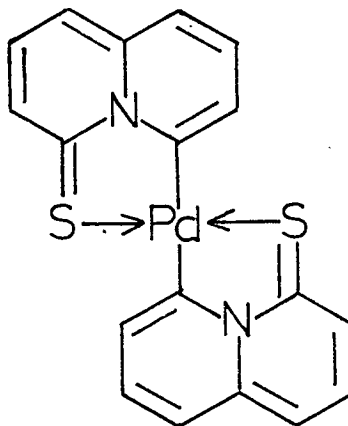
2
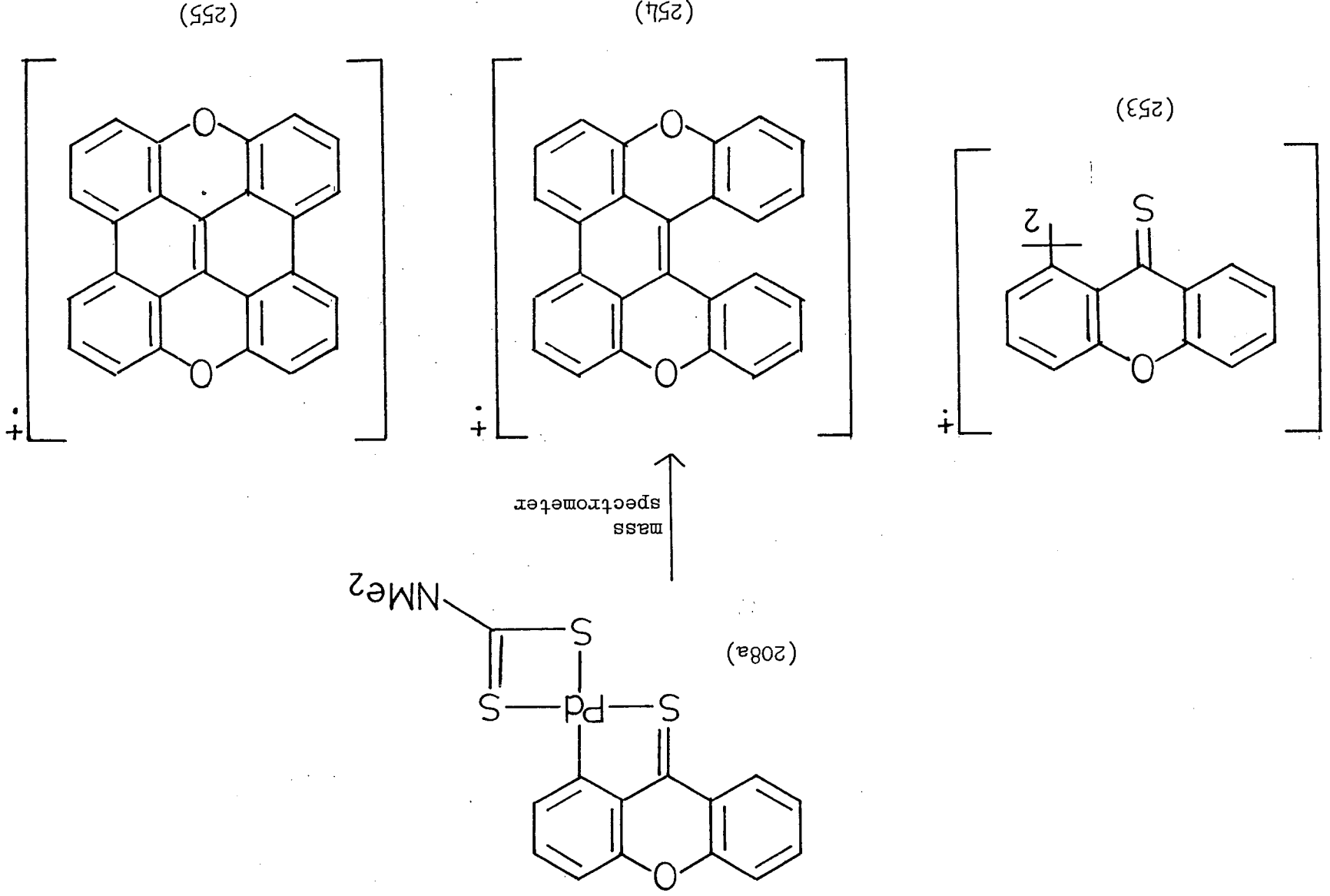
Davis[41] reported the same ion (252) in the mass spectrum of di-μ-chlorobis(4-thioxoquinolizin-6-yl)dipalladium(II), (53).

(b)   Complexes containing sulphur donor ligands other than thioamides.

example: 9-Thioxoxanthen-1-yl(N,N-dimethyl-dithiocarbamato)palladium(II), (208a).

The mass spectrum of the complex (208a), showed peaks with a palladium isotope pattern at $^m/e$ 437 and 346 and palladium-free ions at $^m/e$ 422, 358 and 356. The peak at $^m/e$ 437 corresponds to the parent ion of the complex (208a) while $^m/e$ 346 is again due to the ion (251) of bis(N,N-dimethyldithiocarbamato)palladium. The palladium-free ions at $^m/e$ 422, 358 and 356 were attributed to 9,9'-dithioxo-1,1'-bixanthenyl (253), the benzobisxanthene (254), and the naphthobisxanthene (255), respectively. Exact mass measurements confirmed the compositions of the $^m/e$ 358 and 356 ions.

Bimolecular processes must again be responsible for the formation of these anomalous ions; (254) may arise either from (253), by loss of sulphur, or directly from the original complex; (255) is probably formed from (254) by a normal mass spectrometric process.

When the complex (208a) was heated at 300°C in an evacuated (0.2mm) sublimation apparatus, a maroon sublimate was obtained. This was shown to be a mixture of xanthone and xanthenethione and the black involatile residue was thought to be palladium and/or palladium sulphide. The failure to obtain any products corresponding to the anomalous ions in the mass spectrum suggests that these ions are formed directly from the complex, by election-impact, rather than by ionisation of thermally generated molecular products.

(238a; X = H)

(233)

$-2\,S$

$-S$

(258)

(257)

$-2\,S$

$-S$

(259)

(256)

Scheme 23
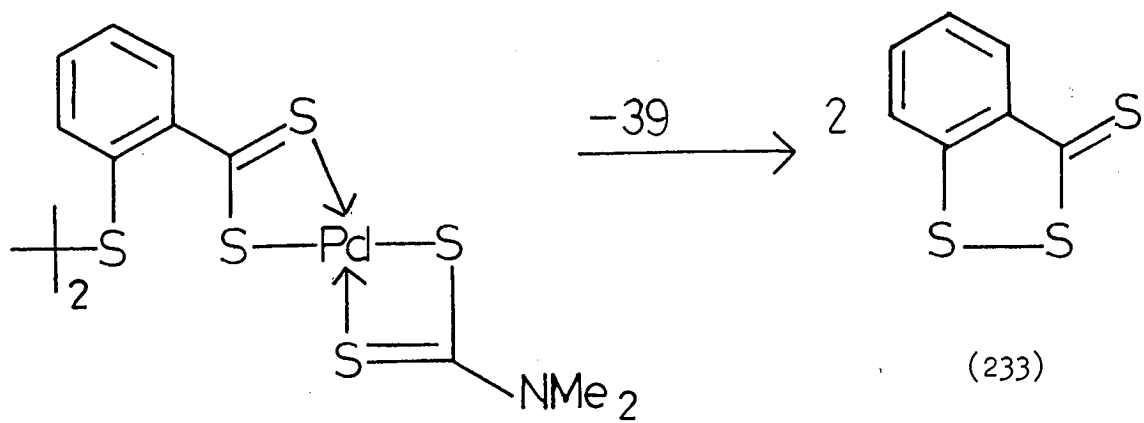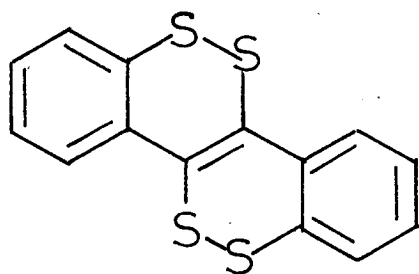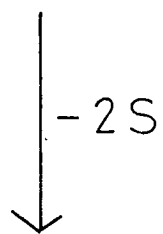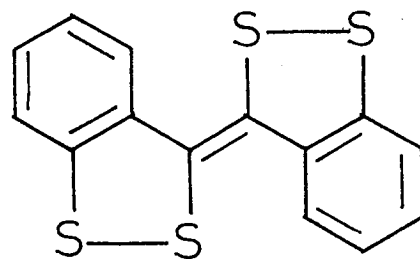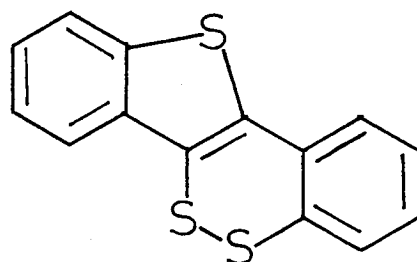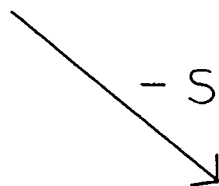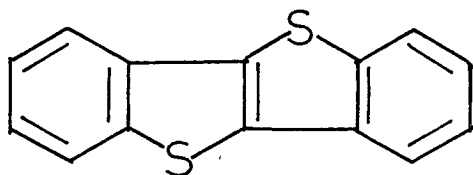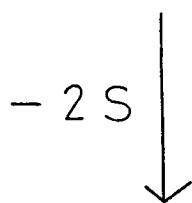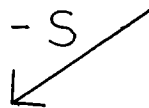
(c)   · Complexes derived from 1,2-dithiole-3-thiones.

example: [2,2'-Dithiobis(dithiobenzoato)]
bis[(N,N-dimethyldithiocarbamato)palladium
(II)], (238a;X=H).

The mass spectrum of complex (238a;X=H) showed strong palladium-
containing ions at ^{m}/e 346 and 226 [due to (251) and (248), respect-
ively] and palladium-free ions at ^{m}/e 240 and 184, assigned to the
molecular ions of [1]benzothieno[3,2-b]-[1]benzothiophene (256) and
4,5-benzo-1,2-dithiole-3-thione (233) respectively. It is thought
that the thienothiophene (256) may be formed from compound (233) via
the dibenzotetrathiafulvalene (257) as illustrated in Scheme 22 but
it is not known whether these processes occur thermally or after
electron impact.

Behringer and Meinetsberger[112] have shown that the related
tetrathiafulvalene (260) loses sulphur on being heated and rearranges
to the thienothiophene (261).

(260)   (261)
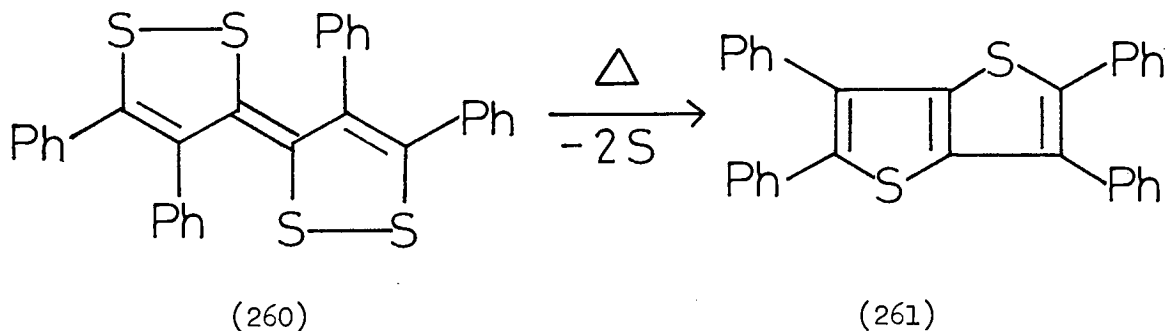
A possible mechanism for this type of reaction is shown in
Scheme 22 and involves rearrangement of (257), by disulphide bond
cleavage and reformation, to the tetrathiachrysene (258). Stepwise
extrusion of sulphur would then give (259) and finally (256). The
presence of a weak peak at ^{m}/e 272, possibly corresponding to (259),
lends some support to these suggestions.

EXPERIMENTAL

General Notes

1.   Melting Points were determined using a Koflar hot-stage
      apparatus and are uncorrected.

2.   Elemental analyses were carried out on a Perkin-Elmer
      Elemental Analyser 240 by Mr. J. Grunbaum, of the
      University of Edinburgh.

3.   Infra-red spectra were recorded on a Perkin-Elmer 157G
      spectrophotometer.

4.   Nuclear Magnetic Resonance spectra were recorded on a
      Varian Associates E.M.360 (60MHz) and a Varian Associates
      H.A.100 (100 MHz) spectrometer. Chemical shifts are
      recorded in parts per million (δ) using tetramethyl
      silane as internal standard. The spectra were recorded
      in 10-15% weight/volume solutions in deuteriochloroform
      unless otherwise stated.
      ^{13}C n.m.r. spectra were recorded on a Varian CFT-20
      spectrometer and ^{31}P n.m.r. spectra were recorded on a
      JEOL JNM-FX 60Q spectrometer.

5.   Mass spectra and exact mass measurements were recorded
      on an A.E.I. MS902 double-focussing mass spectrometer.
      $^{m}/e$ values reported for ions containing palladium, refer
      to ^{106}Pd which is the main isotope of palladium.

6.   Alumina for chromatography was Spence Type "H", which was
      deactivated (6% or 10%) with 10% aqueous acetic acid.

7.   Solvents used were previously dried over anhydrous magnesium
      sulphate or molecular sieve type 4A, unless stated otherwise.

ABBREVIATIONS

b.p.   boiling point

m.p.   melting point

t.l.c. thin-layer chromatography

n.m.r. nuclear magnetic resonance

  s singlet   bs broad singlet

  d doublet   dd doublet of doublets

  t triplet   td doublet of triplets

  q quartet

  p pentet

  m multiplet   bm broad multiplet

M^+ mass of molecular ion

$^m/e$ mass to charge ratio

Section one.   The Synthesis of Acene Polysulphides

Synthesis of Anthra (1,9,8-bcde:5,10,4-b'c'd'e')bis(thiathiophthen)

("Hexathioanthracene")

1,4,5,8-Tetrachloranthraquinone (13.8g) was added to a stirred
solution of sodium sulphide nonahydrate (85.8g) in water (200 cm^3)
and dimethyl formamide (400 cm^3) and the solution was maintained
under reflux for 8 hours. During the refluxing a green product with
a metallic lustre was precipitated. The product was extracted in a
Soxhlet apparatus with dimethyl formamide for 24 hours followed by
1,2,4-trichlorobenzene for 72 hours and then washed with acetone and
ether.

Yield 5.6g (38%) m.p.>360°C[lit.[18]m.p.>325°C]

Analysis: Found: C,46.1; H,1.1%

$C_{14}H_4S_6$ requires: C,46.1; H,1.1%

Infra-red spectrum: $\sqrt{}$ $_{max}$ 1420, 1305, 1180, 1050, 1030, 820, 730 cm^{-1}

Mass spectrum: ^{m}/e 364(M$^+$), 348, 333, 320, 302, 220, 207, 206, 182.

Conversion of Hexathioanthracene into 1,4,5,8-Tetra(methylthio)anthracene

Hexathioanthracene (1.0g), sodium dithionite (24.0g) and 2N sodium
hydroxide (500 cm^3) were maintained under reflux until the solution
became reddish-orange (approx.30 mins.), then dimethyl sulphate (20 cm^3)
was added. The mixture was maintained under reflux for 7 hours during
which a yellow solid was precipitated. The solid was filtered off,
washed with water, dried and recrystallised from ethyl benzoate, and
then from nitrobenzene, to give yellow plates (0.7g;70%), m.p.282-283°C.

Analysis: Found: C,59.6; H,5.0%

   $C_{18}H_{18}S_4$ requires: C,59.7; H,5.0%

Infra-red spectrum: ν_{max} 1590, 1285, 1260, 1215, 990, 955, 940, 800, 790 cm^{-1}

^{1}H n.m.r. spectrum: δ 9.3(s,1H), 7.5(s,2H), 2.6(s,6H)

Mass spectrum: ^{m}/e 362(M^+), 347(M^+-Me), 332(M^+-Me$_2$), 302(M^+-Me$_4$), 283, 181, 174, 166

Conversion of Hexathioanthracene into 5,10-Di(methylthio)anthraceno [1,9-cd: 5,10-c'd']bis(1,2-dithiole)

Hexathioanthracene (1.1g) and methyl fluorosulphonate (15 cm^3) were maintained under reflux for 6 hours. On cooling a green product (1.4g) crystallised and this was filtered off and dried. [This product was assumed to be the bisdithiolium bisfluorosulphonate (134), yield 97%].

The fluorosulphonate (1.3g) was added to a stirred solution of sodium dithionite (0.5g) in water (50 cm^3) and stirred at ambient temperature for 2 hours. The suspended solid was then filtered off, washed with water and dried. The solid was extracted with 1,1,2-tri-chloroethane and the solution chromatographed on 6% deactivated alumina eluting with carbon disulphide. Concentration of the solvent gave a deep purple solid that was sublimed at 250°C and 0.5 mm to yield 5,10-di(methylthio)anthraceno[1,9-cd:10-c'd']bis(1,2-dithiole) (0.3g;34%), m.p.297-298°C.

Analysis: Found: C,48.8; H,2.9%

              $C_{16}H_6S_6$ requires: C,48.7; H,2.5%

Infra-red spectrum: γ_{max} 1560, 1490, 1300, 1285, 1200, 995, 805 cm^{-1}

^{1}H n.m.r. spectrum: δ 7.4(d), 6.9(d), 2.4(s)

Owing to the low solubility of the product the ^{1}H n.m.r. spectrum was obtained by the pulsed Fourier Transform method using a Varian XL100 spectrometer.

Mass spectrum: ^{m}/e 394(M$^+$), 379(M$^+$-Me), 364(M$^+$-Me$_2$), 320, 197, 189, 166.

The residue (0.3g), after extraction with 1,1,2-trichloroethane, was a brown-green colour; infra-red and mass spectroscopy indicated that the residue was hexathioanthracene.

Oxidation of Hexathioanthracene

(a) With bromine.

Hexathioanthracene (0.3g) was dissolved in concentrated sulphuric acid (10 cm^3) and bromine (0.3 cm^3) was added. The resultant solution was stirred for 1 hour at ambient temperature and then ethyl acetate was added. The dark brown precipitate was collected, washed with ethyl acetate and dried (0.28g), m.p.>300°C.

Analysis: Found: C,23.4; H,0.9%

(b) With hydrogen peroxide.

The above reaction was repeated with 30% hydrogen peroxide (5 cm^3) as oxidant instead of bromine (0.22g), m.p.>300°C.

Analysis: Found: C,13.8; H,3.7%

Reaction of Cyclohexane-1,4-dione with Carbon Disulphide

Dimethylacetamide (7.5 cm^3) was added dropwise over 15 minutes to a stirred and cooled (external ice-bath), mixture of cyclohexane-1,4-dione(2.1g), 60% sodium hydride-oil dispersion (3.0g), carbon disulphide (3.6 cm^3) iodomethane (7.5 cm^3) and toluene (75 cm^3). When the addition was complete, the mixture was stirred for 20 minutes at 0°C and 30 minutes at ambient temperature, and then the mixture was poured onto ice-dilute hydrochloric acid (300 cm^3). Filtration and drying gave a light brown solid which was purified by Soxhlet extraction with chloroform followed by acetonitrile, leaving a dark green residue of 4,8-dihydro-4,8-dioxo-1,3,5,7-tetra(methylthio)benzo[1,2-c:4,5-c'] dithiophene (2.0g;26%), m.p.>300°C.

For analytical purposes, a small sample was recrystallised from pyridine.

Analysis: Found: C,41.6; H,2.9%

        $C_{14}H_{12}O_2S_6$ requires: C,41.6; H,3.0%

Infra-red spectrum: ν_{max} 1630, 1140, 1020, 915, 760 cm^{-1}

Mass spectrum: ^{m}/e 404(M$^+$), 389(M$^+$-Me), 371(M$^+$-SH), 356,

                338, 323, 305, 202

Exact mass measurement:

            ^{m}/e 403.9167 ($C_{14}H_{12}O_2S_6$ requires 403.9162)

Reaction of the Dithiophene (136) with thionating agents

(a) The dithiophene (0.28g) phosphorus pentasulphide (0.30g) and pyridine (20 cm^3) were maintained under reflux for 3 hours. On cooling a green solid was formed and this was filtered off, washed with water, acetone and dried (0.22g), m.p.>300°C.

Infra-red and mass spectroscopy indicated that the solid was starting material, and there was no evidence of the desired product.

(b) The dithiophene (0.20g), phosphorus pentasulphide (1.0g) and xylene (25 cm^3) were maintained under reflux for 6 hours, and then filtered hot. Analysis of the residue indicated that the solid was starting material and there was no evidence of the thiathiophthen derivative (137).

(c) The dithiophene (0.20g), phosphorus pentasulphide (0.33g) and sulpholane (20 cm^3) were stirred at ambient temperature while sodium hydrogen carbonate (0.25g) was added during 5 minutes. The resulting solution was then stirred at ambient temperature for 10 minutes and at 150°C. for 2 hours. Cooling and acidification with dilute hydrochloric acid gave a green solid (0.17g), m.p. >300°C.

Infra-red and mass spectroscopy indicated that the solid was starting material.

(d) The dithiophene (0.30g) was dissolved in O,O-diethyldithio-phosphate (10 cm^3) and then benzene (40 cm^3) was added and the resulting solution was maintained under reflux for 24 hours. Con-centration of the solution gave a dark green residue (0.30g), m.p. >300°C, identified as starting material.

(e) The dithiophene (0.43g) was added to a stirred solution of sodium sulphide nonahydrate (1.72g) in water (10 cm^3) and dimethyl formamide (20 cm^3). The reddish-brown solution was then stirred under reflux for 8 hours. Acidification of the cold solution produced a dark green solid (0.3g), m.p. >300°C, the mass spectrum of which showed weak peaks at ^{m}/e 404 (starting material) and 376 (desired

product), but the major peak was at $^m/e$ 390 with fragments at $^m/e$ 375, 358 and 344, corresponding to the compound (142).

This product (0.30g) was added to a solution of sodium sulphide nonahydrate (1.72g) in water (10 cm^3) and dimethyl formamide (20 cm^3) and stirred under reflux for 8 hours. Acidification produced a black precipitate which was filtered off, washed and dried (0.25g), m.p.>300°C.

A Nujol mull showed no absorptions in the infra-red and the product was insufficiently volatile to obtain a mass spectrum.

Attempts to repeat the formation of compound (142) under the conditions of experiment (e), or with replacement of sodium sulphide nonahydrate by anhydrous sodium hydrogen sulphide and sulphur, gave similar black decomposition products.

Synthesis of 1,4-Dibromodurene

This was synthesised by the method of Smith[91] in 92% yield, m.p.197-199°C.[lit.m.p.198-199°C.].

Synthesis of 1,4-Dibromo-2,3,5,6-tetra(bromomethyl)benzene

The title compound was synthesised by the method of Hopff[92] in 50% yield, m.p.261-262°C.[lit.m.p.262°C.].

Reactions of Hexabromodurene

(a)   With Sulphur and sodium n-propoxide.

Sodium (0.37g) was dissolved in n-propanol (50 cm^3) and then sulphur (0.64g) and hexabromodurene (1.22g) were added. The resulting deep green solution was then maintained under reflux for 24 hours and hot filtered to remove sodium bromide. Concentration of the filtrate

gave a deep purple solid which, on treatment with dilute hydrochloric acid (25 cm^3), yielded a dark coloured solid. The solid was collected, washed with water and dried (0.52g), m.p. >300°C.

Infra-red and mass spectroscopy gave no evidence for the desired product and the solid resembled the products from reaction of the dithiophene (136) with sodium sulphide.

(b) With Sulphur in dimethyl formamide.

Hexabromodurene (0.61g) and sulphur (0.32g) were dissolved in dimethyl formamide (35 cm^3) and the turquoise coloured solution was maintained under reflux for 15 hours. Concentration, under vacuum, gave a deep purple solid (0.33g), m.p. >300°C.

The product was similar to that isolated from reaction (a) since no infra-red or mass spectrum could be obtained.

Tetraethyl ethylenetetracarboxylate

The title compound was synthesised in 92% yield from diethyl malonate by the method described in Organic Syntheses[112], b.p. 154-160°C, at 0.35 mm[lit. b.p. 220°C. at 15 mm].

Infra-red spectrum: ν max 2995, 1730, 1455, 1370, 1035, 860, 775, 720 cm^{-1}

^{1}H n.m.r. spectrum: δ 4.4(q,2H), 1.35(t,3H)

1,4,5,8-Tetrahydroxypyridazino[4,5-d]pyridazine

This was synthesised by the method of Adembri[95] in 50% yield, m.p. >350°C.(decomp.),[lit.m.p. >340°C.].

<u>Infra-red spectrum</u>: ν_{max} 3140, 1640, 1560, 1450, 1345, 1290, 1210, 950, 760, 685 cm^{-1}.

1,4,5,8-Tetrachloropyridazino[4,5-d]pyridazine

This was synthesised by a procedure similar to that of Adembri[95].

1,4,5,8-Tetrahydroxypyridazinopyridazine (3.7g), phosphorus pentachloride (34g) and redistilled phosphoryl chloride (250 cm^3) were maintained under reflux for 24 hours. On cooling pale yellow crystals were precipitated. Concentration of the filtrate to approximately one-third volume produced a further crop of crystals, that were collected and dried.

Total yield 1.7g (33%) m.p.>330°C.[lit.m.p.>300°C.].

<u>Infra-red spectrum</u>: ν_{max} 1400, 1340, 1285, 845, 640 cm^{-1}.

<u>Mass spectrum</u>:   274, 272, 270, 268 (M$^+$,4 chlorine pattern), 250, 181, 179, 177, 146, 144, 142, 120, 118, 111, 109.

Reaction of 1,4,5,8-Tetrahydroxypyridazino[4,5-d]pyridazine with phosphorus pentasulphide

A solution of 1,4,5,8-Tetrahydroxypyridazino[4,5-d]pyridazine (0.44g) and phosphorus pentasulphide (1.50g) in pyridine (25 cm^3) was maintained under reflux for 3 hours and then poured into boiling water (100 cm^3). The dark coloured precipitate was filtered, washed with water and dried. It was then washed with warm dimethylformamide and with acetone and dried again to give a brown-red solid 0.26g (40%), m.p.>300°C.

Infra-red spectrum: ν_{max} 1520, 1490, 1255, 1075, 800 cm^{-1}

Mass spectrum: 288(M$^+$), 256(M$^+$-S), 242, 226, 196, 156, 112, 100

Exact mass measurements,

287.8700 ($C_6N_4S_5$ requires 287.8726)

255.9001 ($C_6N_4S_4$ requires 255.9006)

225.9446 ($C_6N_4H_2S_3$ requires 225.9442)

155.9170 (C_5S_3 requires 155.9162)

Reaction of 1,4,5,8-tetrachloropyridazino[4,5-d]pyridazine with sodium hydrogen sulphide

A solution of sodium hydrogen sulphide (0.45g) in ethanol (25 cm^3) was added dropwise to a stirred suspension of 1,4,5,8-tetrachloro-pyridazinopyridazine (0.54g) in ethanol (30 cm^3) and the resulting brown solution was stirred under reflux for 3 hours. After refluxing the solution was evaporated to dryness and the residue was washed with water (20 cm^3) and dried to yield a brown solid 0.4g (69%), m.p. >340°C.

Analysis: Found: C,28.1; H,1.2; N,19.4%

$C_6N_4S_5$ requires: C,25.0; H,0.0; N,19.4%

Infra-red spectrum: ν_{max} 1525, 1260, 1150, 1080, 800, 720 cm^{-1}

Mass spectrum: 288(M$^+$), 256(M$^+$-S), 226, 192, 156, 112, 100

Attempts to identify the product (^{m}/e 288)

(a) Reduction with alkaline sodium dithionite.

The unknown solid (0.1g) was added to a stirred solution of sodium dithionite (0.13g) and sodium hydroxide (0.06g) in water (10 cm^3).

The resulting maroon solution was stirred at ambient temperature for 30 minutes and then filtered. Acidification of the filtrate with dilute hydrochloric acid gave starting material (0.09g).

A second experiment carried out under apparently identical conditions gave a dark brown solid (28%), m.p.>300°C. ^{m}/e 226(M^+).

(b) Desulphurisation with triphenylphosphine.

A solution of the unknown sulphur compound (0.09g) and triphenyl-phosphine (0.08g) in dimethylformamide (25 cm^3) was maintained under reflux for 2 hours in an atmosphere of nitrogen. Concentration under reduced pressure gave a brown solid that was extracted with chloroform (to remove triphenylphosphine sulphide) to yield a dark brown solid, 0.06g, m.p.>300°C.

An infra-red spectrum contained no absorptions and the sample was too involatile to obtain a mass spectral trace.

(c) Vacuum sublimation of ^{m}/e 288.

The unknown compound (0.1g) was heated at 300°C and 0.1 mm pressure in a sublimation apparatus. A small amount of sublimate was obtained (m.p.>300°C.) and a black involatile residue (m.p.>300°C.).

Analysis: Sublimate C, 18.3; H, 1.5; N, 13.0%

               Residue: C, 36.3; H, 0.8; N, 22.5%

$C_6N_4S_4$ requires: C, 28.1; H, 0.0; N, 21.9%

Since the elemental analyses indicated that decomposition had taken place, the experiment was discontinued.

Section two.   The Synthesis of 4-thioacyl-1,2-dithiole-3-

thiones and Related Compounds

(i)   The Reaction of Malonic Acid Derivatives with Carbon

Disulphide and Sulphur

5-Amino-4-carboxamido-1,2-dithiole-3-thione

This was synthesised by the method of Gewald[97] in 31% yield,

m.p. 235° decomp.[lit.m.p.260-264°C].

Mass spectrum: $^m/e$ 192(M^+), 175, 164, 160, 132, 127, 110.

Reactions of 5-amino-4-carboxamido-1,2-dithiole-3-thione with

phosphorus pentasulphide

(a)   In xylene

The title compound (0.5g), phosphorus pentasulphide (0.5g) and

xylene (10 cm^3) was stirred under reflux for 2 hours and the solution

was filtered hot.   The filtrate contained no material and analysis of

the residue showed only the presence of starting material.

(b)   In 1,2-dichloroethane

This method was based on a procedure described by Steven[98].

A mixture of the title compound (0.77g), phosphorus pentasulphide

(1.86g) and 1,2-dichloroethane (50 cm^3) was stirred at ambient temp-

erature while bromine (0.24 cm^3) was added.   The resulting mixture

was stirred at ambient temperature for 5 minutes and under reflux

for 4 hours.   Hot filtration and analysis of the residue indicated

that the residue was starting material, (0.7g), m.p. 237°C.(decomp.).

(c) In pyridine

The title compound (0.43g), phosphorus pentasulphide (0.66g) and pyridine (20 cm^3) were maintained under reflux for 4 hours. Acidification, with dilute hydrochloric acid, produced a maroon oil that was extracted into chloroform. The extract was dried over magnesium sulphate, filtered and concentrated under reduced pressure to give a maroon gum which on trituration with glacial acetic acid gave a small amount of red-brown solid, (0.1g), m.p.>300°C. Attempts to recrystallise the product were unsuccessful, resulting in the formation of maroon oils.

Crude analysis: Found: C,20.7; H,1.6; N,10.4%

$C_4H_4N_2S_5$)
) required: C,20.0; H,1.7; N,11.6%
$C_4H_4N_2O_2S_4$)

Infra-red spectrum: ν max 1600, 1140, 970, 720 cm^{-1}

Mass spectrum: $^m/e$ 240(M$^+$), 216, 184, 176, 174, 154, 112, 100

Cyanothioacetamide

Malononitrile (1.32g) was dissolved in absolute ethanol (30 cm^3) and triethylamine (1 cm^3). The solution was saturated with hydrogen sulphide (approx. 40 minutes) and concentrated to dryness to give a grey-white solid (1.5g;75%), m.p.119-120°C.[lit.[99] m.p.121°C.], from ethanol.

Reaction of cyanothioacetamide with carbon disulphide and sulphur

Cyanothioacetamide (0.5g) and carbon disulphide (0.38g) were added to a stirred solution of sodium (0.23g) in methanol (10 cm^3). Sulphur (0.2g) was added to the solution and the resulting mixture was stirred under reflux for 1 hour. The hot solution was poured into 50% acetic

acid (10 cm^3) and kept overnight. The orange needles that precipitated were filtered off and recrystallised from aqueous dimethyl formamide to give 5-amino-4-cyano-1,2-dithiole-3-thione (0.4g;46%), m.p. 230°C. (decomp.)[lit.[97] m.p. 230°C.(decomp.)].

<u>Infra-red spectrum:</u> $\vee_{max}$ 3250, 3170, 2210, 1610, 1305, 1005 cm^1

<u>Mass spectrum:</u> ^{m}/e 174(M$^+$), 151, 129, 109, 83

Reaction of 5-amino-4-cyano-1,2-dithiole-3-thione with hydrogen sulphide

The title compound (0.17g) was dissolved in a mixture of ethanol, picoline and 2-dimethylaminoethanol (5:2:1;10 cm^3) and hydrogen sulphide was passed through the resulting solution for 5 hours. Concentration of the solution produced a maroon gum which, on trituration with ether, gave an orange-brown solid. Recrystallisation from aqueous dimethyl-formamide yielded a yellow solid (0.3g), m.p. 148-150°C. (Found: C,29.9; H,4.1; N,1.9%), ^{m}/e 196, 168, 137 and 97.

Reaction of 5-amino-4-cyano-1,2-dithiole-3-thione with O,O-diethyl dithiophosphate

(a) The title compound (0.35g) was dissolved in 1,2-dimethoxyethane (50 cm^3) and O,O-diethyl dithiophosphate (0.5 cm^3) and water (0.5 cm^3) were added. The solution was maintained under reflux for 18 hours, in an atmosphere of nitrogen. Concentration to dryness, under reduced pressure, and recrystallisation of the residue gave starting material (0.32g), m.p. 228-230°C.(decomp.).

(b) The cyanodithiolethione (0.3g), water (1 cm^3) and 0,0-diethyl dithiophosphate (10 cm^3) were stirred on a steam-bath, under an atmosphere of nitrogen, for 9 hours. Concentration under reduced pressure produced a deep red, foul smelling oil from which no characterisable product could be obtained.

Dithiomalonamide

Malononitrile (1.0g) was dissolved in a mixture of ethanol, α-picoline and 2-dimethylaminoethanol (5:2:1;7 cm^3). The solution was cooled to 0°C. and stirred while hydrogen sulphide was passed through. The pale yellow crystals that precipitated were collected and dried. The filtrate was cooled and saturated with hydrogen sulphide to give a second crop of crystals. The two crops were combined and recrystallised from acetic acid to give the thioamide (1.3g;64%), m.p. 210-212°C. (decomp.)[lit[99] m.p. 212°C.].

(ii) The Reaction of 2-Methylthio-1,3-dithiolanylium methosulphate with Derivatives of Malonic Acid

(a) With dithiomalonamide.

Ethylene trithiocarbonate (0.27g) and dimethyl sulphate (0.2 cm^3) was stirred on a steam-bath for 30 minutes and the resulting oil was dissolved in glacial acetic acid (2 cm^3). Dithiomalonamide (0.27g) and pyridine (0.3 cm^3) were added and the solution was stirred under reflux for 1 hour. When the hot solution was poured into water dithiomalonamide (0.2g) was recovered as a pale yellow solid.

(b) With malonamide.

Dimethyl sulphate (0.25 cm^3) and ethylene trithiocarbonate (0.27g) were stirred on a steam-bath for 30 minutes and the resulting oily

dithiolanylium salt was dissolved in acetic acid (2.5 cm^3). Malon-amide (0.25g) and pyridine (0.35 cm^3) were then added to the solution and the mixture stirred under reflux for 1 hour. The hot solution was added to water (20 cm^3) and the resulting yellow precipitate was collected and recrystallised from acetic acid to yield 1,3-dithiolan-2-ylidene malonamide (0.1g;25%), yellow microcrystals, m.p. 252-254°C. (decomp.).

<u>Analysis</u>:   Found: C,35.4; H,4.1; N,13.4%

   C$_6$H$_8$N$_2$O$_2$S$_2$ requires: C,35.3; H,3.9; N,13.7%

<u>Infra-red spectrum</u>: $\nu$$_{max}$ 3400, 1685, 1640, 1600, 1285, 1095

                         855, 790, 740, 680, 655, 635 cm^{-1}

<u>Mass spectrum</u>: ^{m}/e   204(M$^+$), 176, 159, 145, 128

(c) With malononitrile.

   The reaction was carried out by the procedure described by Gompper[33] and from 0.35g malononitrile, 0.6g (67%) of 1,3-dithiolan-2-ylidenemalononitrile was isolated, m.p. 199°C.[lit. m.p. 199-200°C.].

<u>Reactions of 1,3-dithiolan-2-ylidenemalonamide with phosphorus pentasulphide</u>

(a) In xylene.

   The malonamide derivative (0.2g), phosphorus pentasulphide (0.8g) and xylene (25 cm^3) were stirred under reflux for 3 hours and the solution was filtered hot. The residue was washed with boiling xylene (10 cm^3) and the combined filtrate and washings were concen-trated to dryness. Recrystallisation of the residue led to recovery of 1,3-dithiolan-2-ylidene malonamide (0.16g), m.p. 252-254°C.(decomp.).

(b) In pyridine.

The diamide (0.2g), phosphorus pentasulphide (0.8g) and pyridine (25 cm^3) were stirred under reflux for 3 hours and then poured into water (75 cm^3). A yellow precipitate was filtered off, recrystallised from acetic acid and identified as starting material (0.15g) m.p. 251-254°C.(decomp.).

Reactions of 1,3-dithiolan-2-ylidenemalononitrile with hydrothionating agents

(a) With hydrogen sulphide.

1,3-Dithiolan-2-ylidenemalononitrile (0.2g) was dissolved in a mixture of ethanol, α-picoline and 2-dimethylaminoethanol (5:2:1; 10 cm^3) and the solution was saturated with hydrogen sulphide. After 3 hours the solution was concentrated to dryness and the residue was recrystallised from ethanol to give starting material (0.16g) m.p. 198-200°C.

(b) With O,O-diethyl dithiophosphate.

1,3-Dithiolan-2-ylidenemalononitrile (0.18g), diethyl dithio-phosphate (0.3g) and benzene (20 cm^3) were maintained under reflux for 10 hours. Concentration under reduced pressure gave a red oil which, on trituration with acetic acid, produced an orange solid that was filtered off and dried. Recrystallisation from ethanol yielded S-[2-cyano-2-(1,3-dithiolan-2-ylidene)acetimidoyl]O,O-diethyl dithiophosphate (0.2g;55%), orange microcrystals, m.p. 109-110°C.

Analysis: Found: C,33.8; H,4.2; N,7.7%

$C_{10}H_{15}N_2O_2PS_4$ requires: C,33.9; H,4.2; N,7.9%

Infra-red spectrum: ν_{max} 3340, 2200, 1285, 1240, 1010, 910,

785, 660 cm^{-1}

^{1}H n.m.r. spectrum: δ 8.0(bs,1H), 4.3(q,4H), 3.6(s,4H), 1.4(t,6H)

Mass spectrum: $^m/e$ 354(M$^+$), 326, 298, 270, 214, 186, 168,

153, 142, 125, 109

(c) A solution containing 1,3-dithiolan-2-ylidenemalononitrile (0.2g),

0,0-diethyl dithiophosphate (0.5g) and water (0.5 cm^3) in benzene

(20 cm^3) was maintained under reflux, in an atmosphere of nitrogen,

for 24 hours. Evaporation of the solution and trituration of the

residue with glacial acetic acid gave a yellow solid that was filtered

off and recrystallised from ethanol to yield 1,3-dithiolan-2-ylidene-

cyanothioacetamide (0.2g;83%), m.p. 190-191°C.(decomp.). This compound

could not be isolated in a pure form despite repeated recrystallisation.

Analysis: Found: C,34.4; H,3.1; N,12.9%

$C_6H_6N_2S_3$ requires: C,35.6; H,3.0; N,13.9%

Infra-red spectrum: ν_{max} 2200, 1610, 1335, 820 cm^{-1}

Mass spectrum: $^m/e$ 202(M$^+$), 174, 149, 126, 109, 60

1,3-Dithiolan-2-ylidenecyanothioacetamide was also isolated by

hydrolysis of the dithiophosphate obtained by procedure (b).

The dithiophosphate (0.1g) was stirred in boiling water (5 cm^3)

for 15 minutes, during which the colour gradually changed from orange

to yellow. Filtration and recrystallisation of the residue from

ethanol gave 1,3-dithiolan-2-ylidenecyanothioacetamide (50 mgs;88%),

m.p. 188-190°C.(decomp.).

This compound was recovered in 90% yield after further treatment

(100 hr.) with diethyl dithiophosphate and water in boiling benzene.

Reaction of hexachloro-p-xylene and sulphur

(a) In sulpholane.

Hexachloro-p-xylene (0.31g) and sulphur (0.52g) were dissolved in sulpholane (20 cm^3) and the solution was stirred at 150°C. After 1 hour pyridine (1 cm^3) was added and heating and stirring were continued for a further 3 hours. On cooling the solution deposited sulphur (0.5g;96% recovery), m.p. 110-115°C. The filtrate was poured into water (100 cm^3) and a black solid was filtered off and dried (0.25g), m.p. >300°C.

No infra-red or mass spectrum could be obtained.

(b) In N-methylpyrrolidine-2-one.

The hexachloro-compound (0.31g) and sulphur (0.52g) were dissolved in N-methylpyrrolidine-2-one (25 cm^3) and the solution was maintained under reflux for 18 hours. The solution was concentrated to dryness under reduced pressure to give a black solid from which sulphur (0.41g) was obtained by extraction with carbon disulphide. The black residue (0.2g), m.p. >300°C was too insoluble and involatile to be characterised.

(c) In methanol containing sodium methoxide.

Sulphur (0.26g) and the hexachloro-compound (0.31g) were added to a solution of sodium methoxide (from 0.1g sodium) in methanol (30 cm^3). The resulting mixture was maintained under reflux for 18 hours and then filtered hot (to remove sodium chloride). The filtrate was concentrated to dryness and treated with dilute hydrochloric acid (25 cm^3) to yield a red oil. Extraction with chloroform and evaporation of the dried extract gave a bright red solid (0.3g), m.p. 150-155°C, ^{m}/e 350 (weak), 304, 301, 267.

N.B. Only those peaks containing ^{35}Cl are listed.

(d) In propan-1-ol containing sodium 1-propoxide.

Hexachloro-p-xylene (0.31g) and sulphur (0.26g) were added to

a solution of sodium 1-propoxide (from 0.1g sodium) in propon-1-ol

(20 cm^3) and the mixture was maintained under reflux for 18 hours.

The solution was filtered hot (to remove sodium chloride), and

concentrated, under reduced pressure, to give a dark brown-red solid.

The brown-red solid was washed with dilute hydrochloric acid and with

water and dried. Extraction with carbon disulphide (to remove unreacted

sulphur) followed by chloroform yielded slightly impure 1,2,3,4,5,6,7,

8-octathiadicyclopenta[cd,ij]-s-indacene (0.1g;28%) as a brown-red

solid, m.p. >300°C. (Found: C,25.3; H,1.0%,M$^+$ 351.77638; C_8S_8

requires: C,27.2; H,0.0%, M$^+$ 351.77658).

Infra-red spectrum: ν_{max} 1260, 1145, 880, 720 cm^{-1}

Reaction of $\alpha,\alpha,\alpha^1,\alpha^1$-2,3,5,6-octachloro-p-xylene with sulphur

Octachloro-p-xylene (0.35g) and sulphur (0.26g) were added to

a solution of sodium 1-propoxide (from 0.1g sodium) in propan-1-ol

(25 cm^3). The purple solution was maintained under reflux for 24 hours

and then filtered hot. Concentration of the filtrate gave sulphur

(0.2g) m.p. 115-118°C. The residue was washed with water and then

extracted in a Soxhlet apparatus with chloroform yielding a brown-red

residue (0.3g), m.p. 278-281°C.(decomp.). (Found: C,25.0; H,1.5%)

^{m}/e 418.

Section three.   The Synthesis and Reactions of Complexes

containing Cyclopalladated Nitrogen and

Sulphur Donor Ligands

Synthesis of 1-phenylpyrazole

Phenylhydrazine hydrochloride (4.34g) and 1,1,3,3,-tetraethoxy-propane (6.60g) were stirred on a steam-bath for 2 hours. To the cold mixture ether (20 cm^3) and water (20 cm^3) were added and the whole mixture was neutralised with sodium carbonate. The ether extract was removed and the aqueous phase re-extracted with ether. The combined extracts were dried over magnesium sulphate and filtered and the filtrate was concentrated under reduced pressure to yield a red oil that was redistilled, b.p. 85°C. at 0.05 mm (yield 3.6g;83%).

Infra-red spectrum: ν max 3100, 2900, 1715, 1590, 1510, 1490, 1385, 1335,
1115, 1040, 1030, 960, 750, 690, 655 cm^{-1}

^{1}H n.m.r. spectrum: δ 7.3(m,3H), 6.85(m,4H), 5.9(d,1H)

Mass spectrum: ^{m}/e 144(M^+), 117, 104, 91, 78

Synthesis of 4,4'-dimethoxythiobenzophenone

4,4'-Dimethoxybenzophenone (0.24g), phosphorus pentasulphide (0.44g) and xylene (25 cm^3) were stirred under reflux for one hour. The blue solution was filtered hot, the filtrate concentrated to dryness and the residue recrystallised from ethanol to give the thione (0.3g;97%) m.p. 119-120°C.[lit.[115] m.p. 116-118°C.].

Synthesis of xanthenethione

Xanthenethione was obtained in 70% yield by the method described for 4,4'-dimethoxythiobenzophenone m.p. 155-156°C.[lit.[116] m.p. 156°C.].

Synthesis of thioxanthenethione

Thioxanthenethione was synthesised from thioxanthenone and phosphorus pentasulphide in 65% yield, m.p. 173-175°C.[lit.[117] m.p. 172-175°C.].

Synthesis of quinolizine-4-thione

The thione was synthesised by the method of Van Allen and Reynolds[118].

Synthesis of N-methylisoquinolin-1-one

The method of Elpern and Hamilton was used and the compound was obtained in 67% yield, m.p. 54-55°C.[lit.[110] m.p. 53-54°C.].

Synthesis of N-methylisoquinoline-1-thione

N-Methylisoquinolin-1-one (1.5g) and freshly distilled phosphoryl chloride (10 cm^3) were heated on a steam-bath for 20 minutes, and the resultant solution was concentrated to dryness under vacuum to yield a maroon oil. The oil was added to a solution of sodium hydrogensulphide (1.25g) in absolute ethanol (50 cm^3) and maintained under reflux for 6 hours. The mixture was filtered hot and the filtrate cooled. The yellow crystals that formed were collected and recrystallised from ethanol to yield the thione, (1.0g;61%), m.p. 111-112°C. [lit.[120] m.p. 112°C.].

Synthesis of N-methylquinolin-4-one

The compound was synthesised from diethyl anilinomethylene-malonate by the procedure of Markees and Schwab[127], m.p. 151-152°C. [lit. m.p. 149-152°C.].

Synthesis of N-methylquinoline-4-thione

The compound was synthesised in 70% yield by the method described for N-methylisoquinolinethione, m.p. 207-209°C.[lit.[122] m.p. 208-209°C.].

Synthesis of N,N-dimethylthiobenzamide

The compound was obtained in 80% yield from benzyl chloride using the method of Brown and Thompson[123], m.p. 66-67°C.[lit. m.p. 67°C.].

Synthesis of p-methyl-N,N-dimethylthiobenzamide

A mixture of N,N-dimethyl-p-toluamide (2.59g) and phosphorus pentasulphide (3.33g) in benzene (70 cm^3) was stirred under reflux for 2 hours. The solution was filtered hot and the filtrate concentrated to dryness. The residue was recrystallised from ether to yield the thioamide (2.2g;75%), m.p. 49-50°C.[lit.[124] m.p. 49-50°C.].

Synthesis of 4,5-benzo-1,2-dithiole-3-thione

The method of Klingsberg and Schreiber[125] was used and the compound was isolated in 67% yield, m.p. 95-96°C.[lit. m.p. 94-96°C.].

Synthesis of 6-chloro-4,5-benzo-1,2-dithiole-3-thione

The compound was synthesised in 60% yield by the above procedure from 4,4'-dichloro-2,2'-dithiobenzoic acid m.p. 174-176°C.[lit.[126] m.p. 174-176°C.].

Synthesis of tetraethylammonium N,N-dimethyldithiocarbamate

Tetraethylammonium chloride (5.51g) and sodium N,N-dimethyl-dithiocarbamate (4.29g) were stirred in ethanol (30 cm^3) at ambient temperature for 10 minutes. The mixture was filtered to remove sodium chloride and the filtrate was concentrated under reduced pressure to give a colourless product (5.5g;73%) that was dried over phosphorus pentoxide in vacuum.

Infra-red spectrum: ν max 1625, 1245, 1175, 1165, 1100, 1000, 970, 785 cm^{-1}

The Synthesis of Acetate- and Chloride-bridged Dimeric Cyclopalladated Complexes

Reaction of benzo[h]quinoline with palladium acetate

The reaction was carried out by a method adapted from that of Hay and Leaver[127].

Benzo[h]quinoline (1.39g), palladium acetate (1.73g) and glacial acetic acid (75 cm^3) were maintained under reflux for one hour. The brown solution was evaporated to dryness to give a brownish-yellow solid that was chromatographed on 10% deactivated alumina eluting with chloroform. A single yellow eluate was obtained, evaporation

of which gave a yellow residue. Recrystallisation from toluene gave di-μ-acetatobis(benzo[h]quinolin-10-yl)dipalladium(II), (2.0g;75%) as yellow crystals, m.p. 210°C.(decomp.)[lit.[127] m.p. 210°C.(decomp.)].

<u>Infra-red spectrum</u>: ν_{max} 1700, 1605, 1560, 1550, 835 cm^{-1}

^{1}H n.m.r. spectrum: δ 8.8(d,1H), 7.1(m,6H), 6.4(dd,1H), 2.3(s,3H)

Reaction of 1-phenylpyrazole with palladium acetate

A solution of 1-phenylpyrazole (0.72g) and palladium acetate (1.12g) in glacial acetic acid (50 cm^3) was maintained under reflux for 1 hour, and the resulting dark solution was concentrated to dryness to give a brown solid. Chromatography on 6% deactivated alumina, eluting with chloroform, yielded a fawn solid (1.20g;78%) identified as di-μ-acetatobis[2-(1-pyrazolyl)phenyl]dipalladium(II), m.p. 227-228°C. Attempts to recrystallise the complex failed or resulted in decomposition.

<u>Analysis</u>:   Found: C,42.0; H,3.3; N,8.2%

  $C_{22}H_{20}N_4O_4Pd_2$ requires: C,42.8; H,3.4; N,9.0%

<u>Infra-red spectrum</u>: ν_{max} 1700, 1580, 1560, 1550, 1450, 1400, 1330,
                      1100, 1080, 760 cm^{-1}.

^{1}H n.m.r. spectrum: δ 7.4(d,1H), 6.9-6.6(m,5H), 5.9(d,1H), 2.3(s,3H)

<u>Mass spectrum</u>: ^{m}/e 392(Pd), 308(M$^+$,Pd), 249(Pd), 219, 144

Di-μ-chlorobis[2-(phenylazoxy)phenyl]dipalladium(II)

The title complex was synthesised by the method of Balch and Petridis[44] in 73% yield, m.p. >300°C.[lit. m.p. >320°C.].

<u>Di-μ-chlorobis[5-methoxy-2-(4-methoxythiobenzoyl)phenyl]dipalladium(II)</u>

This complex was synthesised by the method of Alper[40] in 99% yield, m.p. 258-260°C.(decomp.)[lit. m.p. 261-263°C.].

<u>Reaction of xanthene-9-thione with sodium tetrachloropalladate</u>

To a solution of xanthenethione (0.21g) in methanol (50 cm^3) was added sodium tetrachloropalladate [made from palladium chloride (0.18g) and sodium chloride (0.12g) in methanol (20 cm^3)]. A reddish-brown precipitate formed immediately and the suspension was stirred at ambient temperature for 30 minutes and at reflux for 10 minutes. The complex was filtered off and washed with chloroform to give di-μ-chlorobis-(9-thioxoxanthen-1-yl)dipalladium(II), (0.27g;77%), m.p. >310°C.

<u>Analysis:</u>　　　　　　　　Found:　C,42.1;　H,2.0%

$C_{26}H_{14}Cl_2O_2S_2Pd_2$　requires:　C,44.2;　H,2.0%

<u>Infra-red spectrum:</u> ν max 1570, 1560, 1280, 1210, 1135, 1000, 900, 760, 720 cm^{-1}

<u>Mass spectrum:</u>　　　　^{m}/e 422(M$^+$), 358, 356, 212

<u>Reaction of thioxanthene-9-thione with sodium tetrachloropalladate</u>

The reaction was carried out as for the reaction of xanthenethione to yield di-μ-chlorobis(9-thioxothioxanthen-1-yl)dipalladium(II)(94%), as a purple solid m.p. >300°C.

<u>Analysis:</u>　　　　　　　　Found:　C,39.9;　H,1.8%

$C_{26}H_{14}Cl_2S_4Pd_2$　requires:　C,42.3;　H,1.9%

<u>Infra-red spectrum:</u> ν max 1600, 1550, 1520, 1250, 1235, 1100, 765, 755, 715 cm^{-1}

Mass spectrum: ^{m}/e 454(M^+), 420, 390, 228

Di-μ-chlorobis(4-thioxoquinolizin-6-yl)dipalladium(II)

This was synthesised by a method adapted from that of R.C. Davis[41].

A solution of sodium tetrachloropalladate [from sodium chloride
(0.23g) and palladium dichloride (0.35g) in methanol (25 cm^3)] was
added to quinolizine-4-thione (0.32g) in methanol (30 cm^3). A preci-
pitate was formed and the suspension was stirred at ambient temperature
for 20 minutes and at reflux for 20 minutes. The product was collected,
washed with chloroform and dried to give an orange-brown residue
(0.54g;90%), m.p. >310°C.[lit. m.p. >300°C.].

Analysis: Found: C,34.2; H,2.1; N,4.1%

   $C_{18}H_{12}Cl_2N_2S_2Pd_2$ requires: C,35.8; H,2.0; N,4.6%

Infra-red spectrum: $\sqrt{}$ $_{max}$ 1635, 1605, 1560, 1335, 1290, 1225,
                    1170, 815, 800, 745, 720 cm^{-1}

Mass spectrum: No trace was obtained as the sample was

                     too involatile.

Reaction of N-methylisoquinoline-1-thione with sodium tetrachloropalladate

The reaction was carried out under conditions identical with those
of the preceding reaction to give di-μ-chlorobis(1-thioxo-N-methyliso-
quinolin-8-yl)dipalladium(II)(89%), as an orange solid m.p. >300°C.

Analysis: Found: C,37.2; H,2.6; N,4.2%

   $C_{20}H_{16}Cl_2N_2S_2Pd_2$ requires: C,38.0; H,2.6; N,4.4%

Infra-red spectrum: $\sqrt{}$ $_{max}$ 1620, 1535, 1380, 1340, 1200, 810, 770 cm^{-1}

Reaction of N-methylquinoline-4-thione with sodium tetrachloro-palladate

The reaction was carried out under conditions identical with those of the preceding reaction to give an orange solid (89%), thought originally to be di-μ-chlorobis(4-thioxo-N-methylquinolin-5-yl)dipalladium(II) but yielding unsatisfactory analytical results.

Analysis: Found: C,31.8; H,2.6; N,3.6%

$C_{20}H_{16}Cl_2N_2S_2Pd_2$ requires: C,38.0; H,2.5; N,4.4%

Infra-red spectrum: λ_{max} 1610, 1595, 1560, 1520, 1100, 925, 850, 765 cm^{-1}

Reaction of N,N-dimethylthiobenzamide with sodium tetrachloropalladate

A solution of sodium tetrachloropalladate [made from sodium chloride (0.35g) and palladium dichloride (0.53g) in methanol (40 cm^3)] was added to a stirred solution of N,N-dimethylthiobenzamide (0.48g) in methanol.   A brown solid was precipitated and the resulting suspension was stirred at ambient temperature for 20 minutes and at reflux for 20 minutes.   When cool the complex was filtered off and washed with chloroform to yield a brown solid (0.67g), m.p. 210-213°C, thought to be mainly di-μ-chlorobis(N-methyl-N-thiobenzoylaminomethyl)-dipalladium(II) but yielding unsatisfactory analytical results.

Analysis: Found: C,28.7; H,2.8; N,3.3%

$C_{18}H_{20}Cl_2N_2S_2Pd_2$ requires: C,35.3; H,3.3; N,4.6%

Infra-red spectrum: λ_{max} 1585, 1260, 970, 900, 755, 685 cm^{-1}

Reaction of p-methyl-N,N-dimethylthiobenzamide with sodium
tetrachloropalladate

The reaction was carried out under conditions identical with
those of the preceding reaction to give di-µ-chlorobis(N-methyl-N-
p-methylthiobenzoylaminomethyl)dipalladium(II)(78%), as a brown solid
m.p. 181-184°C.

Analysis: Found: C,36.3; H,3.7; N,4.2%

    $C_{20}H_{24}Cl_2N_2S_2Pd_2$ requires: C,37.5; H,3.8; N,4.4%

Infra-red spectrum: γ max 1600, 1310, 1300, 1265, 1180, 980, 810 cm^{-1}

Conversion of Dimeric Chloride-bridged Complexes into
Monomeric Phosphine Complexes

Reaction of di-µ-chlorobis(9-thioxanthen-1-yl)dipalladium(II)
with triethylphosphine

Triethylphosphine (0.12g) was added to a stirred suspension of
the title complex (0.35g) in dichloromethane (30 cm^3) and the resulting
maroon solution was stirred at ambient temperature, under nitrogen,
for 30 minutes. The solution was concentrated to a small volume and
then chromatographed on 6% deactivated alumina with dichloromethane
as eluant. A maroon solid recovered from the eluate was identified
as chloro-(9-thioxoxanthen-1-yl)triethylphosphinepalladium(II),
(0.29g;62%), m.p. 167-169°C.(decomp.).

Analysis: Found: C,48.5; H,4.7%

    $C_{19}H_{22}ClOPSPd$ requires: C,48.5; H,4.7%

Infra-red spectrum:γ max 1570, 1550, 1275, 1145, 1125, 1025, 990, 760 cm^{-1}

[underline]^{1}H n.m.r. spectrum:[/underline]	δ 8.3-8.6(m,*ca.*1.5H), 7.1-7.9(m,*ca.*5.5H),
	2.0(q,6H), 1.2(m,9H)
[underline]^{31}P n.m.r. spectrum:[/underline]	24.4(s) and 12.2(s) p.p.m.
[underline]Mass spectrum:[/underline]	^{m}/e 422(M^{+}), 358, 356, 118

Reaction of di-μ-chlorobis(9-thioxothioxanthen-1-yl)dipalladium(II) with triethylphosphine

The reaction was carried out under conditions identical with those of the preceding reaction. Chloro-(9-thioxothioxanthen-1-yl) triethylphosphinepalladium(II) was isolated as purple microcrystals (75%), m.p. 181-182°C.

[underline]Analysis:[/underline]   Found: C,46.7; H,4.6%

$C_{19}H_{22}ClPS_2Pd$ requires: C,46.7; H,4.5%

[underline]Infra-red spectrum:[/underline] $\vee$ $_{max}$ 1600, 1560, 1550, 1520, 1255, 1230, 1160, 1100, 1040, 765, 725 cm^{-1}

[underline]^{1}H n.m.r. spectrum:[/underline] δ[9.0(d) and 8.8(t)](*ca.*1.5H), 7.2-7.8(m,*ca.*5.5H), 2.0(m,6H), 1.3(m,9H)

[underline]^{13}C n.m.r. spectrum:[/underline] 178.0, 170.8 (C=S); 137.2-121 (19 lines, aromatic carbon resonances), 15.6 14.6, (3 lines, P-CH$_2$CH$_3$), 8.8, 8.3 (2 lines, PCH$_2$CH$_3$)

[underline]^{31}P n.m.r. spectrum:[/underline] 22.7(s) and 11.9(s) p.p.m.

[underline]Mass spectrum:[/underline] ^{m}/e 456(Pd), 412(Pd), 228

Reaction of di-μ-chlorobis(4-thioxoquinolizin-6-yl)dipalladium(II) with triphenylphosphine

Triphenylphosphine (0.14g) was added to a stirred suspension of the title complex (0.16g) in dichloromethane (25 cm^3) and the result-ing solution was stirred at ambient temperature, under nitrogen, for

1 hour. The solution was concentrated to a small volume and chromato-graphed on 6% deactivated alumina eluting with dichloromethane. A single yellow fraction was obtained that gave chloro-(4-thioxoquino-lizin-6-yl)triphenylphosphinepalladium(II), (0.25g;85%) as a yellow solid m.p. 184-185°C.

Analysis: Found: C,57.7; N,3.9; N,2.4%

$C_{27}H_{21}ClNPSPd$ requires: C,57.5; H,3.7; N,2.5%

Infra-red spectrum: ν_{max} 1615, 1560, 1305, 1295, 1225, 1100, 810, 750 cm^{-1}

^{1}H n.m.r. spectrum: δ 9.1(dd,1H), 7.9-7.3(m,21H)

^{31}P n.m.r. spectrum: 19.7 (s) p.p.m.

Mass spectrum: ^{m}/e 558(Pd), 426(Pd), 377, 287, 262, 216, 183, 160

Reaction of di-μ-chlorobis(4-thioxoquinolizin-6-yl)dipalladium(II) with triethylphosphine

The reaction was carried out by the procedure described by Davis[41] to yield chloro-(4-thioxoquinolizine-6-yl)triethylphosphinepalladium(II) in 90% yield, m.p. 174-175°C.[lit.m.p. 173-175°C.].

Reaction of di-μ-chlorobis(1-thioxo-N-methylisoquinolin-8-yl) dipalladium(II) with triethylphosphine

The reaction was carried out under conditions identical with those of the corresponding reaction of di-μ-chlorobis(9-thioxoxanthen-1-yl)dipalladium(II). A yellowish-orange complex (91%), m.p. 198-200°C. was isolated.

Analysis: Found: C,41.4; H,5.9; N,2.3%

$C_{16}H_{23}ClNPSPd$ requires: C,44.3; H,5.3; N,3.2%

Infra-red spectrum: ν_{max} 1625, 1530, 1335, 1195, 1030, 920, 870, 810, 770 cm^{-1}

^{1}H n.m.r. spectrum: δ 8.6(t,<u>ca</u>.0.5H), 7.7-7.2(m,<u>ca</u>.3.5H), 7.0(d,1H),

4.1-4.0(s,3H), 1.9(q,8H), 1.1(p,12H)

Mass spectrum: ^{m}/e 458(Pd), 414(Pd), 341(Pd), 313(Pd), 285(Pd),

216, 173, 118

Reaction of di-μ-chlorobis(4-thioxo-N-methylquinolin-5-yl) dipalladium(II) with triethylphosphine

The reaction was carried out under conditions identical with those of the preceding reaction. An orange complex (91%), m.p. 220-222°C. (decomp.), was isolated.

Analysis: Found: C,40.7; H,5.0; N,3.1%

$C_{16}H_{23}ClNPSPd$ requires: C,44.3; H,5.3; N,3.2%

Infra-red spectrum:ν_{max} 1600, 1525, 1190, 1165, 1110, 1030, 945,
760, 730 cm^{-1}

^{1}H n.m.r. spectrum: the spectrum was not well resolved and contained

five broad resonances.

Mass spectrum: ^{m}/e 412(Pd), 300, 265, 175, 118

Reaction of di-μ-chlorobis(N-methyl-N-thiobenzoylaminomethyl) dipalladium(II) with triethylphosphine

The reaction was carried out under conditions identical with those of the preceding experiment and chloro(N-methyl-N-thiobenzoylamino-methyl)triethylphosphinepalladium(II)(62%), was isolated as a yellowish-orange solid, m.p. 150-151°C.

Analysis: Found: C,42.5; H,6.1; N,2.9%

$C_{15}H_{25}ClNPSPd$ requires: C,42.5; H,5.9; N,3.3%

Infra-red spectrum:ν_{max} 1580, 1140, 1030, 760, 725 cm^{-1}

^{1}H n.m.r. spectrum: δ 7.2-7.5(m,5H), 4.2(d,2H), 3.1(s,3H), 1.9(m,8H),

1.2(p,12H)

^{13}C n.m.r. spectrum: 194.7(s,C=S), 137.2(s,C-1), 130.5(d,C-4),

128.7(d,C-2), 126.9(d,C-3), 55.5(td,N.$\underline{C}$H$_2$Pd),

45.6(q,N-CH$_3$), 15.1; 13.8(td,P.CH$_2$),

8.1(q,P.CH$_2$$\underline{C}H_3$)

The multiplicities reported are those observed with single frequency off-resonance proton decoupling.

Mass spectrum: ^{m}/e 412(Pd), 341(Pd), 311(Pd), 280(Pd), 195,

165, 164, 118

Reaction of di-μ-chlorobis(N-methyl-N-p-methylthiobenzoylamino-methyl)dipalladium(II) with triethylphosphine

The reaction was carried out under conditions identical with those of the preceding reaction and gave chloro-(N-methyl-N-p-methylthio-benzoylaminomethyl)triethylphosphinepalladium(II)(80%), as a reddish-brown solid, m.p. 157-158°C.(decomp.).

Analysis: Found: C,43.6; H,5.7; N,3.0%

   C$_{16}$H$_{27}$ClNPSPd requires: C,43.9; H,6.1; N,3.2%

Infra-red spectrum: ν_{max} 1585, 1310, 1265, 1190, 1040, 980, 815,

770, 730 cm^{-1}

^{1}H n.m.r. spectrum: δ 7.2(m,4H), 4.2(d,2H), 3.2(s,3H), 2.4(s,3H),

1.9(p,6H), 1.2(p,9H)

Mass spectrum: 458(Pd), 437(M$^+$,Pd), 412(Pd), 401(Pd,M$^+$-HCl),

265, 178, 118

Reaction of di-µ-thiocyanatobis(N,N-dimethyldithiocarbamato) dipalladium(II) with triethylphosphine

Triethylphosphine (0.12g) was added to a stirred suspension of di-µ-thiocyanatobis(N,N-dimethyldithiocarbamato)dipalladium(II), (0.28g) in dichloromethane (30 cm³). The resulting solution was stirred at ambient temperature, under nitrogen, for 30 minutes. Evaporation gave a maroon gum which, on trituration with ether, yielded a yellow solid that was extracted in a Soxhlet apparatus with acetone. On cooling the extract thiocyanato-(N,N-dimethyl-dithiocarbamato)triethylphosphine palladium(II) (0.30g;75%) crystallised as yellow needles m.p. 150°C.

<u>Analysis:</u>　　　　Found:　C,30.0;　H,5.3;　N,7.0%

$C_{10}H_{21}N_2PS_3Pd$　requires:　C,29.9;　H,5.2;　N,6.9%

<u>Infra-red spectrum:</u> ν_{max} 2080, 1550, 1260, 1035, 740 cm^{-1}

^{13}C n.m.r. spectrum: 148.7, 137.8(C=S), 129.3, 123.6(SCN), 38.7, 38.0(NMe$_2$), 17.5, 16.0, 14.6(P.$\underline{C}$H$_2$CH$_3$), 8.1, 8.0(P.CH$_2$$\underline{C}H_3$)

<u>Mass spectrum:</u>　　^{m}/e 402(M$^+$,Pd), 370(Pd), 346(Pd), 226(Pd), 150, 122

Conversion of Dimeric Chloride-bridged Complexes into Monomeric Dithiocarbamato-Complexes

Reaction of di-µ-acetatobis(benzo[h]quinolin-10-yl)dipalladium(II) with tetraethylammonium N,N-dimethyldithiocarbamate

The reaction was carried out by a method adapted from Hay[127].

To the title complex (1.74g) in dichloromethane (100 cm^3) was added a solution of tetraethylammonium N,N-dimethyldithiocarbamate (1.27g) in dichloromethane (25 cm^3). The resulting solution was stirred at ambient temperature overnight and then filtered to remove tetraethylammonium acetate. The filtrate was concentrated to a small volume and chromatographed on 6% deactivated alumina, eluting with dichloromethane to give a yellow solid. The complex was recrystallised from toluene and identified as benzo[h]quinolin-10-yl(N,N-dimethyl-dithiocarbamato)palladium(II), (1,1g;51%), m.p. 249-250°C.(decomp.).

<u>Analysis:</u>   Found: C,47.4; H,3.4; N,6.7%

          C$_{16}$H$_{14}$N$_2$S$_2$Pd requires: C,47.5; H,3.5; N,6.9%

<u>Infra-red spectrum:</u> ν_{max} 1650, 1610, 1310, 1140, 960, 820, 810, 750,

                    710 cm^{-1}

<u>Reaction of di-µ-acetatobis[2-(1-pyrazolyl)phenyl]dipalladium(II)</u>

<u>with tetraethylammonium N,N-dimethyldithiocarbamate</u>

The reaction was carried out under conditions identical with those of the preceding reaction and [2-(1-pyrazolyl)phenyl](N,N-dimethyl-dithiocarbamato)palladium(II) was isolated, (74%), as a pale yellow solid m.p. 209-210°C.(decomp.).

<u>Analysis:</u>   Found: C,39.0; H,3.5; N,11.2%

          C$_{12}$H$_{13}$N$_3$S$_2$Pd requires: C,39.0; H,3.5; N,11.4%

<u>Infra-red spectrum:</u> ν_{max} 1520, 1145, 1100, 1070, 1050, 1020, 960,

                    745, 730, 720 cm^{-1}

^{1}<u>H n.m.r. spectrum:</u>   δ 7.9(d,1H), 7.8-7.1(m,5H), 6.5(t,1H), 3.4(s,3H),

                    3.3(s,3H)

Mass spectrum: ^{m}/e 369(M$^+$,Pd), 346(Pd), 326(Pd), 281, 194, 175, 144

Reaction of di-μ-chlorobis[2-(phenylazoxy)phenyl]dipalladium(II) with sodium N,N-dimethyldithiocarbamate

Sodium N,N-dimethyldithiocarbamate (0.14g) was added to a stirred suspension of the title complex (0.34g) in dimethylformamide (30 cm^3) and the resulting solution was stirred at ambient temperature overnight. The solution was evaporated to dryness and the residue was extracted with dichloromethane. The extract was filtered, to remove the sodium chloride, concentrated to small volume, and chromatographed on 6% deactivated alumina eluting with dichloromethane. 2-[(Phenylazoxy)phenyl](N,N-dimethyldithiocarbamato)palladium(II) was obtained as a yellow powder (0.35g;83%), m.p. 226-227°C.(decomp.).

Analysis: Found: C,42.6; H,3.6; N,9.8%

     C$_{15}$H$_{15}$N$_3$OS$_2$Pd requires: C,42.6; H,3.4; N,9.9%

Infra-red spectrum:$\vee$$_{max}$ 1590, 1540, 1325, 1305, 1160, 1045, 970,
                        865, 815, 685 cm^{-1}

^{1}H n.m.r. spectrum: δ 7.8-7.1(m,9H), 3.4(s,3H), 3.3(s,3H)

Mass spectrum: ^{m}/e 423(M$^+$,Pd), 407(Pd,M$^+$-O), 390(Pd,M$^+$-S$_4$), 387,
                        346(Pd), 319(Pd), 303, 290(Pd), 226(Pd), 194(Pd)

Reaction of di-μ-chlorobis[5-methoxy-2-(4-methoxythiobenzoyl)phenyl] dipalladium(II) with sodium N,N-dimethyldithiocarbamate

The reaction was carried out under conditions identical with those of the preceding reaction and [5-methoxy-2-(4-methoxythiobenzoyl) phenyl](N,N-dimethyldithiocarbamato)palladium(II) was isolated (61%) as a maroon solid m.p. 178-179°C.

Analysis: Found: C,44.9;   H,4.0;   N,2.9%

$C_{18}H_{19}NO_2S_3Pd$ requires: C,44.7;   H,3.9;   N,2.9%

Infra-red spectrum: ν_{max} 1580, 1555, 1325, 1290, 1250, 1255, 1160,

                     1020, 835, 790, 720 cm^{-1}

^1H n.m.r. spectrum: δ 7.6(d,2H), 7.3(d,1H), 6.9(d,2H and d,1H),

                     6.5(dd,1H), 3.9(s,3H), 3.8(s,3H), 3.4(s,6H)

Mass spectrum: $^m/e$ 483(M^+,Pd), 450, 363, 346(Pd), 298, 176

Exact mass measurement:

           $^m/e$ 450.1844 ($C_{30}H_{26}O_4$ requires 450.1831)

Reaction of di-μ-chlorobis(9-thioxoxanthen-1-yl)dipalladium(II) with sodium N,N-dimethyldithiocarbamate

The reaction was carried out under conditions identical with those of the preceding reaction and 9-thioxoxanthen-1-yl(N,N-dimethyldithiocarbamato)palladium(II) was isolated (52%) as maroon needles, m.p. 235°C.(decomp.).

Analysis: Found: C,43.8;   H,3.1;   N,3.1%

$C_{16}H_{13}NOS_3Pd$ requires: C,43.9;   H,3.0;   N,3.2%

Infra-red spectrum: ν_{max} 1600, 1570, 1560, 1530, 1275, 1150, 1135,

                     1000, 965, 900, 825, 780 cm^{-1}

Mass spectrum: $^m/e$ 437(M^+,Pd), 422, 358, 356, 346(Pd), 317(Pd),

                     265, 226(Pd), 212, 194(Pd)

Exact mass measurements:

           $^m/e$ 358.0988 ($C_{26}H_{14}O_2$ requires 358.0994)

           $^m/e$ 356.0834 ($C_{26}H_{12}O_2$ requires 356.0837)

Reaction of di-μ-chlorobis(9-thioxothioxanthen-1-yl)dipalladium(II) with sodium N,N-dimethyldithiocarbamate

The reaction was carried out under conditions identical with those of the preceding reaction, and 9-thioxothioxanthen-1-yl(N,N-dimethyldithiocarbamato)palladium(II) was isolated (66%) as purple microcrystals, m.p. 235-236°C.

Analysis: Found: C,42.2;   H,3.0;   N,3.1%

$C_{16}H_{13}NS_4Pd$ requires: C,42.4;   H,2.9;   N,3.1%

Infra-red spectrum: ν_{max} 1550, 1250, 1150, 1100, 995, 780, 765, 740, 713 cm^{-1}

Mass spectrum: $^m/e$ 453(M$^+$,Pd), 390, 346(Pd), 333(Pd), 298, 228

Reaction of di-μ-chlorobis(4-thioxoquinolizin-6-yl)dipalladium(II) with sodium N,N-dimethyldithiocarbamate

Sodium N,N-dimethyldithiocarbamate (0.29g) was added to a stirred suspension of the title complex (0.60g) in dimethylformamide (150 cm^3) and the resulting maroon solution was stirred at ambient temperature overnight. The solution was evaporated to dryness and the residue was extracted with dichloromethane in a Soxhlet extractor for 24 hours. Evaporation of the extract gave an orange gum which, on trituration with diethyl ether, gave 4-thioxoquinolizin-6-yl(N,N-dimethyldithio-carbamato)palladium(II), (0.6g;78%), as an orange powder m.p. 257-258°C.

Analysis: Found: C,37.0;   H,3.1;   N,6.7%

$C_{12}H_{12}N_2S_3Pd$ requires: C,37.3;   H,3.1;   N,7.2%

Infra-red spectrum: ν_{max} 1660, 1550, 1210, 1145, 800 cm^{-1}

Mass spectrum: $^m/e$ 386(M$^+$,Pd), 346(Pd), 266(Pd), 226(Pd), 160

Reaction of di-μ-chlorobis(1-thioxo-N-methylisoquinolin-8-yl

dipalladium(II) with sodium N,N-dimethyldithiocarbamate

The reaction was carried out under conditions identical with those of the preceding reaction, except the product from extraction was recrystallised from dimethyl sulphoxide. 1-Thioxo-N-methyliso-quinolin-8-yl(N,N-dimethyldithiocarbamato)palladium(II) was isolated (80%) as a yellow powder, m.p. 195-196°C.(decomp.).

Analysis: Found: C,39.1; N,3.5; N,7.1%

$C_{13}H_{14}N_2S_3Pd$ requires: C,39.0; N,3.5; N,7.0%

Infra-red spectrum: ν_{max} 1620, 1530, 1340, 1260, 1190, 1140, 815 cm^{-1}

^{1}H n.m.r. spectrum: δ 7.9(d,1H;J=7Hz), 7.5(bm,3H), 7.3(d,1H;J=7Hz),

4.1(s,3H), 3.3(s,3H), 3.2(s,3H)

Mass spectrum: ^{m}/e 400(M$^+$,Pd), 346(Pd), 312(Pd), 280(Pd),

266(Pd), 175

Reaction of the putative di-μ-chlorobis(4-thioxo-N-methylquinolin-

5-yl)dipalladium(II) with sodium N,N-dimethyldithiocarbamate

The reaction was carried out under conditions identical with those of the corresponding reaction of di-μ-chlorobis(4-thioxoquinolizin-6-yl)-dipalladium(II). An orange solid was isolated (ca. 75%), m.p. 256-258°C. (decomp.).

Analysis: Found: C,33.4; H,3.7; N,6.5%

$C_{13}H_{14}N_2S_3Pd$ requires: C,39.0; H,3.5; N,7.0%

Infra-red spectrum: ν_{max} 1670, 1600, 1540, 1190, 1165, 1110, 950,

825, 770, 665 cm^{-1}

Mass spectrum: $^m/e$ 400(M$^+$,Pd), 346(Pd), 330, 314(Pd), 300, 282(Pd), 226(Pd), 194(Pd), 175

Reaction of di-μ-chlorobis(N-methyl-N-thiobenzoylaminomethyl) dipalladium(II) with sodium N,N-dimethyldithiocarbamate

The reaction was carried out under conditions identical with those of the preceding reaction, and (N-methyl-N-thiobenzoylamino-methyl)(N,N-dimethyldithiocarbamato)palladium(II) was isolated (74%) as a sandy powder, m.p. 184-186°C.

Analysis: Found: C,36.7; H,4.0; N,6.7%

$C_{12}H_{16}N_2S_3Pd$ requires: C,36.9; H,4.1; N,7.1%

Infra-red spectrum: ν_{max} 1575, 1540, 1250, 970, 760, 700 cm^{-1}

^{1}H n.m.r. spectrum: δ 7.6-7.3(m,ca.5H), 4.5(s,ca.2H), 3.3(s,3H), 3.2(s,3H)

Mass spectrum: $^m/e$ 434(Pd), 390(M$^+$Pd), 346(Pd), 259(Pd), 226(Pd), 195, 165, 164

Reaction of di-μ-chlorobis(N-methyl-N-p-methylthiobenzoylaminomethyl)-dipalladium(II) with sodium N,N-dimethyldithiocarbamate

The reaction was carried out under conditions identical with those of the preceding reaction and (N-methyl-N-p-methylthiobenzoylamino-methyl)(N,N-dimethyldithiocarbamato)palladium(II) was isolated (78%) as a pale orange powder, m.p. 228-230°C.

Analysis: Found: C,38.5; H,4.3; N,6.5%

$C_{13}H_{18}N_2S_3Pd$ requires: C,38.6; N,4.4; N,6.9%

Infra-red spectrum: ν_{max} 1590, 1530, 1275, 1140, 965, 815 cm^{-1}

<u>^{1}H n.m.r. spectrum:</u>   δ 7.3(s,4H), 4.4(s,2H), 3.3(s,<u>ca.</u>6H),

3.2(s,3H), 2.4(s,3H)

<u>Mass spectrum:</u> ^{m}/e 462(Pd), 451(Pd), 404(M$^+$,Pd), 361(Pd),

346(Pd), 298, 273(Pd), 226(Pd), 179, 178

<u>Reactions of Cyclopalladated Complexes containing Dithio-
carbamate Ligands with Bromine and with Thiocyanogen</u>

<u>Reaction of benzo[h]quinolin-10-yl(N,N-dimethyldithiocarbamato)
palladium(II) with thiocyanogen</u>

A solution of bromine (0.1 cm^3) in chloroform (2 cm^3) was added
to a suspension of lead thiocyanate (0.6g) in chloroform (5 cm^3) at
0-5°C. and, after filtration, the resulting solution of thiocyanogen
was added to a stirred solution of the title complex (1.42g) in chloro-
form (100 cm^3). The solution immediately became deep blood-red and
after 5 minutes stirring a pale yellow solid was precipitated and the
solution became pale orange. The stirring was continued at ambient
temperature overnight and then di-μ-thiocyanatobis(N,N-dimethyldithio-
carbamato)dipalladium(II), (0.86g;86%) was filtered off. The filtrate
was concentrated to small volume and chromatographed on 6% deactivated
alumina, eluting with toluene-diethyl ether (90:10) to give a yellow
solid that was recrystallised from ethanol to yield 10-thiocyanato-
benzo[<u>h</u>]quinoline (0.56g;68%) as a cream solid m.p. 173-174°C.(decomp.)
[lit.[127] m.p. 174°C.].

<u>Infra-red spectrum:</u> ν $_{max}$ 2130, 1205, 830, 815, 750, 650 cm^{-1}
<u>^{1}H n.m.r. spectrum:</u> δ 8.9(dd,1H), 8.3(m,2H), 7.8(m,5H)
<u>Mass spectrum:</u> ^{m}/e 236(M$^+$), 210(M$^+$-CN), 179, 166, 118

<u>Reaction of [2-(1-pyrazolyl)phenyl](N,N-dimethyldithiocarbamato)</u>

<u>palladium(II) with thiocyanogen</u>

The reaction was carried out under conditions identical with those of the previous reaction and 1-(2-thiocyanatophenyl)pyrazole was isolated (50%) as white crystals (from 80-100° light petroleum) m.p. 150-151°C.

<u>Analysis:</u>   Found: C,56.7; H,3.7; N,19.8%

$C_{10}H_7N_3S$ requires: C,59.7; H,3.5; N,20.9%

Attempts to purify the compound further were unsuccessful.

<u>Infra-red spectrum:</u>ν_{max} 2140, 1070, 1040, 1015, 935, 745 cm^{-1}

<u>^{1}H n.m.r. spectrum:</u> δ 7.9(m,3H), 7.5(m,3H), 6.5(t,1H)

<u>Mass spectrum:</u> ^{m}/e 201(M^+), 175(M^+-CN), 174(M^+-HCN), 148, 116, 90

<u>Reaction of 2-(phenylazoxy)phenyl(N,N-dimethyldithiocarbamato)</u>

<u>palladium(II) with thiocyanogen</u>

The reaction was carried out under conditions identical with those of the previous reaction, and 2-thiocyanatoazoxybenzene was isolated (67%) as an orange powder, m.p. 115-118°C.(decomp.). Attempts to purify the product by chromatography or by recrystallisation led to decomposition.

<u>Analysis:</u>   Found: C,59.9; H,3.6; N,16.3%

$C_{13}H_9N_3OS$ requires: C,61.2; H,3.5; N,16.5%

<u>Infra-red spectrum:</u>ν_{max} 2150, 1300, 1275, 755, 680 cm^{-1}

<u>^{1}H n.m.r. spectrum:</u> δ 8.5-8.0(m,4H), 7.8-7.4(m,5H)

<u>Mass spectrum:</u> ^{m}/e 255(M^+), 226, 198, 175, 142

Reaction of [5-methoxy-2-(4-methoxythiobenzoyl)phenyl](N,N-dimethyl-dithiocarbamato)palladium(II) with thiocyanogen

The reaction was carried out under conditions identical with those of the preceding reaction except that evaporation of the chloro-form filtrate gave a maroon gum that was triturated with diethyl ether to yield 4,4'-dimethoxy-2-thiocyanatothiobenzophenone (95%) as a reddish-brown solid, m.p. 102-105°C. (decomp.). Attempts to purify the product were unsuccessful and led to decomposition.

Infra-red spectrum: ν_{max} 2095, 1575, 1255, 1240, 1170, 1010, 830, 750 cm^{-1}

Mass spectrum: $^{m}/e$ 315(M^{+}), 289, 282, 271, 238, 251, 220, 208

Reaction of 9-thioxoxanthen-1-yl(N,N-dimethyldithiocarbamato) palladium(II) with thiocyanogen

(a) In concentrated solution.

The reaction was carried out under conditions identical with those of the previous reaction. A mixture of 1-thiocyanatoxanthene-9-thione and di-µ-thiocyanatobis(N,N-dimethyldithiocarbamato)dipal-ladium(II) was isolated. Attempts to separate the mixture were unsuccessful.

(b) In dilute solution.

A solution of bromine (0.1 cm^3) in chloroform (2 cm^3) was added to a suspension of lead thiocyanate (0.38g) in chloroform (5 cm^3) at 0-5°C. and, after filtration, the resulting solution of thiocyanogen was added to a stirred solution of the title complex (0.51g) in chloroform (250 cm^3). The solution immediately became deep blood-red

and after 5 minutes stirring a yellow solid was precipitated and the solution became light red. The stirring was continued at ambient temperature overnight and then di-μ-thiocyanatobis(N,N-dimethyldithiocarbamato)dipalladium(II), (0.31g;94%) was filtered off. The filtrate was evaporated to yield a reddish-brown solid identified as 1-thiocyanatoxanthene-9-thione (0.20g;64%), m.p. 143-145°C. (decomp.). Attempts to purify the product were unsuccessful.

<u>Infra-red spectrum</u>: ν max 1570, 1250, 910, 785, 760 cm^3

<u>Mass spectrum</u>: ^{m}/e 269(M$^+$), 243(M$^+$-CN), 205, 196, 192, 149, 105, 76

Exact mass measurements

^{m}/e 268.9973 ($C_{14}H_7NOS_2$ requires 268.9969)

^{m}/e 242.9930 ($C_{13}H_7OS_2$ requires 242.9938)

<u>Reaction of 9-thioxothioxanthen-1-yl(N,N-dimethyldithiocarbamato)</u>
<u>palladium(II) with thiocyanogen</u>

The reaction was carried out under conditions identical with those of the preceding reaction and 1-thiocyanatothioxanthene-9-thione was isolated (75%) as a purple powder, m.p. 161-164°C. (decomp.).

<u>Infra-red spectrum</u>: ν max 1550, 1260, 1100, 800 cm^{-1}

<u>Mass spectrum</u>: ^{m}/e 285(M$^+$), 259(M$^+$-CN), 228, 221, 212, 184, 177, 149, 139

Reaction of 4-thioxoquinolizin-6-yl(N,N-dimethyldithiocarbamato)
palladium(II) with thiocyanogen in dichloromethane

A solution of thiocyanogen (0.16g) in dichloromethane (10 cm^3) was added to a stirred solution of the title complex (0.53g) in dichloromethane (150 cm^3) and the resulting solution was stirred at ambient temperature overnight. On addition of the thiocyanogen, the solution changed from orange to deep maroon which then slowly lightened with precipitation of di-μ-thiocyanatobis(N,N-dimethyldithiocarbamato) dipalladium(II), (0.38g;98%), m.p. 262-264°C. (decomp.). The palladium complex was filtered off and evaporation of the filtrate gave a yellow solid identified as quinolizine-4-thione (0.20g;90%), m.p. 102-104°C. [lit.[118] m.p. 104°C.].

An identical reaction in chloroform gave the same products.

Reaction of 4-thioxoquinolizin-6-yl-(N,N-dimethyldithiocarbamato)
palladium(II) with bromine in dichloromethane

The reaction was carried out under conditions identical with those of the preceding reaction except that bromine was used instead of thiocyanogen. The only products isolated were di-μ-bromobis(N,N-dimethyldithiocarbamato)dipalladium(II), (98%) and quinolizine-4-thione (95%).

Reaction of 4-thioxoquinolizin-6-yl(N,N-dimethyldithiocarbamato)
palladium(II) with iodine

(a) A solution of iodine (0.25g) in chloroform (10 cm^3) was added to a stirred solution of the title complex (0.39g) in dichloromethane (200 cm^3) and the resulting solution was stirred at ambient temperature

overnight. No precipitate was formed and evaporation of the solution yielded iodine (0.21g) and the title complex (0.38g).

(b) The preceding reaction was repeated except that the solution was maintained under reflux for 18 hours. The only products isolated were iodine (0.2g) and the title complex (0.36g).

Reaction of 4-thioxoquinolizin-6-yl(N,N-dimethyldithiocarbamato) palladium(II) with N-bromosuccinimide

(a) A solution of the title complex (0.19g) and N-bromosuccinimide (0.09g) in chloroform (100 cm^3) was stirred at ambient temperature for 3 days. A white solid was collected, dried and identified as succinimide (0.05g). Evaporation of the filtrate yielded only the title complex (0.19g;100% recovery).

(b) The preceding reaction was repeated except that the solution was maintained under reflux for 24 hours. The only products isolated were succinimide and the title complex.

Reaction of 4-thioxoquinolizin-6-yl(N,N-dimethyldithiocarbamato) palladium(II) with thiocyanogen in Arklone

A solution of thiocyanogen (0.10g) in 1,1,2-trichloro-1,2,2-trifluoroethane, Arklone (5 cm^3) was added to a stirred solution of the title complex (0.20g) in Arklone (300 cm^3). The orange solution became deep maroon and, after stirring for 10 minutes, the colour began to fade and di-μ-thiocyanatobis(N,N-dimethyldithiocarbamato) dipalladium(II) was precipitated (0.14g;99%), m.p. 262-264°C. (decomp.). The mixture was stirred at ambient temperature overnight and then filtered to remove the palladium complex. Evaporation of the

filtrate gave an orange residue that could not be recrystallised
(0.12g), m.p. 205-210°C. (decomp.).

Analysis: Found: C,30.4; H,3.1; N,8.5%

Infra-red spectrum: ν max 2100, 1595, 1550, 1050, 760 cm^{-1}

Mass spectrum: ^{m}/e 255(M$^+$), 224, 192, 175, 160, 128

A ^{1}H n.m.r. spectrum could not be obtained owing to the insolubility of the product.

Reaction of chloro-(4-thioxoquinolizin-6-yl)triphenylphosphine palladium(II) with bromine

The title complex (0.28g) was dissolved in Arklone (250 cm^3) and bromine (0.08g) was added. A reddish-brown precipitate was formed. The mixture was stirred at ambient temperature overnight, and then filtered to give a reddish-brown solid (0.31g), m.p. >300°C. Evaporation of the filtrate gave no residue.

Analysis: Found: C,38.4; H,2.7; N,1.8%

Infra-red spectrum: ν max 1610, 1550, 1090, 805, 685 cm^{-1}

The product was extremely insoluble and involatile so no ^{1}H n.m.r. or mass spectra could be obtained.

Reaction of the above product with triethylphosphine

The product (0.25g) was suspended in dichloromethane (30 cm^3) and triethylphosphine (0.3 cm^3) was added. The maroon solution was stirred under nitrogen at ambient temperature for 30 minutes, and then evaporated to dryness. Chromatography on 6% deactivated alumina, eluting with

dichloromethane, gave a single maroon band from which a maroon gum was obtained. Attempts to obtain a solid product failed and the ^{1}H n.m.r. spectrum of the gum showed only triethylphosphine resonances.

Reaction of 1-thioxo-N-methylisoquinolin-8-yl(N,N-dimethyldithio-carbamato)palladium(II) with thiocyanogen

The title complex (0.2g) was dissolved in chloroform (250 cm^3) and a solution of thiocyanogen (0.1g) in chloroform (5 cm^3) was added. The yellow solution became dark red and, after 15 minutes, di-μ-thio-cyanatobis(N,N-dimethyldithiocarbamato)dipalladium(II), (0.14g;99%) was precipitated. The mixture was kept at ambient temperature over-night. The palladium complex was filtered off and the filtrate evaporated to dryness to yield a yellow residue, (0.08g), m.p. 103-105°C. (from ethanol).

Spectroscopic analysis of the product showed it to be N-methyl-isoquinoline-1-thione with a small amount of N-methylisoquinolin-1-one.

Reaction of 1-thioxo-N-methylisoquinolin-8-yl(N,N-dimethyldithio-carbamato)palladium(II) with bromine

Bromine (0.08g) was added to a stirred solution of the title complex (0.2g) in chloroform (250 cm^3) and the resulting maroon solution was stirred at ambient temperature overnight. Evaporation of the solution gave a maroon solid (0.2g), m.p. >300°C.

The product could not be recrystallised owing to its poor solubility, and no n.m.r. spectrum could be obtained.

Analysis: Found: C,30.0; H,3.2; N,4.4%

Mass spectrum: ^{m}/e 239/237, 175

Reaction of (N-methyl-N-thiobenzoylaminomethyl)-(N,N-dimethyldithio-carbamato)palladium(II) with thiocyanogen

Thiocyanogen (0.12g) in chloroform (5 cm^3) was added to a stirred solution of the title complex (0.39g) in chloroform (250 cm^3). The mixture became dark maroon and, after 15 minutes, di-μ-thio-cyanatobis (N,N-dimethyldithiocarbamato)dipalladium(II),(0.28g;99%) was precipitated. The mixture was stirred at ambient temperature overnight and, after removal of the palladium complex, the filtrate was evaporated to dryness to give an orange gum. Trituration of the gum with a small amount of ethanol gave N,N-dimethylthiobenzamide (0.16g;97%), m.p. 65-67°C.[lit.[123] m.p. 67°C.].

Reaction of 10-thiocyanatobenzo[h]quinoline with 70% perchloric acid

70% Perchloric acid (0.1 cm^3) was added to a stirred solution of 10-thiocyanatobenzo[h]quinoline (0.1g) in absolute ethanol (35 cm^3) and the resulting pale yellow solution was stirred at ambient temper-ature for 30 minutes. On cooling, in ice, a pale yellow solid crystal-lised and was filtered off and recrystallised from glacial acetic acid containing a little perchloric acid to give 9a-azonia-1-thiacyclopenta-[def]phenanthrene perchlorate (0.11g;85%), m.p. 140°C. (explodes).

Analysis: Found: C,50.2; H,2.9; N,4.4%

   $C_{13}H_8ClNO_4S$ requires: C,50.4; H,2.6; N,4.5%

Infra-red spectrum: ν_{max} 1600, 1560, 1150, 1080, 830 cm^{-1}

^{1}H n.m.r. spectrum: δ 9.6(dd,1H), 8.7-8.1(m,7H)

Attempted cyclisation of 1-(2-thiocyanatophenyl)pyrazole

(a) With 70% perchloric acid.

70% Perchloric acid (0.1 cm^3) was added to a stirred solution of 1-(2-thiocyanatophenyl)pyrazole (0.1g) in absolute ethanol. After stirring at ambient temperature for 30 minutes the solution was cooled. Since no crystallisation occurred, the solution was diluted with water and extracted with ether. Evaporation of the ether extract yielded 0.09g (90%) of starting pyrazole.

(b) Reaction (a) was repeated except that the solution was maintained under reflux for one hour. 80% of the starting material was recovered unchanged.

(c) With bromine.

A solution of 1-(2-thiocyanatophenyl)pyrazole (0.1g) and bromine (0.1g) in absolute ethanol (25 cm^3) was maintained under reflux for 1 hour. Evaporation of the solution gave a dark brown gum. Thin layer chromatography indicated the presence of four compounds and, since only a small amount of 1-(2-thiocyanatophenyl)pyrazole had been used, the experiment was discontinued.

(d) With boron trifluoride diethyl etherate.

1-(2-thiocyanatophenyl)pyrazole (0.1g) and boron trifluoride diethyl etherate (0.12g) were mixed at ambient temperature and left for 60 minutes. Diethyl ether (10 cm^3) was added and the resulting solution was evaporated to dryness to yield the starting pyrazole derivative (0.085g;85%).

(e) Reaction (d) was repeated, except that the reaction was performed at 60°C. Untreated starting material (80%) was isolated.

Reaction of 2-thiocyanatoazoxybenzene with 70% perchloric acid

70% Perchloric acid (0.1 cm^3) was added to a stirred solution of 2-thiocyanatoazoxybenzene (0.1g) in glacial acetic acid (20 cm^3). The solution, originally yellow, became chocolate brown and was stirred at ambient temperature for 2 hours. Diethyl ether (10 cm^3) was added and the solution was cooled to produce a chocolate brown solid. The solid was filtered off, washed with ether, and recrystallised from glacial acetic acid containing a little perchloric acid (yield 0.12g), m.p. 208-211°C.(decomp.).

Analysis: Found: C,33.8;   H,3.3;   N,9.3%

  $C_{13}H_{11}Cl_2N_3O_9S$ requires: C,34.3;   H,2.4;   N,9.2%

Infra-red spectrum: $\sqrt{}_{max}$ 1305, 1070, 760, 720 cm^{-1}

^{1}H n.m.r. spectrum: δ 9.0(dd,1H), 8.8(dd,1H), 8.3(m,4H), 7.9(m,3H)

A small sample of the solid was dissolved in 2M-aqueous sodium hydroxide and the solution was extracted with chloroform. Evaporation of the extract gave a pale yellow solid, m.p. 145-150°C.

Mass spectrum: ^{m}/e 213(w), 77(w)

Reaction of 4,4'-dimethoxy-2-thiocyanatothiobenzophenone with 70% perchloric acid

70% Perchloric acid (0.2 cm^3) was added to a stirred solution of the crude thiocyanato compound (0.2g) in glacial acetic acid (35 cm^3). The resulting orange solution was stirred at ambient temperature for 30 minutes and then cooled. The orange precipitate was filtered off and recrystallised from glacial acetic acid containing a little

perchloric acid to yield 3-p-methoxyphenyl-6-methoxybenzo-1,2-
dithiolium perchlorate as orange crystals (0.23g;95%), m.p. 220°C.
(decomp.).

Analysis: Found: C,46.1; H,3.3%

   $C_{15}H_{13}ClO_6S_2$ requires: C,46.3; H,3.4

Infra-red spectrum: ν_{max} 1580, 1300, 1260, 1240, 1170, 1080, 840,
                          635 cm^{-1}

^{1}H n.m.r. spectrum: δ 8.4(d,1H), 7.9(m,3H), 7.6(dd,1H), 7.3(d,2H),
                          4.2(s,3H), 4.0(s,3H)

Reaction of 1-thiocyanatoxanthene-9-thione with 70% perchloric acid

The reaction was carried out under conditions identical with
those of the preceding reaction to give xantheno(1,9:cd)1,2-dithiolium-
perchlorate (75%) as a red powder, m.p. 235°C.(decomp.).

Analysis: Found: C,45.5; H,2.1%

   $C_{13}H_7ClO_5S_2$ requires: C,45.6; N,2.1%

Infra-red spectrum: ν_{max} 1585, 1560, 1100, 1090, 940, 770 cm^{-1}

^{1}H n.m.r. spectrum: δ 8.5-7.7(m)

Reaction of 1-thiocyanatothioxanthene-9-thione with 70% perchloric acid

The reaction was carried out under conditions identical with those
of the preceding reaction to give thioxantheno(1,9:cd)1,2-dithiolium
perchlorate (63%) as a purple powder, m.p. 235-240°C.(decomp.). This
compound could not be isolated in a pure form despite repeated recrystal-
lisation.

Analysis: Found: C,40.6;   H,2.2;   N,1.4%

   $C_{13}H_7ClO_4S_3$ requires: C,43.5; H,2.0; N,0.0%

Reaction of 4,5-benzo-1,2-dithiole-3-thione with sodium tetrachloropalladate

A solution of sodium tetrachloropalladate (made from sodium chloride, 0.47g, and palladium dichloride, 0.71g) in methanol (50 cm^3) was added to a stirred solution of 4,5-benzo-1,2-dithiole-3-thione (0.73g) in methanol (200 cm^3). On mixing a russet solid was precipitated that persisted while the solution was stirred at ambient temperature for 20 minutes and refluxed for 10 minutes. The product was filtered off and washed with chloroform to yield [2,2'-dithiobis(dithiobenzoato]-bispalladium chloride polymer (1.13g;87%), m.p. 275-277°C. (decomp.).

Analysis: Found: C,26.1;   H,1.3%

   $C_7H_4ClS_3Pd$ requires: C,25.8; H,1.2%

Infra-red spectrum: ν $_{max}$ 1565, 1280, 1230, 1130, 1000, 755 cm^{-1}

Reaction of 6-chloro-4,5-benzo-1,2-dithiole-3-thione with sodium tetra-chloropalladate

6-Chloro-4,5-benzo-1,2-dithiole-3-thione (0.22g) was treated with one equivalent of sodium tetrachloropalladate under conditions identical with those of the preceding reaction. Similar work-up gave a reddish brown solid identified as [2,2'-dithiolbis(4-chlorodithiobenzoato)]bis-palladium chloride polymer (0.25g;83%), m.p. >300°C.

Analysis: Found: C,22.2;   H,1.3%

   $C_7H_3Cl_2S_3Pd$ requires: C,23.3; H,0.8%

Infra-red spectrum: ν $_{max}$ 1580, 1280, 1235, 1140, 1100, 1015 cm^{-1}

Reaction of 4-phenyl-1,2-dithiole-3-thione with sodium tetrachloropalladate

4-Phenyl-1,2-dithiole-3-thione (0.42g) was treated with sodium tetrachloropalladate under conditions identical with those of the preceding reaction. [3,3'-Dithiobis(2-phenylprop-2-enedithioato)] bispalladium chloride polymer (0.50g;71%) was isolated as a brownish-red powder, m.p. 265-266°C.(decomp.).

Analysis: Found: C,32.3; H,1.8%

$C_9H_6ClS_3Pd$ requires: C,30.7; H,1.7%

Infra-red spectrum: γ_{max} 1320, 1300, 1100, 1030, 1015, 830, 750, 690 cm^{-1}

Reaction of 4,5-dimethyl-1,2-dithiole-3-thione with sodium tetrachloropalladate

4,5-Dimethyl-1,2-dithiole-3-thione (0.16g) was treated with sodium tetrachloropalladate under conditions identical with those of the preceding reaction. An orange-brown solid identified as [3,3'-dithiobis-(2,3-dimethylprop-2-enedithioato)]bispalladium chloride polymer was isolated (0.25g;82%), m.p. 245-248°C.

Analysis: Found: C,20.8; H,2.1%

$C_5H_6ClS_3Pd$ requires: C,19.8; H,2.0%

Infra-red spectrum: γ_{max} 1160, 1025, 990, 920, 725 cm^1

Reactions of [2,2'-dithiobis(dithiobenzoato)]bispalladium chloride polymer

(a) With triethylphosphine.

The title complex (0.50g) was suspended in dichloromethane (30 cm^3) and triethylphosphine (0.18g) was added. The resulting maroon solution

was stirred at ambient temperature, in an atmosphere of nitrogen, for 30 minutes. Evaporation of the solution gave a gum that was triturated with acetone to yield a brownish-red solid. Chromatography on 6% deactivated alumina, eluting with dichloromethane, gave [2,2'-dithiobis(dithiobenzoato)]bis[chloro(triethylphosphine)palladium(II)], (0.25g;37%) as a maroon solid, m.p. 193-195°C.(decomp.).

Analysis: Found: C,35.0; N,4.3%

$C_{26}H_{38}Cl_2P_2S_6Pd_2$ requires: C,35.1; H,4.3%

Infra-red spectrum: γ $_{max}$ 1540, 1280, 1230, 1125, 1000, 755 cm^{-1}

Mass spectrum: ^{m}/e 240, 184

(b) With tri-n-butylphosphine.

   The title complex (0.38g) and tri-n-butylphosphine (0.24g) were allowed to react under conditions identical with those of the preceding reaction. Attempts to purify the crude orange phosphine complex (0.1g), m.p. 45-51°C, produced only a gum for which a satisfactory analysis could not be obtained.

Analysis: Found: C,34.7; H,3.9%

$C_{38}H_{62}Cl_2P_2S_6Pd_2$ requires: C,43.2; H,5.9%

Infra-red spectrum: γ $_{max}$ 1580, 1280, 1235, 1125, 1000 cm^{-1}

(c) With sodium N,N-dimethyldithiocarbamate.

   Sodium N,N-dimethyldithiocarbamato (0.25g) was added to a stirred suspension of the title complex (0.56g) in dimethyl formamide (100 cm^3) and the resulting solution was stirred at ambient temperature over-night. The solution was evaporated to give an orange solid which was extracted, using a Soxhlet apparatus, with dichloromethane. The

extract was evaporated under reduced pressure to yield [2,2'-dithio-bis[(N,N-dimethyldithiocarbamato)palladium(II)]. (0.53g;75%), m.p. 257-259°C.(decomp.), as an orange powder.

For analytical purposes a small sample was purified by column chromatography (6% deactivated alumina with dichloromethane as eluant).

<u>Analysis</u>:   Found: C,28.0;   H,2.3;   N,3.0%

$C_{20}H_{20}N_2S_{10}Pd_2$ requires: C,29.3;   H,2.4;   N,3.4%

<u>Infra-red spectrum:</u> ν_{max} 1530, 1280, 1230, 1125, 1000, 715 cm^{-1}

<u>Mass spectrum:</u> $^m/e$ 448, 372, 346(Pd), 272, 240, 184

(d)   With sodium N,N-diethyldithiocarbamate.

The title complex (0.16g) and sodium N,N-diethyldithiocarbamate (0.09g) were allowed to react under conditions identical with those of the preceding reaction and [2,2'-dithiobenzoato)]bis[(N,N-diethyl-dithiocarbamato)palladium(II)](0.19g;88%), was isolated as an orange solid, m.p. 185-186°C.

<u>Analysis</u>:   Found: C,32.7;   H,3.1;   N,3.0%

$C_{24}H_{28}N_2S_{10}Pd_2$ requires: C,32.9;   H,3.2;   N,3.2%

<u>Infra-red spectrum:</u> ν_{max} 1585, 1380, 1280, 1240, 1130, 1010, 755 cm^{-1}

<u>^{1}H n.m.r. (FT) spectrum:</u>   δ 8.2(d), 7.8(m), 7.5(m), 3.7(q), 1.3(m)

<u>Mass spectrum:</u> $^m/e$ 402(Pd), 369(Pd), 354, 293(Pd), 272, 255(Pd), 240, 222(Pd), 184

(e)   With sodium N,N-di-n-butyldithiocarbamate.

The title complex (0.16g) and sodium N,N-di-n-butyldithio-
carbamate (0.12g) were allowed to react under conditions identical
with those of the preceding reaction.   A maroon gum (0.2g,82%) was
obtained that could not be crystallised but was thought to be [2,2'-
dithiobis(dithiobenzoato)]bis[(N,N-di-n-butyldithiocarbamato)palladium
(II)].

^{1}H n.m.r. spectrum: δ 8.0(d,1H), 7.9-7.6(m,2H), 7.5-7.3(m,1H),

3.6(m,4H), 1.9-0.8(m,14H)

Reaction of [2,2-dithiobis(4-chlorodithiobenzoato)bispalladium chloride polymer with sodium N,N-diethyldithiocarbamate

The title complex (0.18g) and sodium N,N-diethyldithiocarbamate
(0.09g) were allowed to react under conditions identical with those
previously described.   The maroon resulting solid (0.19g;85%) was
identified as [2,2'-dithiobis(4-chlorodithiobenzoato)bis](N,N-diethyl-
dithiocarbamato)palladium(II)], m.p. 133-135°C.(decomp.).

Analysis: Found: C,30.0;   H,3.1;   N,3.5%

$C_{24}H_{26}Cl_2N_2S_{10}Pd_2$ requires: C,30.4;   H,2.8;   N,3.0%

Infra-red spectrum: ν$_{max}$ 1660, 1560, 1510, 1275, 1200, 1075 cm^{-1}

^{1}H n.m.r. (FT) spectrum: δ 8.0(d), 7.8(d), 7.5(dd), 3.6(q), 1.3(m)

Mass spectrum: ^{m}/e 443(M^+-C_2H_5), 402(Pd), 369(Pd), 347(Pd),

308, 218

Reaction of [3,3'-dithiobis(2-phenylprop-2-enedithioato)]bispalladium chloride polymer

(a) With triethylphosphine.

The title complex (0.35g) and triethylphosphine (0.12g) were allowed to react under conditions identical with those previously described. A maroon solid was obtained (0.20g;45%) thought to be [3,3'-dithiobis(2-phenylprop-2-enedithioato)]bis[chloro(triethyl-phosphine)palladium(II)], m.p. 147-150°C.

Analysis: Found: C,36.7; H,3.9%

$C_{30}H_{42}Cl_2P_2S_6Pd_2$ requires: C,35.6; H,4.7%

Infra-red spectrum: ν_{max} 1300, 1230, 1030, 840, 755, 695 cm^{-1}

(b) With sodium N,N-dimethyldithiocarbamate.

The title complex (0.15g) and sodium N,N-dimethyldithiocarbamate (0.06g) were allowed to react under conditions identical with those previously described. [3,3'-Dithiobis(2-phenylprop-2-enedithioate)]bis-(N,N-dimethyldithiocarbamato)palladium(II)], (0.16g;86%), m.p. >300°C, was isolated.

Analysis: Found: C,34.7; H,2.9; N,2.6%

$C_{24}H_{24}N_2S_{10}Pd_2$ requires: C,33.1; H,2.8; N,3.2%

Infra-red spectrum: ν_{max} 1550, 1010, 830, 750, 690 cm^{-1}

Mass spectrum: $^{m}/e$ 436(M^{2+},Pd), 346(Pd), 292, 226(Pd), 210

Reaction of [3,3'-dithiobis(2,3-dimethylprop-2-enedithioato)]bis-
palladium chloride polymer with sodium N,N-diethyldithiocarbamate

The palladium complex (0.15g) and sodium N,N-diethyldithiocarbamate
(0.09g) were allowed to react under conditions identical with those
previously described.   A maroon gum was isolated (0.19g;92%) and was
presumed to be [3,3'-dithiobis(2,3-dimethyldithioprop-2-enedithioato)
bis[(N,N-diethyldithiocarbamato)palladium(II)].   On standing a small
amount of the gum solidified [m.p. 61-63°C.(decomp.)] but satisfactory
analytical results could not be obtained.

Analysis: Found: C,33.1;   H,4.1;   N,2.3%

   $C_{30}H_{32}N_2S_{10}Pd_2$ requires: C,28.9;   H,3.9;   N,3.3%

Infra-red spectrum: ν max 1515, 1150, 1020, 720 cm^{-1}

^{1}H n.m.r. spectrum: δ 3.7(q,4H), 2.6(s,3H), 2.2(s,3H), 1.3(t,6H)

Mass spectrum: ^{m}/e 402(Pd), 309(Pd), 254(Pd), 242, 196, 162

Thermolysis of 9-thioxoxanthen-1-yl(N,N-dimethyldithiocarbamato)
palladium(II)(207a)

The title complex (0.1g) was heated at 300°C. and 0.2 mm pressure
in a sublimation apparatus for several hours.   Maroon needle-like
crystals formed on the cold finger and were identified as a mixture
of xanthen-9-one and xanthene-9-thione.   A black involatile residue
was thought to be palladium and/or palladium sulphide.

No evidence of 9,9'-dithioxo-1,1'-bixanthenyl (251) or of the
benzobisxanthene (252) was found.

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