APPLICATIONS OF TRANSITION METAL COMPLEXES

IN HETEROCYCLIC SYNTHESIS

by

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DECLARATION

I declare that this thesis is my own composition and that the work described within has been carried out by myself and has not been submitted previously for any Higher Degree. This thesis describes the results of research carried out in the Department of Chemistry, University of Edinburgh, under the supervision of Dr. D. Leaver between November 1977 and September 1980.

The following lecture courses were attended during the three years of research.

Organic Chemistry Seminars (three years attendance).

'Strategy in Organic Synthesis', 5 lectures by Dr. I. Gosney, University of Edinburgh.

'Flash Vacuum Pyrolysis', 5 lectures by Dr. H. McNab, University of Edinburgh.

'Basic and Advanced Stereochemistry', 5 lectures by Dr. H. McNab, University of Edinburgh.

'Frontier Orbitals and Organic Reaction Paths', 5 lectures by Dr. J.T. Sharp, University of Edinburgh.

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'Chemistry at its most Colourful', 5 lectures by the Staff of I.C.I. Organics Division, Blackley.

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INTRODUCTION

D I S C U S S I O N

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Finally, I would like to thank Mrs. A. Simpson for her efficient typing of this manuscript.

Abstract

A series of cyclopalladated complexes was prepared from sulphur donor ligands containing thiocarbonyl groups and from nitrogen donor ligands containing azomethine groups. The initial dimeric complexes were converted into monomeric dithiocarbamato-derivatives and the reactions of the latter with various potential sulphur-transfer reagents were studied. Upon treatment with two molar equivalents of morpholine-N-sulphenyl chloride the S-donor complexes yielded 1,2-dithiolium salts and the N-donor complexes yielded isothiazolium salts. Quinolizine-4-selone was synthesised and treated with sodium tetrachloropalladate to yield the first example of a cyclopalladated selenium donor ligand, i.e. di-μ-chloro-bis-(4-selenoxoquinolizin-4-yl)dipalladium (II). The corresponding complex derived from quinolizine-4-thione was converted into [1,2,4]dithiazolo[3,4,5-de]quinolizinylium chloride and some reactions of this new heterocyclic system were studied.

The reactions of several 1,3-disubstituted allenes with various potential sulphur-transfer reagents were studied. 1,3-Dibenzoylallene reacted with bis(p-perthiotoluato)zinc(II) to yield 2,5-diphenyl-1,6,6aλ^4-dioxathiapentalene. 1,3-Dimethoxycarbonyl-allene reacted with the same reagent to yield a compound which was thought to be 3-methoxycarbonylmethylene-4-methoxycarbonyl-5-p-tolyl-1,2-dithiole.

INTRODUCTION

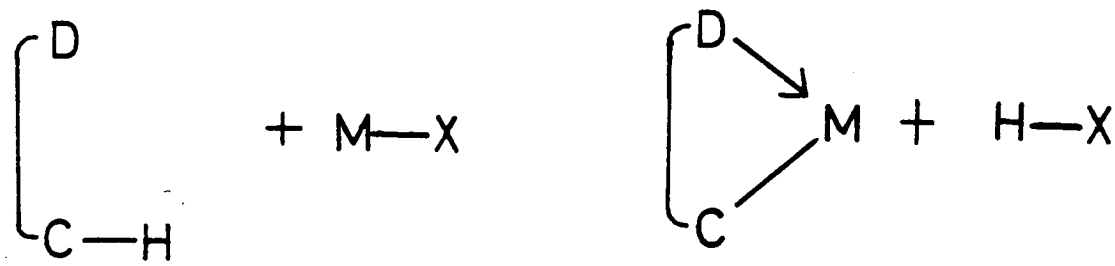
(1) GENERAL INTRODUCTION

The term "cyclometallation" was introduced by Trofimenko[1] to describe reactions of transition metal complexes in which a ligand undergoes an intramolecular (or more rarely, intermolecular) metallation with the formation of a chelate ring containing a metal-carbon σ-bond. The general reaction is illustrated in figure (i). Cyclometallation reactions have been comprehensively reviewed recently by Bruce[2], and so in order to avoid unnecessary repetition, only those aspects of cyclometallation reactions which are either (i) very recent or (ii) relevant to this work will be discussed herein. Attention will be focussed mainly on cyclopalladated complexes since only these complexes were used in this work. The aspects of cyclometallation reactions covered in this discussion will include the formation and general reactions of cyclometallated complexes as well as the uses of these complexes in organic synthesis.

(1.1) THE FORMATION OF CYCLOPALLADATED COMPLEXES

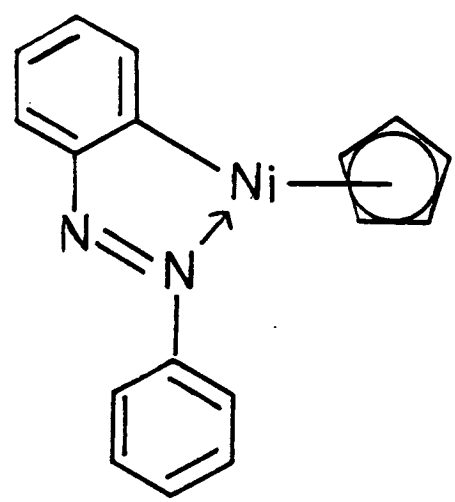
Following a report by Kleiman and Dubeck[3] that treatment of azobenzene with nickelocene resulted in the formation of the cyclometallated complex (1), Cope and Siekman[4] prepared the cyclopalladated complex (2) by reaction of azobenzene with potassium tetrachloropalladate. The site of palladation in the phenyl ring was determined by reduction of (2) with lithium aluminium deuteride. The reduction product was identified as azobenzene-2-d_1 and thus confirmed that palladation had occurred in the ortho position.

In general, the structures of cyclometallated complexes are readily established by conventional spectroscopic and analytical methods. Much information can be obtained by ^1H and ^{13}C n.m.r. studies, but the most convincing evidence is obtained from X-ray

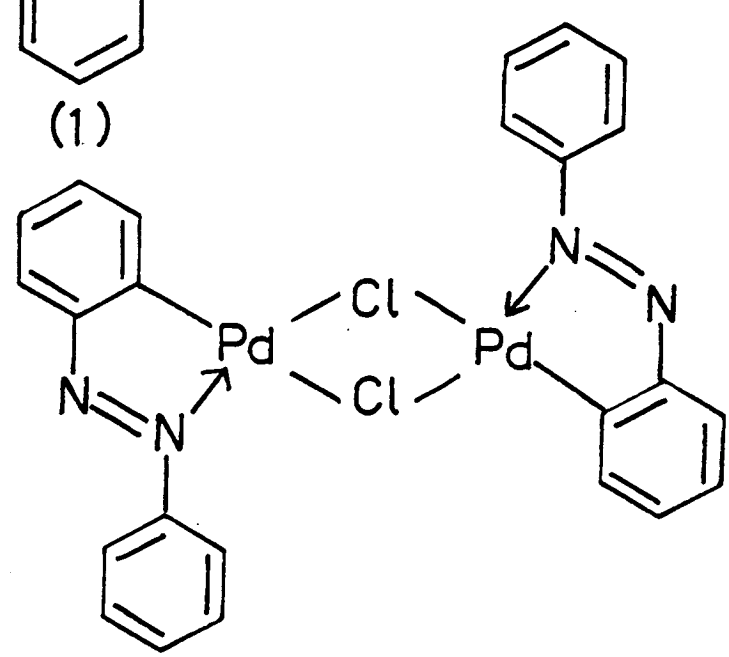


D = donor atom
M = transition metal
X = leaving group

fig(i)



(1)

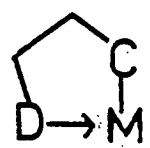


(2)

structure analysis.

(1.2) THE NATURE OF THE SUBSTRATE LIGAND

A large number of cyclometallated ligands are known[2]. A common feature of almost all the known ligands which undergo cyclometallation is the ability to meet a general stereochemical requirement for the formation of a five-membered chelate ring. This general stereochemical requirement is depicted in figure (ii).



C = carbon atom
D = donor atom
M = metal atom

fig(ii)

The types of ligands which undergo cyclometallation are best classified by the nature of the donor atom. The donor atom may be nitrogen, sulphur, oxygen, phosphorus or arsenic. In this work, only cyclopalladated nitrogen and sulphur donor ligands were studied, and so the following discussion will be limited to these donor ligands only.

(1.3) THE NATURE OF THE PALLADIUM REAGENT

The most common palladium reagents are sodium (or lithium) tetrachloropalladate and palladium acetate. The tetrachloropalladates can be looked upon as the reagents of choice through virtue of their facile preparation[5]. Despite a more involved preparation,

palladium acetate[6] has the additional advantage in that it can effect cyclopalladation in most cases where the tetrachloropalladates do not.[7,8] Less frequent in their use as reagents for effecting cyclopalladation are palladium chloride,[9] palladium acetylacetonate[10] and bis (benzonitrile) palladium (II) dichloride.[11] In a recent report, di-μ-chloro-bis (2-methyl-2-methoxy-3-^{t}butylthiopropyl, 1-C,S) palladium (II)has also been shown to effect cyclopalladation.[12]

In those cases where tetrachloropalladates are employed, the reaction solvent is generally either methanol or aqueous methanol. Other solvents such as aqueous dioxan[4] or dimethyl sulphoxide[13] have been used in a limited number of cases. In the case of palladium acetate, the solvent is usually acetic acid, although chloroform has also been employed.[14] Benzene[10] and benzene-methanol mixture[9] have been employed in conjunction with palladium acetylacetonate and palladium chloride respectively in a limited number of cases.

(1.4) THE MECHANISM OF CYCLOPALLADATION

Substituent effects on the cyclopalladation of azobenzene have been studied by Takahashi and Tsuji.[15] In their study, a series of mono-p-substituted azobenzenes were cyclopalladated and evidence was obtained for a stage in the reaction involving electrophilic attack by palladium on the aromatic ring. It was found that there was a preference for cyclopalladation to occur in the more electron-rich ring. This was exemplified by the ease of cyclopalladation increasing along the series Cl < H < Me < MeO, and is illustrated in figure (iii).

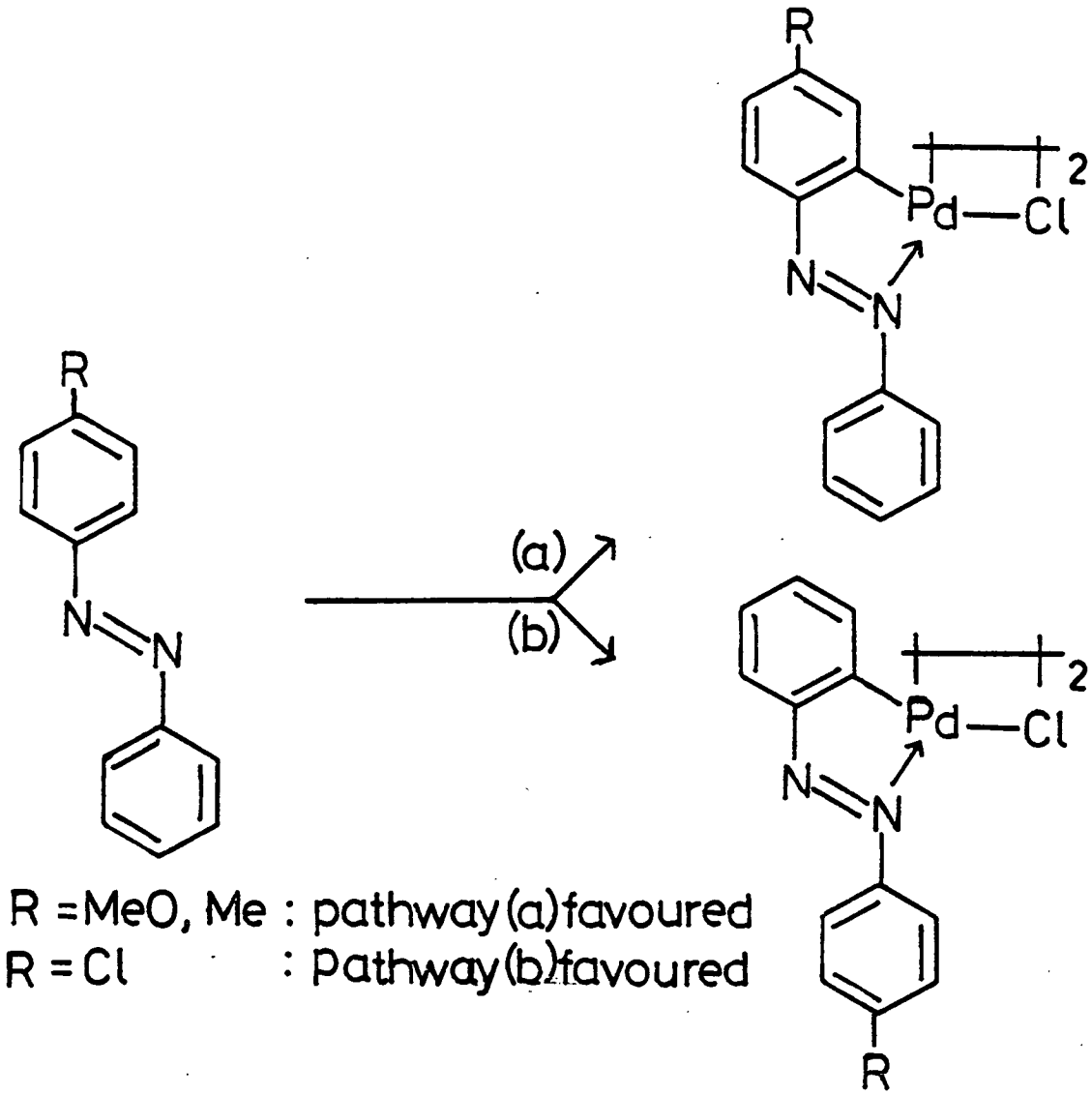
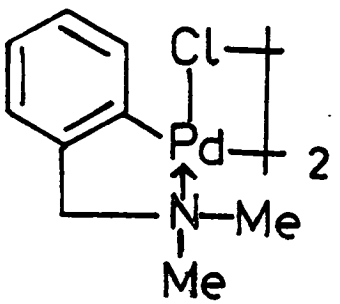
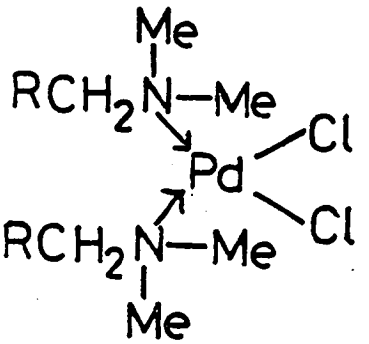


fig (iii)

Further studies on the mechanism of cyclopalladation were carried out by Cope and Friedrich.[16] N,N-Dimethylbenzylamine was allowed to react with lithium tetrachloropalladate, forming the cyclopalladated complex (3). The 4-methoxy-and 3,5-dimethoxy-derivatives were also prepared, but the reaction failed in the case of 4-nitro-N,N-dimethylbenzylamine, which gave rise to a co-ordination complex, bis (4-nitro-N,N-dimethylbenzylamine) palladium (II) dichloride (4).





(3)

(4) R = 4-$NO_2C_6H_4$

(5) R = $PhCH_2$

(6) R = $PhCH_2CH_2$

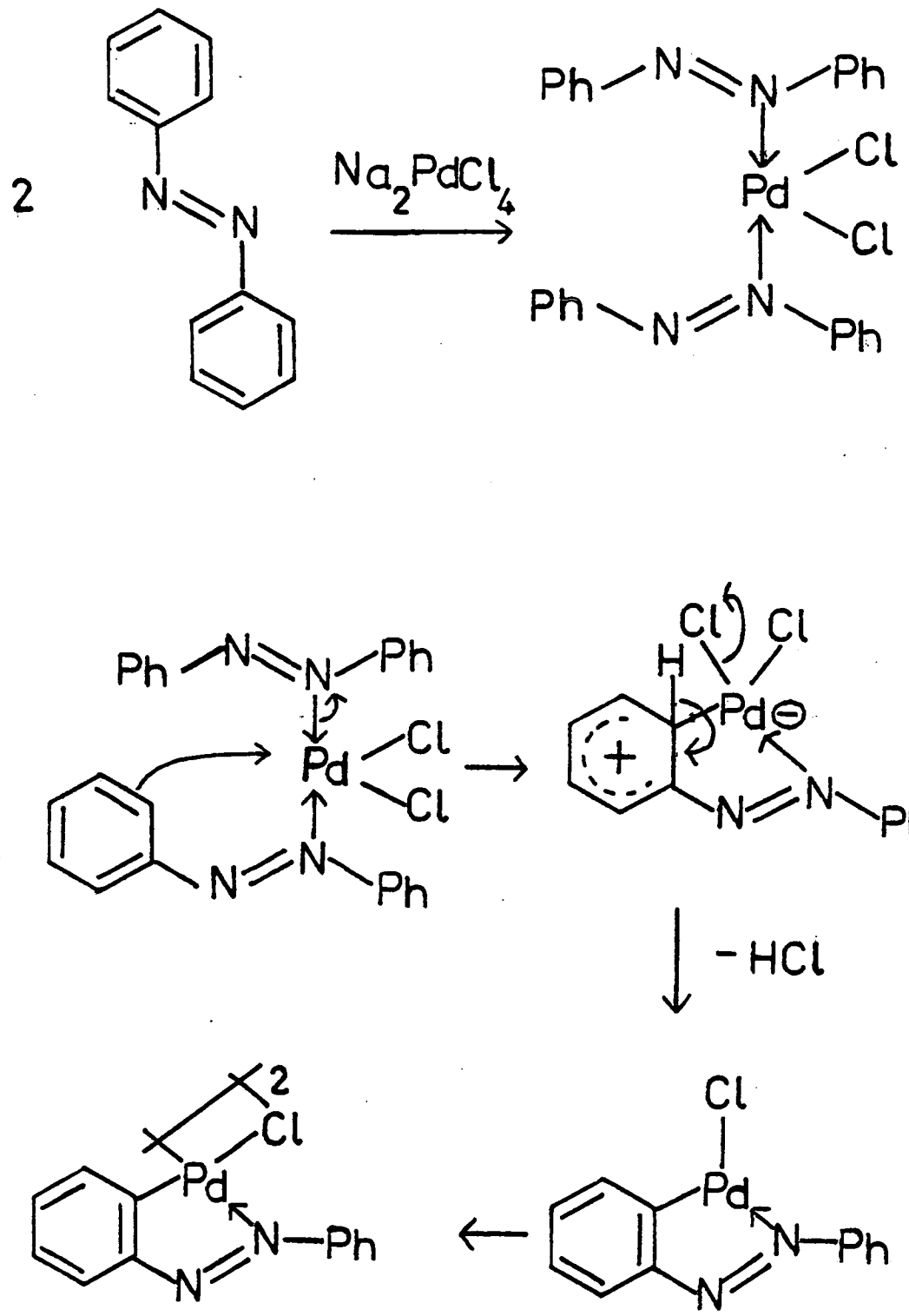
N,N-dimethyl-2-phenyl-1-ethylamine and 3-phenyl-1-propylamine formed only the co-ordination complexes (5) and (6) respectively. The cyclopalladated complexes which would then have contained 6 and 7-membered chelate rings were not formed.

On the basis of these observations, Cope and Friedrich suggested the following:

(i) The initial step in the cyclopalladation reaction involves a rapid co-ordination of the nitrogen to the metal which is then followed by an electrophilic attack by the co-ordinated palladium on the aromatic ring.

(ii) The failure of aromatic substitution to take place in the case of 4-nitro-N,N-dimethylbenzylamine is indicative that Pd (II) must be a weak electrophile.

(iii) The favourable entropy factors for electrophilic attack by the co-ordinated palladium via a 5-membered transition state are necessary to facilitate the aromatic substitution.



Scheme (i)

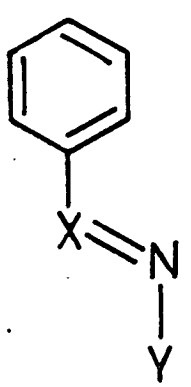
Bruce[17] has studied the cyclometallation of meta-substituted azobenzenes. In the case of cyclopalladation, he obtained results in accord with the previously proposed electrophilic mechanism. However, in the case of cyclomanganation, results were obtained which were in accord with a nucleophilic mechanism. The likely sequence of reaction steps in the cyclopalladation of azobenzene is shown in Scheme (i).

(2) CYCLOPALLADATED NITROGEN DONOR LIGANDS

A large number of cyclopalladated nitrogen donor ligand complexes have been reported.[2] These complexes can be classified according to the nature of the donor ligand. The list of cyclopalladated complexes in each of the following classifications is not intended to be comprehensive but rather, representative of that particular classification.

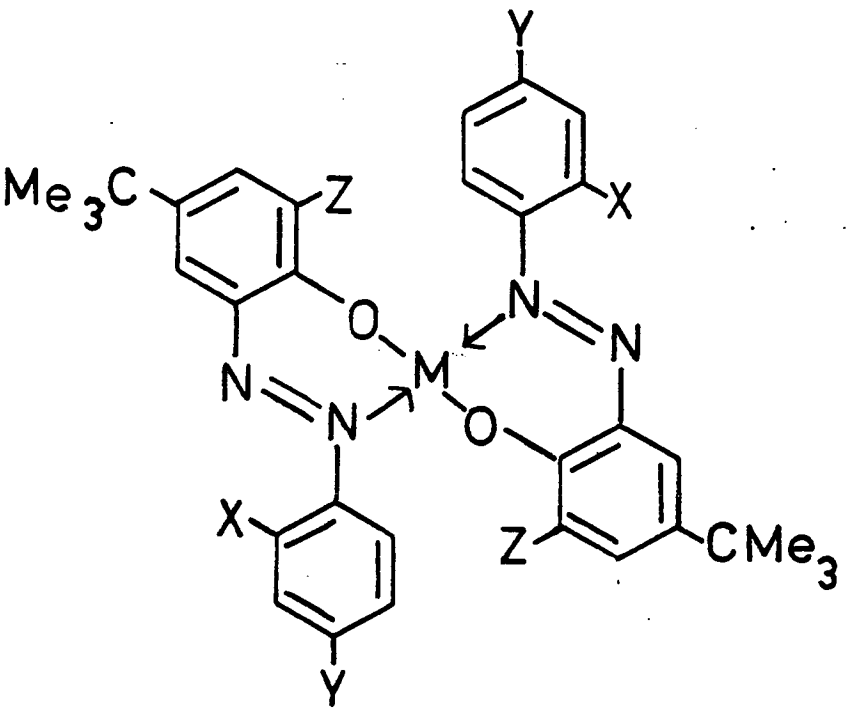
(2.1) CYCLOPALLADATED COMPLEXES OF AZOBENZENE AND ITS ISOSTRUCTURAL ANALOGUES

Azobenzene and its isostructural analogues form the largest category of cyclopalladated nitrogen donor ligands. These ligands have the general structure (7).

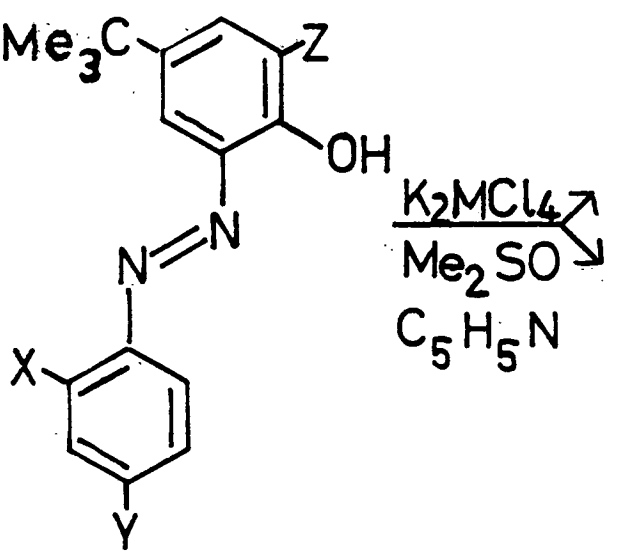


(a) X=N, Y=Ar
(b) X=CH, Y=Ar
(c) X=CR, Y=OH
(d) X=CR, Y=NR_2
(e) X=PAr_2, Y=Ar

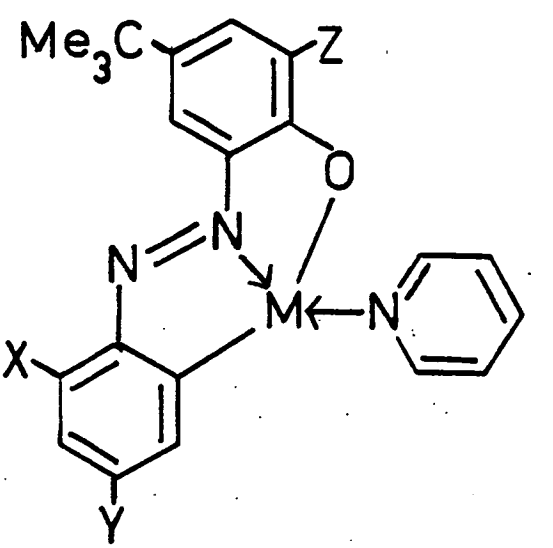
(7)



(9a,b)



(8a,b)



(10a,b)

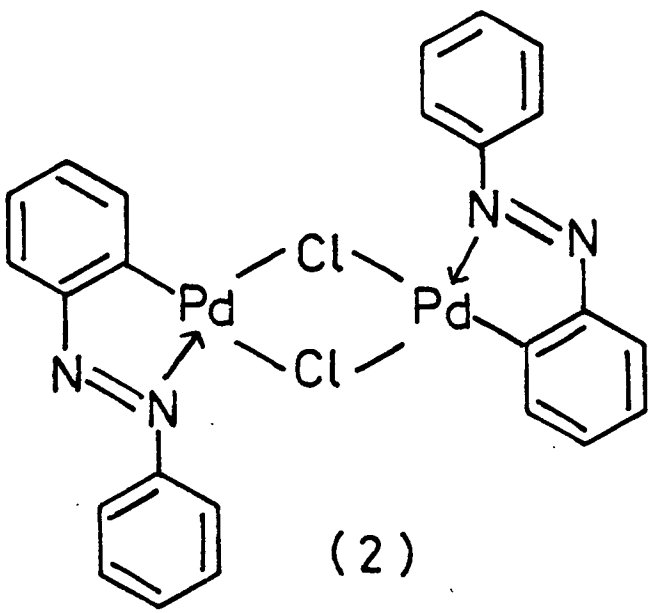
(a) X=Me, Y=H, Z=H

(b) X=H, Y=Br, Z=Me

M = Pd or Pt

Variation of the nature of the atoms or groups X and Y in (7) results in the azobenzenes, Schiff bases, oximes, phenylhydrazones and phosphinimines, (7a-e) respectively.

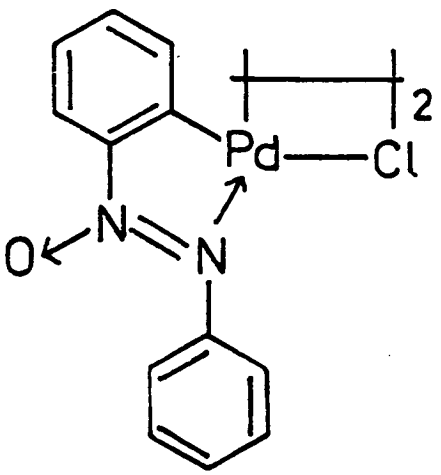
The cyclopalladation of azobenzene, which leads to the formation of the dimeric complex (2) has been discussed before.



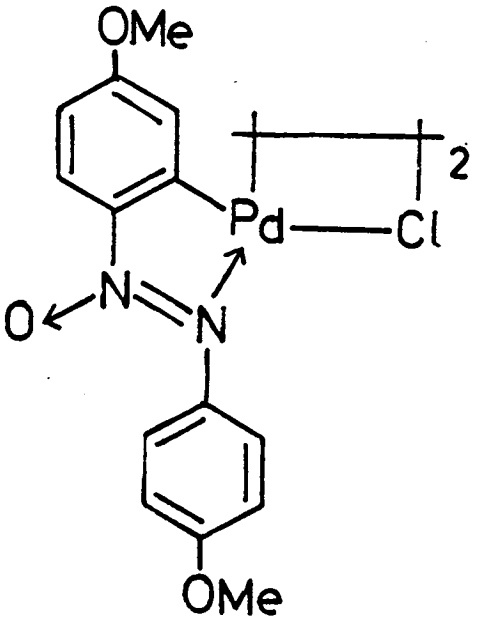
(2)

The cyclopalladation of some 2-hydroxyazobenzene derivatives has been reported recently by Steiner and L'Eplattenier.[13] These workers reported that the 2-hydroxyazobenzenes (8) reacted with potassium tetrachloropalladate in the presence of pyridine in dimethyl sulphoxide yielding the classical complex (9) and the cyclopalladated complex (10). Approximately equal amounts of (9) and (10) were formed and were separated by dry column chromatography. The analogous platinum complexes were also prepared.

In 1969 Balch and Petridis[18] reported that azoxybenzene underwent cyclopalladation yielding the complex (11).



(11)

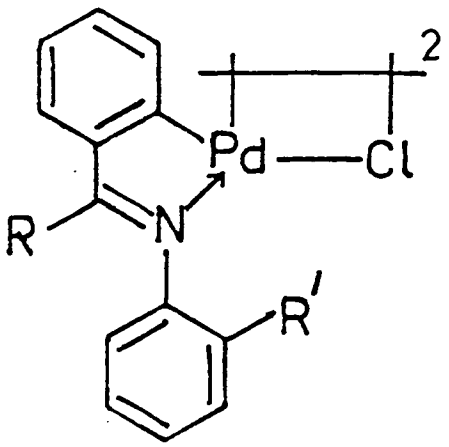


(12)

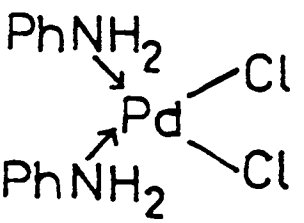
Cyclopalladation was achieved on reaction of azoxybenzene with lithium tetrachloropalladate in methanol under reflux for 48 hours. The resistance of azoxybenzene to cyclopalladation is in marked contrast to that of azobenzene which readily undergoes reaction, and is presumably a consequence of electron withdrawal by the azoxy group which would therefore deactivate the phenyl ring towards electrophilic attack.

Activation of the phenyl rings, as in the case of 4,4'-azoxyanisole had little effect, the cyclopalladated complex (12) being formed after 43 hours under the same reaction conditions.[19]

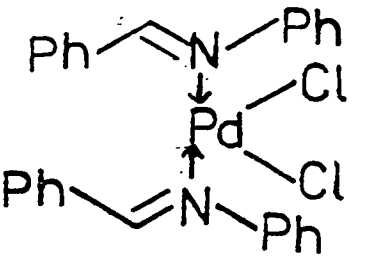
Schiff bases, which are structurally analogous to azobenzenes, might be expected to undergo cyclometallation. Although Pauson[20] in 1965 reported that Schiff bases reacted with di-iron nonacarbonyl, forming cyclometallated complexes, it was not until several years later that the first cyclopalladated Schiff base complexes were reported by Molnar and Orchin.[11] These workers reported that reaction of bis (benzonitrile) palladium (II) dichloride with several Schiff bases yielded cyclopalladated complexes of type (13).



(13)



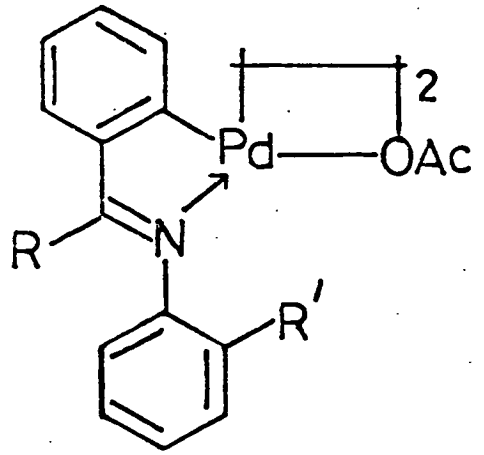
(14)



(15)

However these results have been disputed by several other workers. Onoue and Moritani[7] reported that the reaction of bis (benzonitrile) palladium (II) dichloride with benzylideneaniline yielded a mixture of the non cyclopalladated complexes bis (aniline) palladium (II) dichloride (14) and bis (benzylideneaniline) palladium (II) dichloride (15). Onoue and Moritani, Jardine and McQuillin[21] and later, Lewis et al[22] have suggested that the aniline complex was formed by hydrolysis of the co-ordinated benzylideneaniline ligand.

In the same investigation, Onoue and Moritani reported the synthesis of the acetate-bridged complexes (16) by reaction of the Schiff base with palladium acetate. The corresponding chloride-bridged complexes (13) were prepared by treatment of the acetate analogues with sodium chloride in acetone.



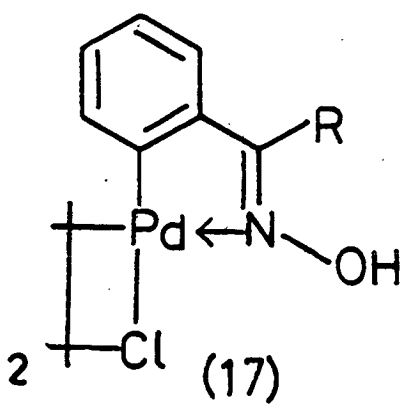
(a) $R = R' = H$

(b) $R = H$, $R' = Me$

(c) $R = Me$, $R' = H$

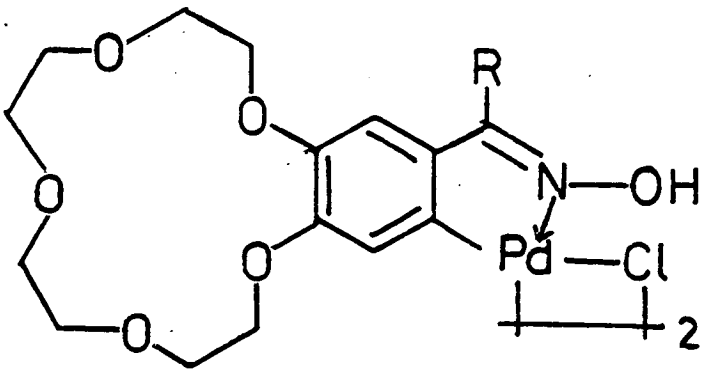
(16)

Another type of cyclometallated nitrogen donor ligand complex which may be included in this category is that formed on metallation of oximes of type (17), several examples of which have been reported.[23,24]

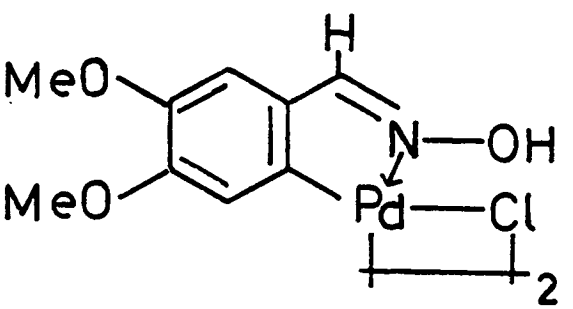


(17)

Recently, some oximes of crown ethers have been reported by Shaw and Shepherd[25] to undergo cyclopalladation. The oximes of 15-formyl-and 15-acetylbenzo- 15-crown-5 were treated with palladium chloride in ethanol in the presence of a small amount of lithium chloride and tetra-n-butylammonium acetate yielding the complexes (18a and 18b) respectively.



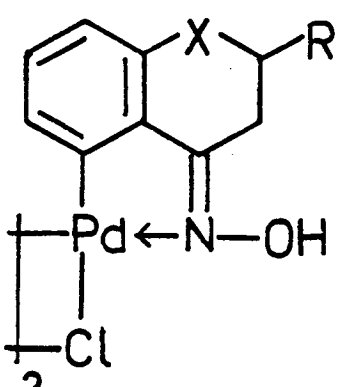
(18a, R = H)
(18b, R = Me)



(19)

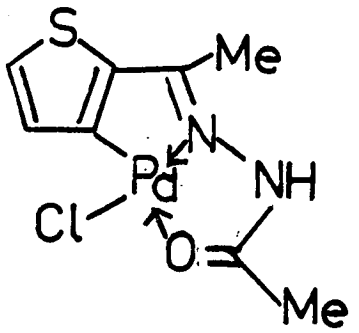
3,4-dimethoxybenzaldoxime also reacted with sodium tetrachloropalladate yielding the cyclopalladated complex (19), which they used for model studies.

Further examples within this category of compounds are the cyclopalladated chromanone and thiochromanone oxime complexes (20a-c), which have been reported recently by Kasahara et al.[26]

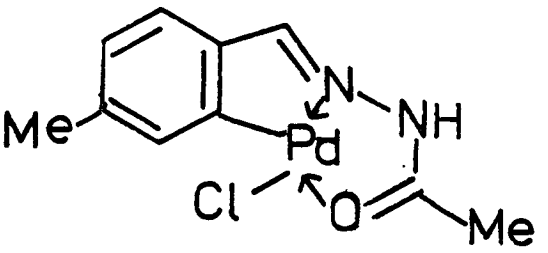


(20)

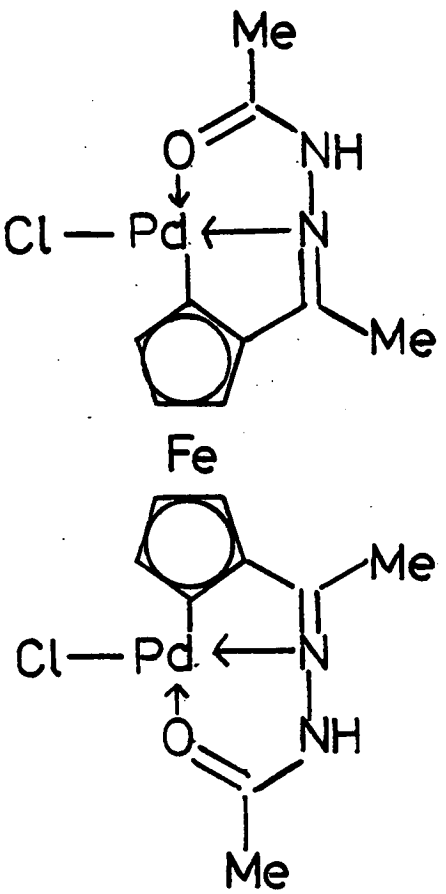
(a) R = H, X = O
(b) R = Ph, X = O
(c) R = Me, X = S



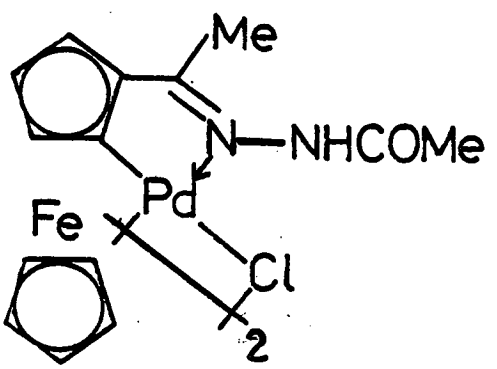
(21)



(22)



(23)



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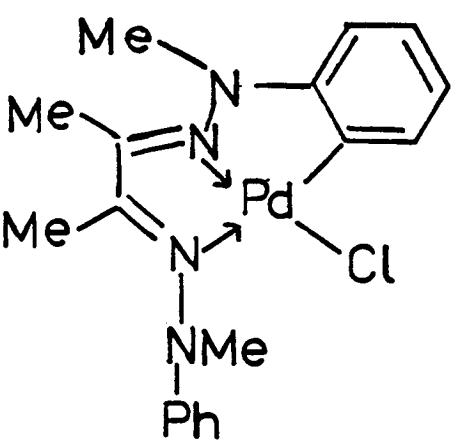
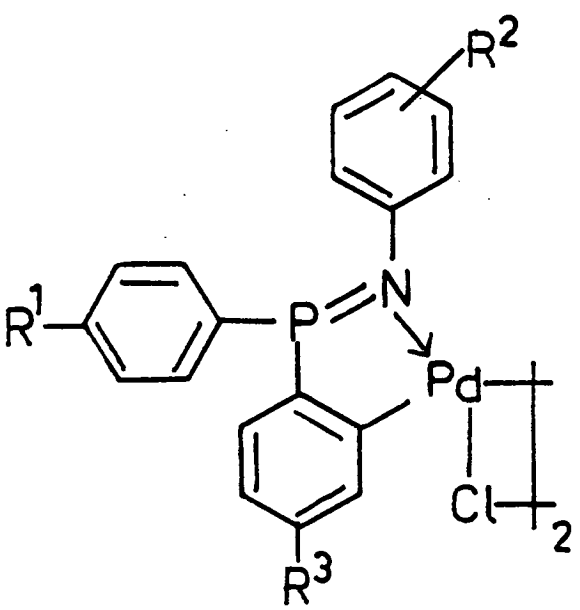


(25)

Some interesting cyclopalladated acetylhydrazone complexes have been prepared by Nonoyama.[27,28] These complexes are interesting in that in most cases, the oxygen atom of the acetylhydrazone moiety co-ordinates to the palladium atom, as exemplified in the acetylhydrazone complexes of 2-acetylthiophene (21), p-methylacetophenone (22) and 1,1'-diacetylferrocene (23). These complexes were prepared by direct reaction of the appropriate ligands with lithium tetrachloropalladate in the presence of sodium acetate in methanol. The complex (23) is also interesting in that it is the first example of a di-cyclometallated ferrocene. However, it was found that acetylferrocene acetylhydrazone reacted with lithium tetrachloropalladate to give the complex (24) in which there was no co-ordination of the oxygen to palladium, as shown by infrared studies.

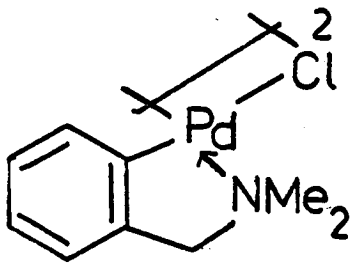
A similar type of co-ordinate bonding is present in the osazone complex (25), prepared by Caglioti et al.[29]

The replacement of one nitrogen atom in azobenzene by a PR_2 group gives rise to a phosphinimine. A series of phosphinimines have been reported by Alper[30] to undergo cyclopalladation upon treatment with sodium tetrachloropalladate yielding complexes of type (26).



	R^1	R^2	R^3
(a)	H	m-Me	H
(b)	H	p-Me	H
(c)	H	p-OMe	H
(d)	Me	p-OMe	Me

(26)



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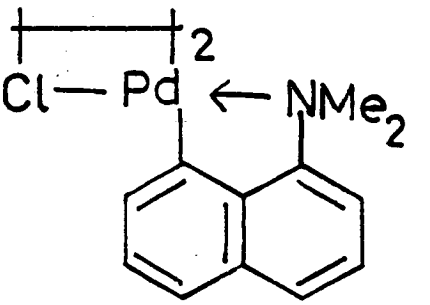

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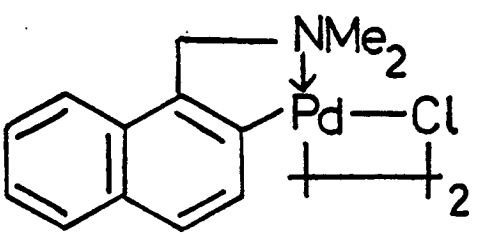

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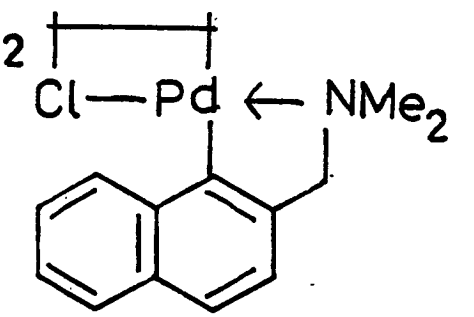

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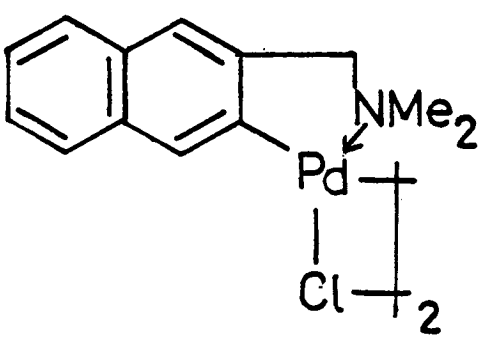


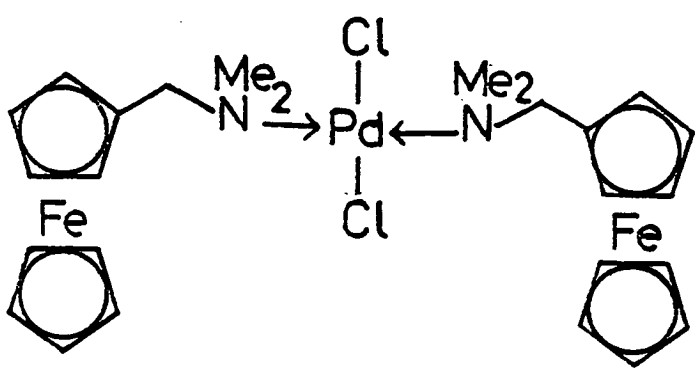
(31)

(2.2) CYCLOPALLADATED COMPLEXES OF BENZYLIC AMINES AND RELATED COMPOUNDS

In 1968 Cope and Friedrich[16] reported that N,N-dimethylbenzylamine and N,N-dimethyl-1-napthylamine formed the cyclopalladated complexes (27) and (28) respectively, upon treatment with lithium tetrachloropalladate. The related compounds 1 and 2-dimethylaminomethylnapthalene have also been shown to react in an analogous manner[31]. In the former case, palladation occurred in the 2-position, as one would expect, yielding the complex (29), but in the latter case two cyclopalladated complexes were formed, one in which palladation had occurred in the 1-position (30) and the other in which palladation had occurred in the 3-position (31). The product ratio (30) : (31) was 2 : 1.

It has been established that a ferrocene ring is much more susceptible to electrophilic attack than a benzene ring.[32] In an attempt to cyclopalladate the ferrocene ring, Moynahan et al[33] reacted dimethylaminomethylferrocene with potassium tetrachloropalladate in aqueous dioxan. However, cyclopalladation did not occur, bis (dimethylaminomethylferrocene) palladium (II) dichloride (32) being formed instead.

Several years later Shaw and Gaunt[34] repeated this reaction but in the presence of sodium acetate. Under these conditions, cyclopalladation occurred, yielding the complex (33).



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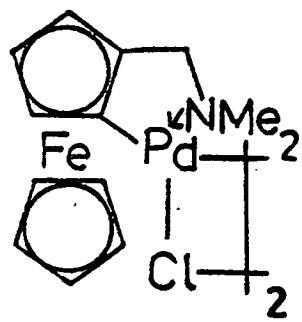


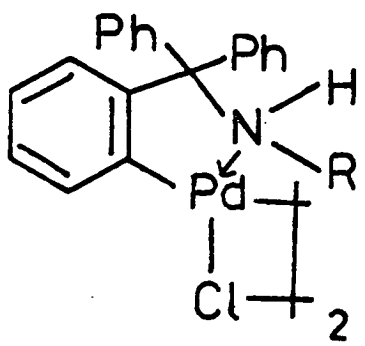
(33)

Further investigations in this area have been carried out by Sokolov et al.[35] Sokolov suggested that the role of the acetate ion was not restricted to the removal of the liberated hydrogen chloride, but rather, that it participated in an early stage in the reaction and that its presence in an intermediate state leading to the cyclopalladated complex (33) was essential. With a view to preparing an optically active complex (33) of high enantiomeric purity, Sokolov assumed that if the carboxylate ion was involved in the transition state of the reaction, then the anion of an optically active carboxylic acid and prochiral dimethylaminomethylferrocene would create conditions for asymmetric induction in the course of cyclopalladation.

In practice, cyclopalladation in the presence of N-acetyl-L-valine yielded optically active (33) of $[\alpha]_D$ 470-500°, (69-74% enantiomeric excess).

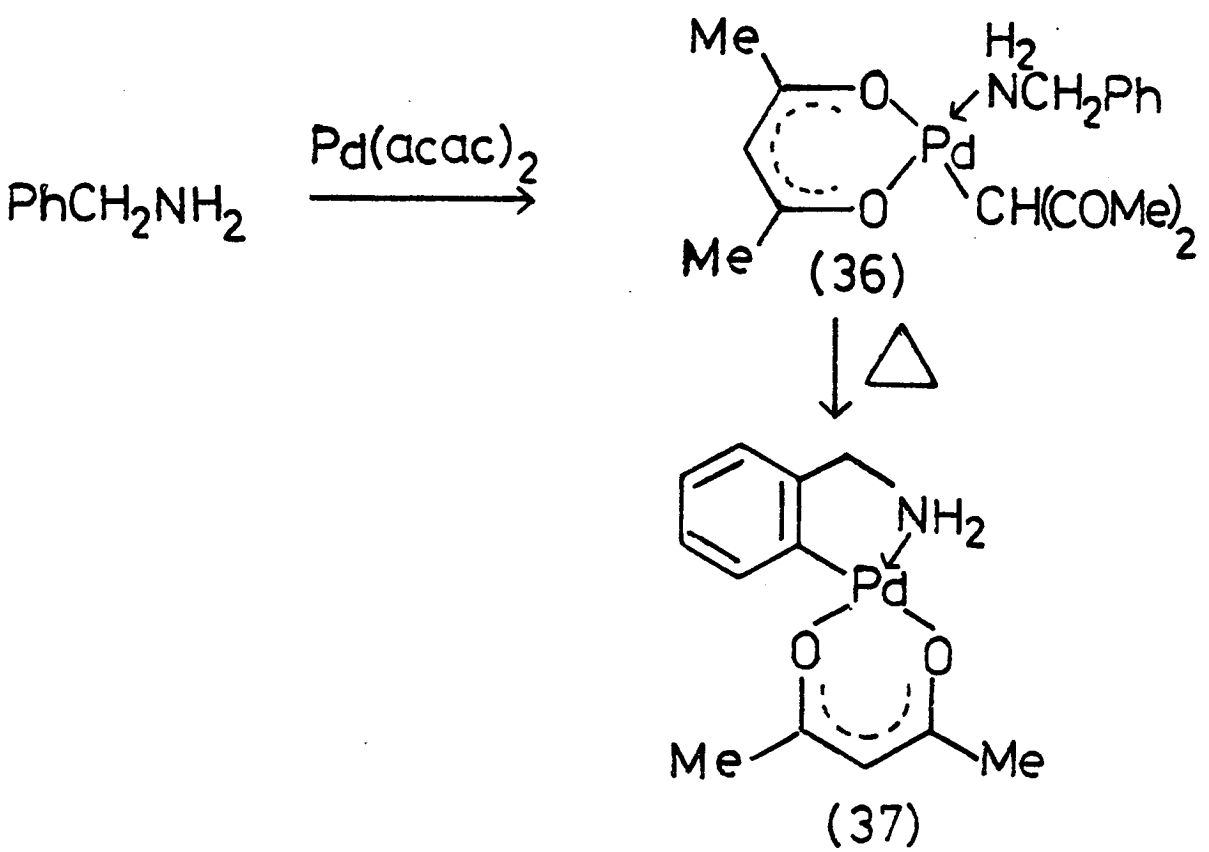
The initial attempts to cyclopalladate primary and secondary

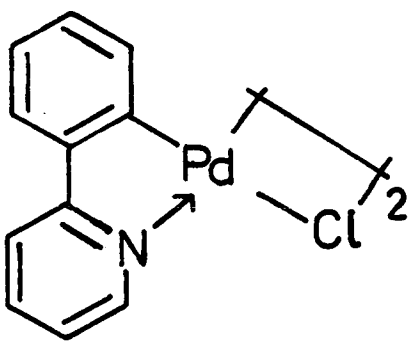
benzylic amines met with failure[16]. In these cases, only co-ordination complexes were formed. The first success in this area was in 1973 when Lewis et al[22] reported the cyclopalladation of triphenylmethylamine and N-methyltriphenylmethylamine which yielded the complexes (34) and (35) respectively.



(34, R=H)
(35, R=Me)

Benzylamine was later reported by Baba and Kawaguchi[10] to undergo cyclopalladation upon treatment with palladium acetylacetonate in benzene. A non-cyclised product (36) was formed initially and this underwent cyclisation upon refluxing of the solution, yielding the complex (37).





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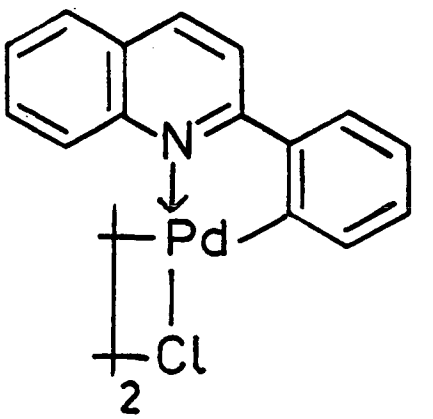
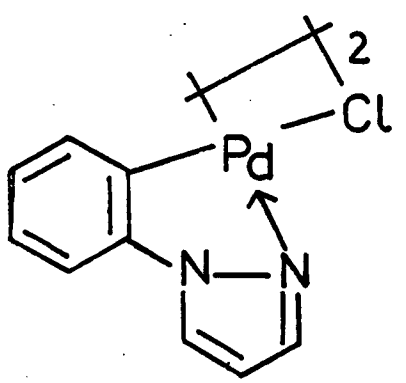
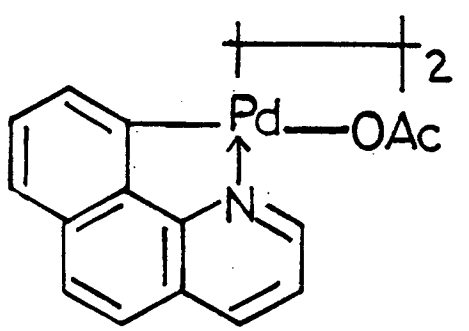


(41)

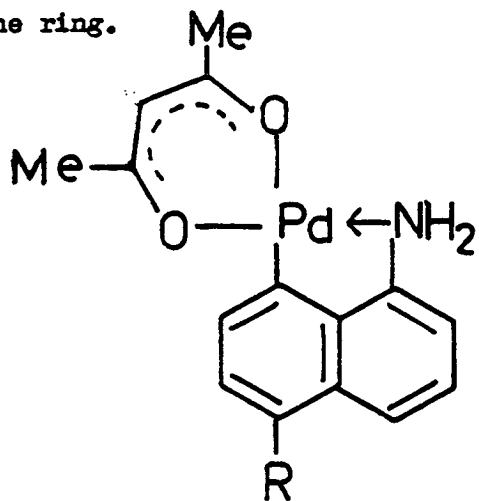


(42)



(43)

1-amino and 1,5-diaminonapthalene underwent cyclopalladation under the same conditions, yielding the complexes (38) and (39) respectively. The rate of cyclopalladation in the latter case was much greater and was attributed to electron donation by the 5-amino group, thus facilitating electrophilic substitution of the napthalene ring.

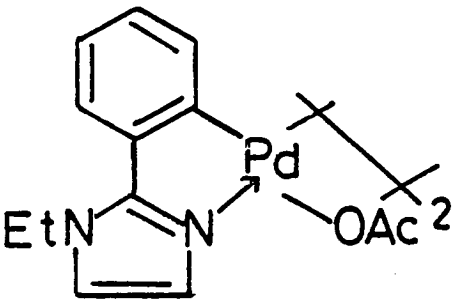


(38, R=H) (39, R= NH_2)

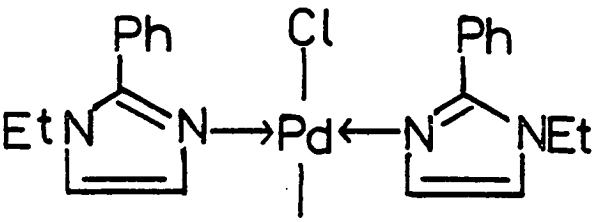
(2.3) PHENYL-SUBSTITUTED NITROGEN HETEROCYCLES

The first examples of this class of compounds to undergo cyclopalladation were 2-phenylpyridine and 2-phenylquinoline[36]. Kasahara[36] prepared the respective cyclopalladated complexes (40) and (41) by reaction of the ligands with sodium tetrachloropalladate. Other cyclopalladated complexes of this type include those of 1-phenylpyrazole[1,19] (42) and benzo [h] quinoline[22,37,38](43).

Recently Hiraki et al[8] reported the cyclopalladation of 1-ethyl-2-phenylimidazole by reaction with palladium acetate which yielded the complex (44). The analogous reaction with lithium tetrachloropalladate yielded only the co-ordination complex bis (1-ethyl-2-phenylimidazole) palladium (II) dichloride (45).

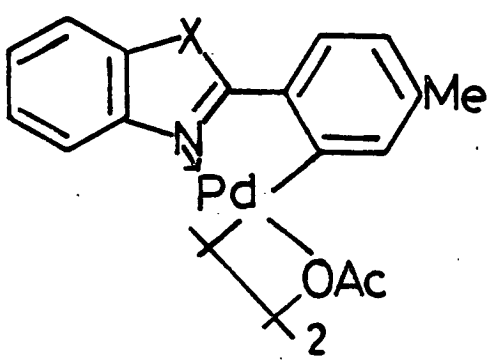


(44)



Cl (45)

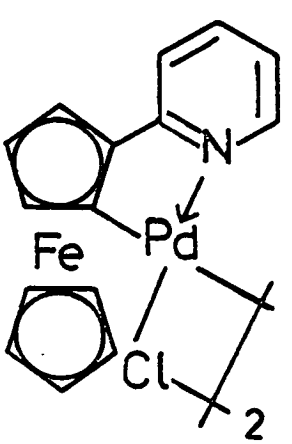
The most recent report of cyclopalladated ligands of this type are those of 2-p-tolylbenzothiazole (46) and 2-p-tolylbenzoxazole[39] (47) which were prepared by reaction of the ligands with palladium acetate. X-ray diffraction studies on these complexes established that they were nitrogen donor complexes and not sulphur or oxygen donors.



(46, X=S)

(47, X=O)

Another cyclopalladated complex which can be included in this particular classification is that of 2-pyridylferrocene (48), which has been reported by Kasahara et al.[40]

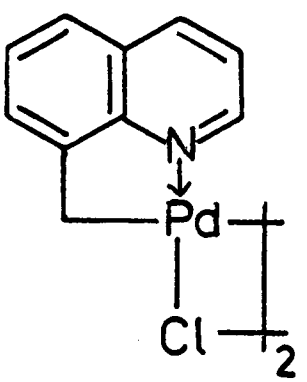


(48)

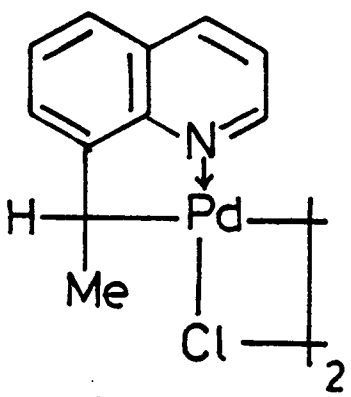
(2.4) 8-ALKYLQUINOLINES AND RELATED COMPOUNDS

In contrast to other nitrogen donor ligands in which the site of cyclopalladation is at an aromatic carbon centre, this class of compounds undergo cyclopalladation at a non-aromatic carbon centre.

The first report of a complex of this type was that of 8-methylquinoline (49), prepared by Hartwell et al[38] in 1970. Sokolov et al[41] have also prepared the 8-ethyl analogue (50) which is of interest in that a chiral centre is formed on the carbon atom bonded to palladium and partial resolution of enantiomers was observed by these workers.

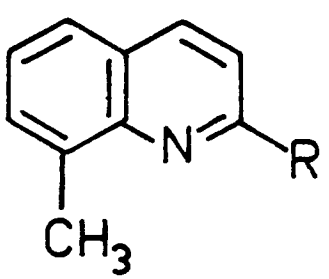


(49)



(50)

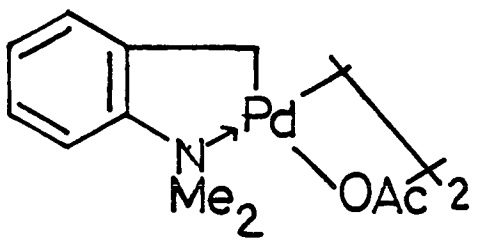
Deeming and Rothwell[14] have investigated the cyclopalladation of several 2-substituted-8-methylquinolines (51 a - g).



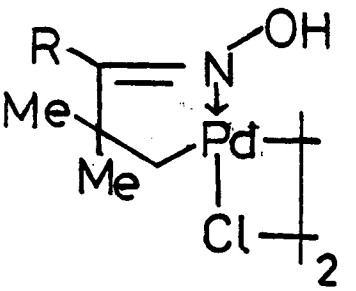
(51)

R

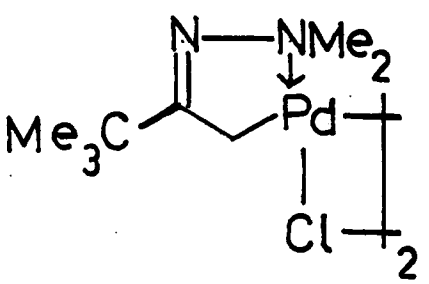
(a) H
(b) Me
(c) Br
(d) CHO
(e) CH=NMe
(f) CO_2H
(g) CH_2OH



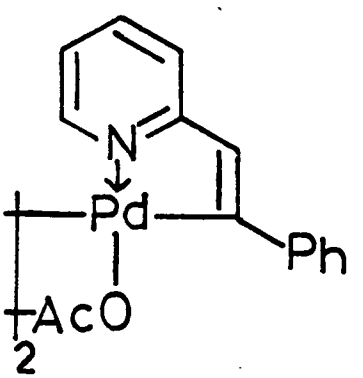
(52)



(53) (a, R=Me)
(b, R=Et)
(c, R=Ph)



(54)



(55)

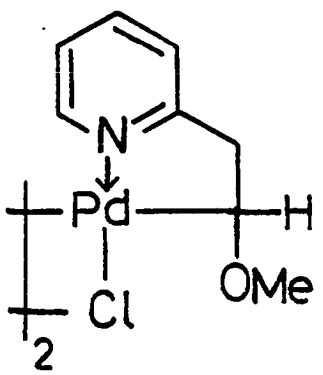
It was observed that the quinolines (51a) and (51 e - g) were readily cyclopalladated by palladium acetate in chloroform but the remaining quinolines (51 b - d) were not cyclopalladated at all. It was proposed that cyclopalladation at the 8-methyl group only occurred when the substituent R was a sufficiently good ligand itself to form a 5-membered chelate ring containing the quinoline nitrogen and thus forcing the 8-methyl group close to the palladium atom in the co-ordination plane. The lack of cyclopalladation of (51 b - d) was not attributed to any significant difference in their ability to co-ordinate, but rather to the inability of these quinolines to rotate easily about the Pd - N bond as a result of steric hindrance of the substituent R with the adjacent cis ligand.

Other examples of the cyclopalladation of C-methyl groups include the complexes of o-(N,N-dimethylamino) toluene [42](52), the methyl, ethyl and phenyl ^{t}butyl ketone oximes (53 a - c) and the dimethylhydrazone of pinacolone[43](54).

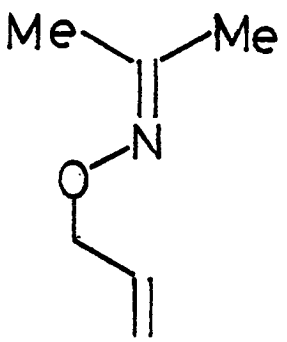
Olefinic C - H bonds have also been reported to undergo cyclopalladation as exemplified by the 2-styrylpyridine complex [44](55). 2-vinylpyridine[45] also undergoes cyclopalladation but the vinyl group also undergoes addition of methanol (from solvent) leading to the 2-methoxy-2(α-pyridyl)ethyl complex (56). In a similar way, oxime O-allyl ethers, eg. (57) undergo cyclopalladation accompanied by nucleophilic attack by methoxide on the terminal allylic carbon leading to the complex[43](58).

(3.1) CYCLOPALLADATED SULPHUR DONOR LIGARDS

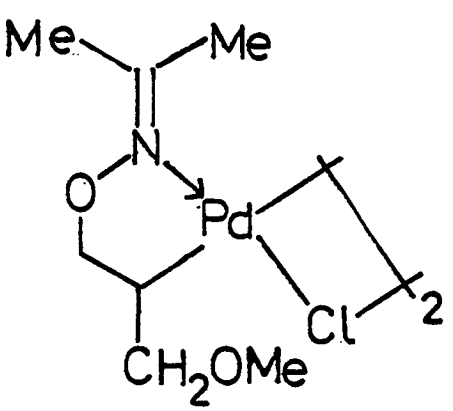
Compared with nitrogen-donor ligands, there have been relatively few reports of cyclopalladated sulphur donor ligands. The first cyclopalladated sulphur-donor ligand complex was that of



(56)

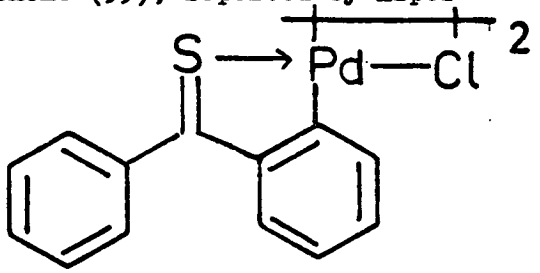


(57)

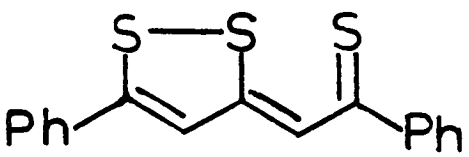


(58)

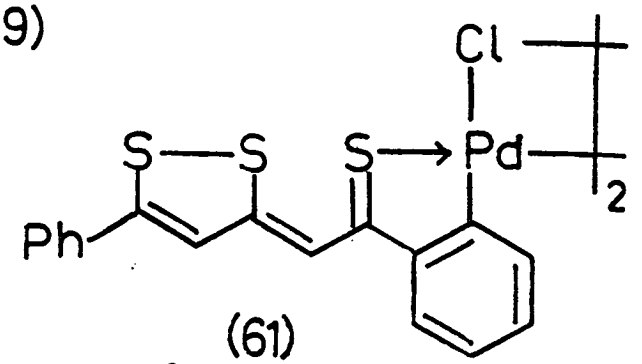
thiobenzophenone (59), reported by Alper[46] in 1973.



(59)



(60)



(61)

Recently Locatelli et al[9] reported that treatment of 2,5-diphenyl-1,6,6aλ^4 - trithiapentalene (60) with palladium chloride in boiling methanol - benzene mixture yielded the cyclopalladated complex (61), the structure of which was confirmed by X-ray analysis.

Several other cyclopalladated sulphur donor ligand complexes have been reported by Davis[44] and Grinter[47] and will be discussed in detail later.

(4) LIGAND EXCHANGE REACTIONS

(4.1) BRIDGE-SPLITTING REACTIONS

The formation of momomeric complexes by the cleavage of ligand-bridged dimers is referred to as a bridge-splitting reaction. This type of reaction is widely used in organometallic chemistry. In the field of cyclometallation, the role of this reaction has been, in general, to facilitate the characterisation of the cyclometallated system.

In the majority of cases, ligand bridged dimeric complexes are insoluble and involatile. Their characterisation is greatly

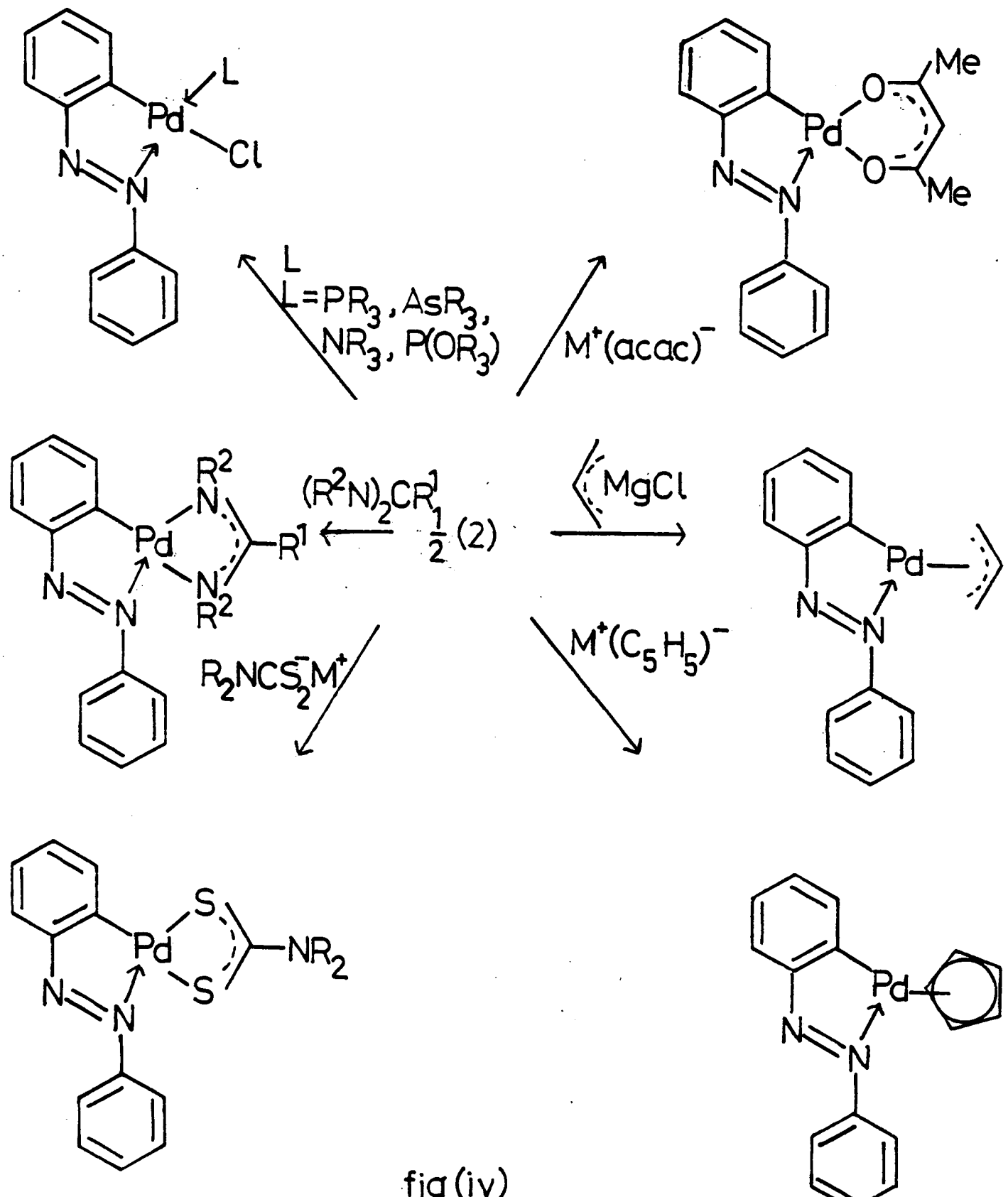

L
Pd
Cl
N
N
L
L=PR3, AsR3,
NR3, P(OR3)
M+(acac)−
Me
O
Pd
O
Me
R2
N
(R2N)2CR1
R1
1/2 (2)
MgCl
Pd
R2
R2NCS2−M+
M+(C5H5)−
S
NR2
S

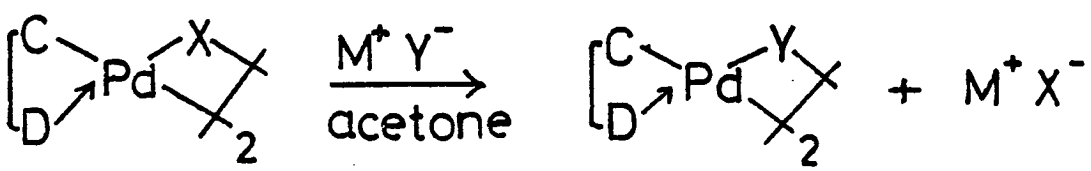
fig (iv)

aided by bridge-splitting reactions, which, on the whole, result in the formation of soluble, crystalline derivatives that are more amenable to characterisation by standard spectroscopic, analytical and crystallographic methods.

The most common bridge-splitting reagents are phosphines, amines, acetylacetone and cyclopentadienide. Less common reagents include arsines, phosphites, amidines and the allyl anion. In this work, dithiocarbamates were used to a greater extent than any of the above as bridge-splitting reagents. Almost all dimeric cyclometallated complexes have been characterised by bridge splitting reactions. The general reaction is illustrated in figure (IV), using the cyclopalladated azobenzene ligand as a typical example.

(4.2) METATHETICAL EXCHANGE REACTIONS

In addition to undergoing bridge-splitting reactions, dimeric ligand-bridged complexes also undergo metathetical exchange in which the nature of the bridging ligands is changed. The most common metathetical exchange reaction is the conversion of acetate-bridged dimers to the chloride-bridged analogues. Ligand exchange is normally effected by treatment of the ligand-bridged complex with an excess of an alkali metal salt of another bridging ligand in acetone. The general reaction is illustrated in figure (V).



C, D = cyclopalladated ligand

M^+ = alkali metal

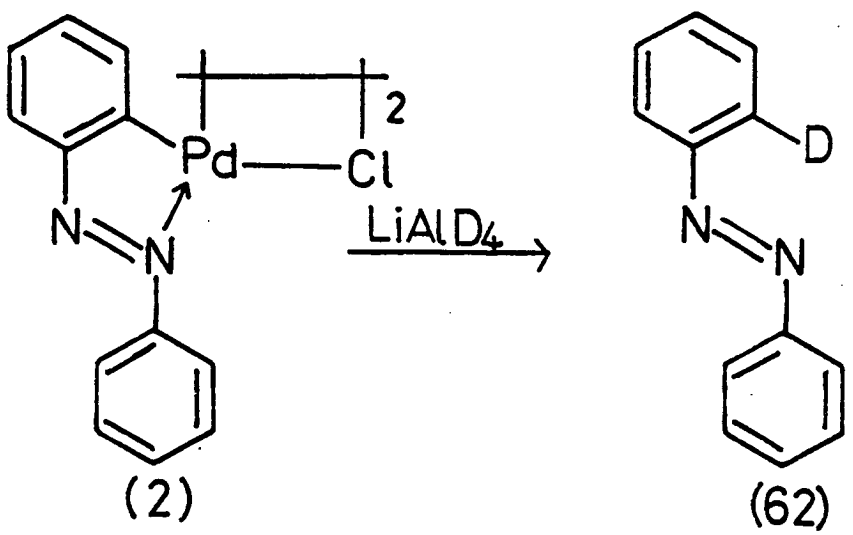
X, Y = Cl, Br, I, SCN, CH_3CO_2, CF_3CO_2

fig (v)

(5) APPLICATIONS OF CYCLOPALLADATED COMPLEXES IN ORGANIC SYNTHESIS

(5.1) DEUTERIATION

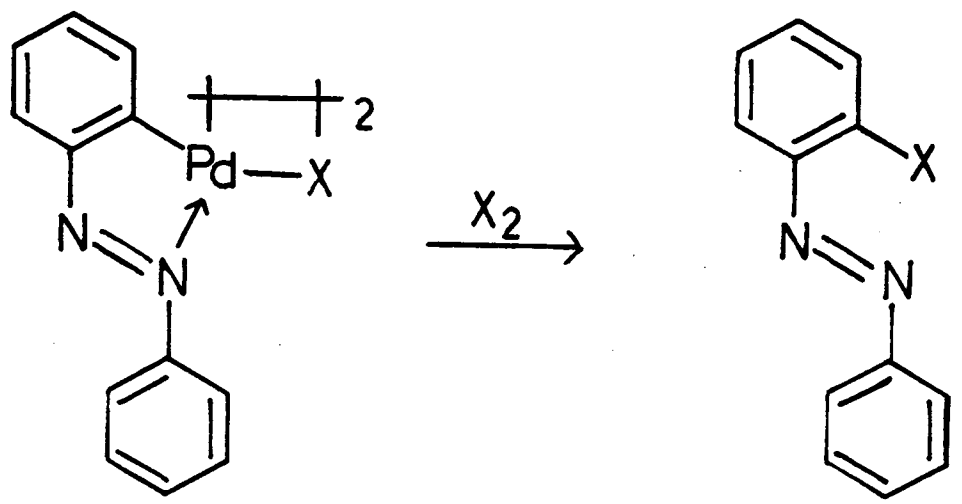
One of the first and simplest applications of cyclopalladated complexes in organic synthesis was the specific ortho-deuteriation of ligands such as azobenzene. As discussed previously, Cope and Siekman[4] established the site of palladation in the azobenzene complex (2) by reduction with lithium aluminium deuteride, the reduction product being azobenzene-2-d_1 (62). This reaction can be extended to many other cyclopalladated ligands.



(2) (62)

(5.2) HALOGENATION

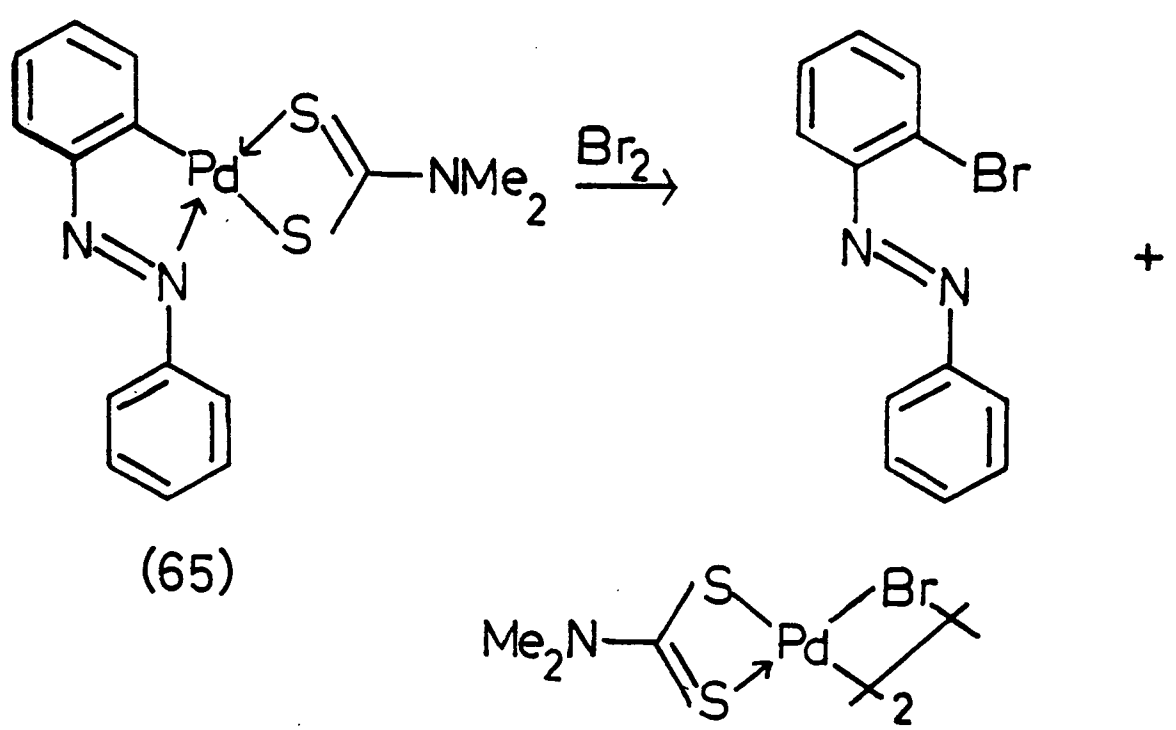
In 1971 Fahey[48] reported the ortho-halogenation of azobenzene in the presence of a catalytic amount of palladium chloride. Chlorination yielded all possible ortho-chlorinated products and exhaustive chlorination led to 2, 2', 6, 6'-tetrachloroazobenzene. The specificity of halogenation was attributed to the formation of the cyclopalladated complex (63), which could be isolated from the reaction mixture, and which then reacted further to yield the products by replacement of palladium in the cyclopalladated complex by a halogen. Further evidence for the intermediacy of a cyclopalladated complex was obtained when Fahey reported that complex (63) reacted with chlorine and bromine forming 2-chloro-and 2-bromoazobenzene (64a) and (64b)



(63) (64)

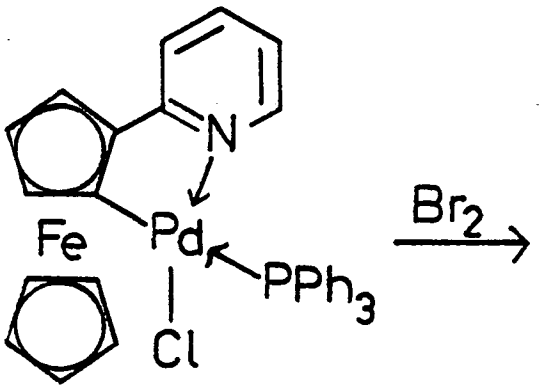
(a, X = Cl)

(b, X = Br)

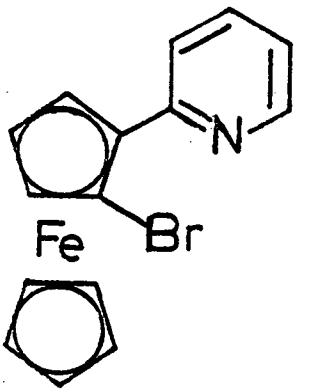


(65)

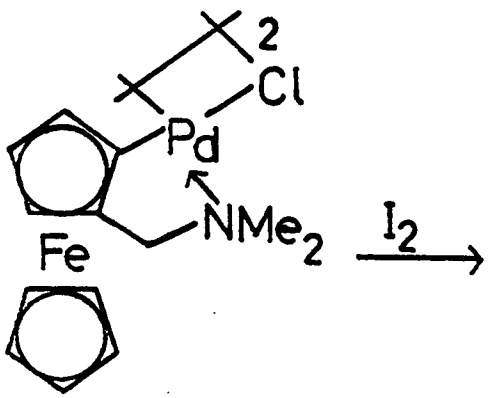
(66)



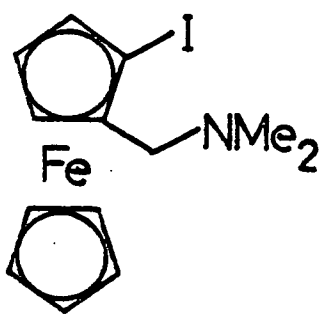
(67)



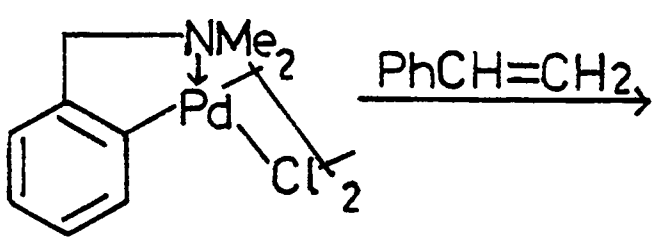
(68)



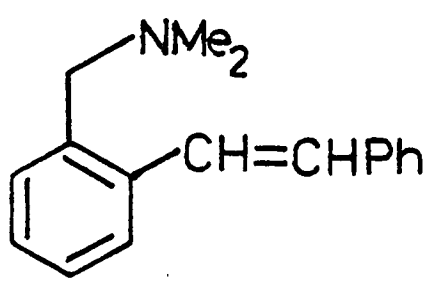
(33)



(69)



(27)



(70)

respectively in quantitative yield.

Davis[44] also reported that the dithiocarbamate complex (65) reacted with bromine forming 2-bromoazobenzene in 80% yield and di-μ-bromo-bis (N,N-dimethyldithiocarbamato) palladium (II) (66).

Other halogenation reactions of cyclopalladated complexes include the synthesis of 2-bromo-1-(2-pyridyl) ferrocene (68) from the complex[40] (67) and 2-iodo-1- (N,N-dimethylaminomethyl) ferrocene (69) from the complex[35] (33).

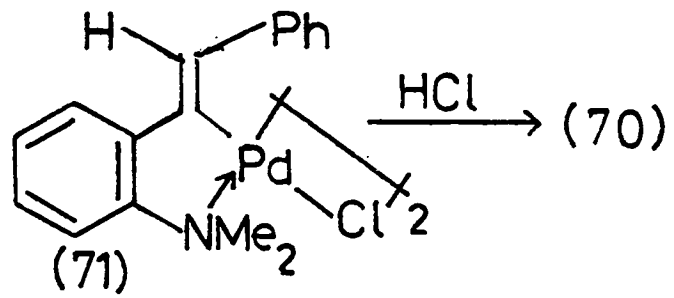
(5.3) VINYLATION

The replacement of palladium in a cyclopalladated complex by a vinyl group was first reported in 1969 by Tsuji[49] who claimed that the dimethylbenzylamine complex (27) reacted with styrene yielding o-dimethylaminomethylstilbene (70). However, no experimental details of this reaction have been published.

Heck[50] attempted to sythesise (70) by reaction of the acetate-bridged analogue of (27) with styrene but was unable to effect this conversion.

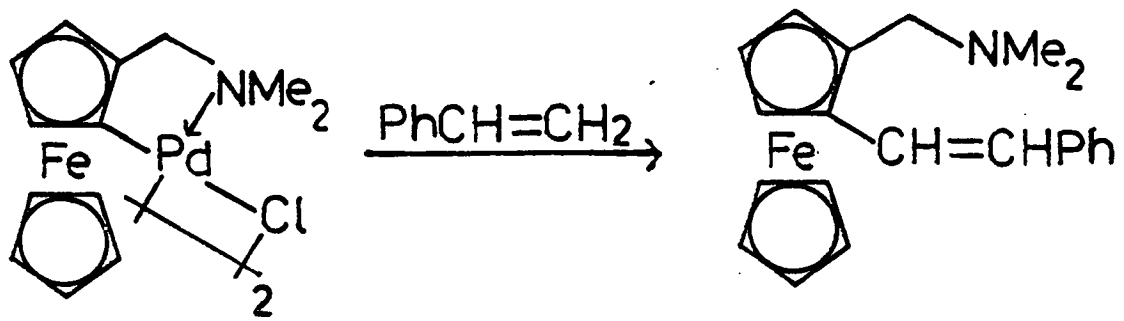
Recently Ryabov and Yatsimirsky[51] reported that (27) reacted with styrene in benzene provided that acetic acid was present. Under these conditions, the reaction product was not (70) but the cyclopalladated complex (71), although this product could be converted to (70) by treatment with hydrochloric acid. The reaction was also found to be more rapid when carried out in the presence of electrolytes such as sodium perchlorate, thus indicating a polar reaction intermediate.

The reaction yield was also improved from 18% to 24% when the electrolyte was present.



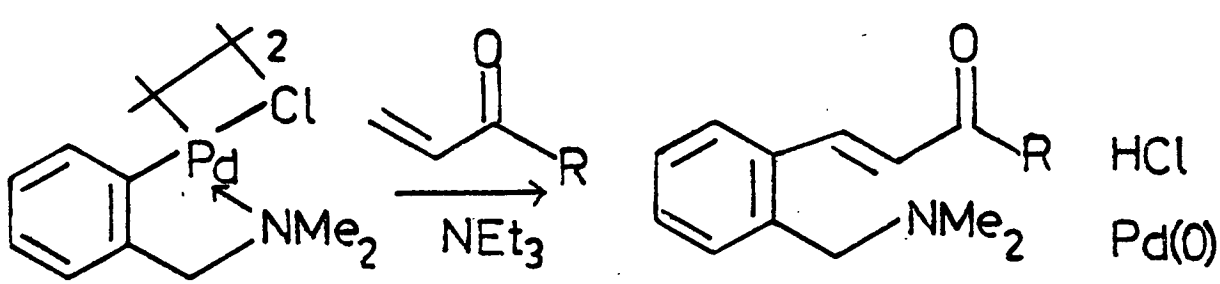
(71)

A successful direct replacement of palladium by styrene has been reported by Kasahara[52] et al who synthesised 2-styryl-(1-N,N-dimethylaminomethylferrocene) (72) from the complex (33) in 33% yield.



(33) (72)

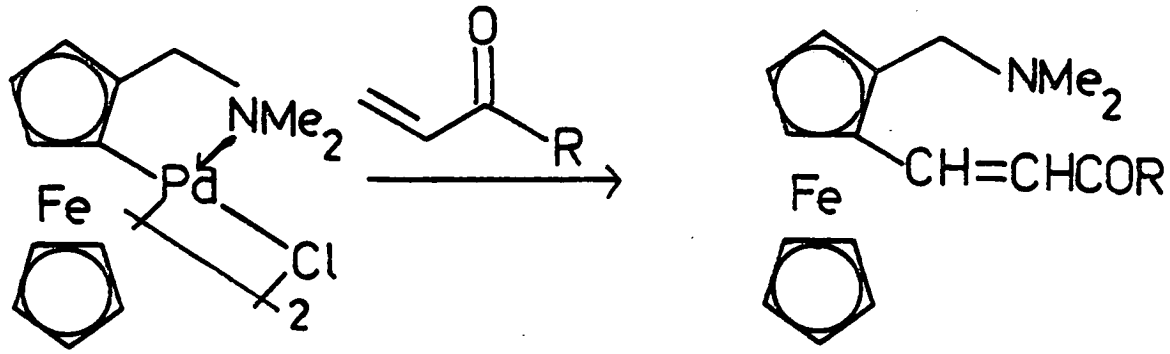
Holton[53] has reported a high yield vinylation of dimethylbenzylamine complexes. The complex (27) reacted with a series of vinyl ketones in boiling benzene or toluene, in the prsence of triethylamine, yielding vinylated dimethylbenzylamines (73). Only the trans isomers were obtained which are potential intermediates in alkaloid synthesis.



(27) (73)

R = Me, Et, c-C_6H_{11}, Ph

Kasahara et al[52] have extended Holton's general reaction to the synthesis of ferrocene derivatives (74), in moderate yields, from the cyclopalladated complex (33).

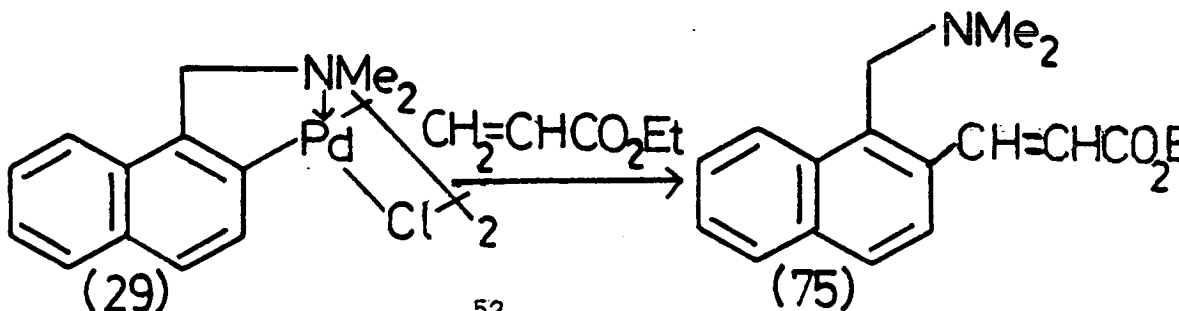


(33) (74)

R = Me, Ph

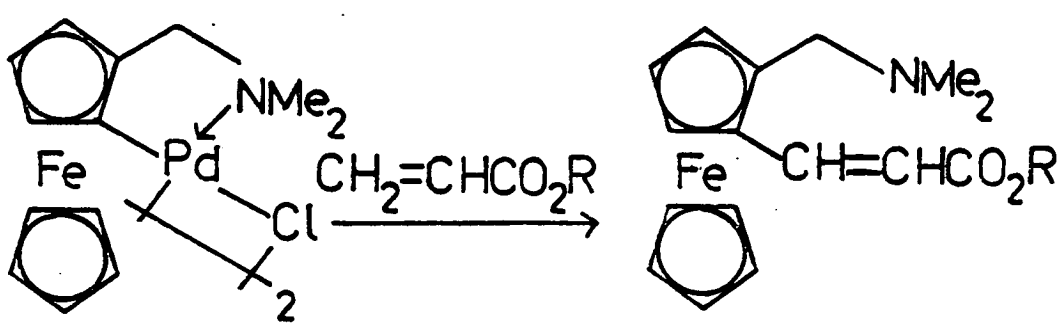
Sokolov et al[35,54] have also carried out the reaction of optically active (33) (59% enantiomeric excess) with methyl vinyl ketone and obtained optically active (74) (R = Me) in 80% yield.

In 1975 Julia et al synthesised ethyl-3-[1-(N,N-dimethylaminomethyl)-2-naphthyl]acrylate (75) in 70% yield by reaction of the complex (29) with ethyl acrylate in acetic acid at 100°.



(29) (75)

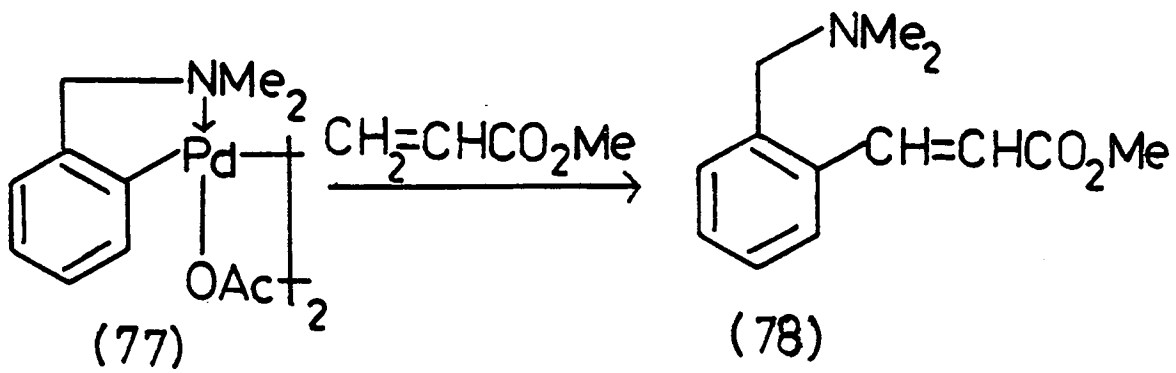
Later Kasahara et al[52] synthesised the ferrocene derivatives (76) in moderate yields by reaction of the complex (33) with methyl and ethyl acrylate in toluene at 100°.



(33) (76)

R = Me, Et

Recently Heck[50] has synthesised methyl o-(N,N-dimethylaminomethyl)-trans-cinnamate (78), in 17.5% yield, by reaction of the acetate-bridge complex (77) with methyl acrylate.



(77) (78)

Heck also observed a more interesting reaction of the Schiff base complex (79) with methyl acrylate in which the former incorporated two methyl acrylate units. The identity of the product was established as the tetralin derivative (80) by X-ray diffraction. Heck postulated a reaction mechanism to account for the formation of the tetralin and this is shown in figure (VI). The initial step is the normal arylation of methyl acrylate yielding trans-methyl-o-(N-phenylimidomethyl) cinnamate (81). Cyclopalladation of (81) forms (82) which, by two consecutive insertion reactions, first of an acrylate unit and then of the imine group, into the palladium-carbon bond is converted to (83). Reaction with acetic acid then generates the tetralin (80) and palladium acetate.

(5.4) ORTHO-ALKYLATION

Murahashi et al[55] treated cyclopalladated complexes of Schiff bases, azobenzenes and benzylamines with alkyl-lithiums and Grignard reagents yielding ortho-alkylated products in high yields. The general reaction scheme is shown in figure (VII). The Schiff base complex (84) was treated with 4 equivalents of triphenylphosphine forming (85). Reaction of (85) with an alkyl-lithium or alkyl Grignard reagent yielded the ortho-alkylated Schiff base (87)

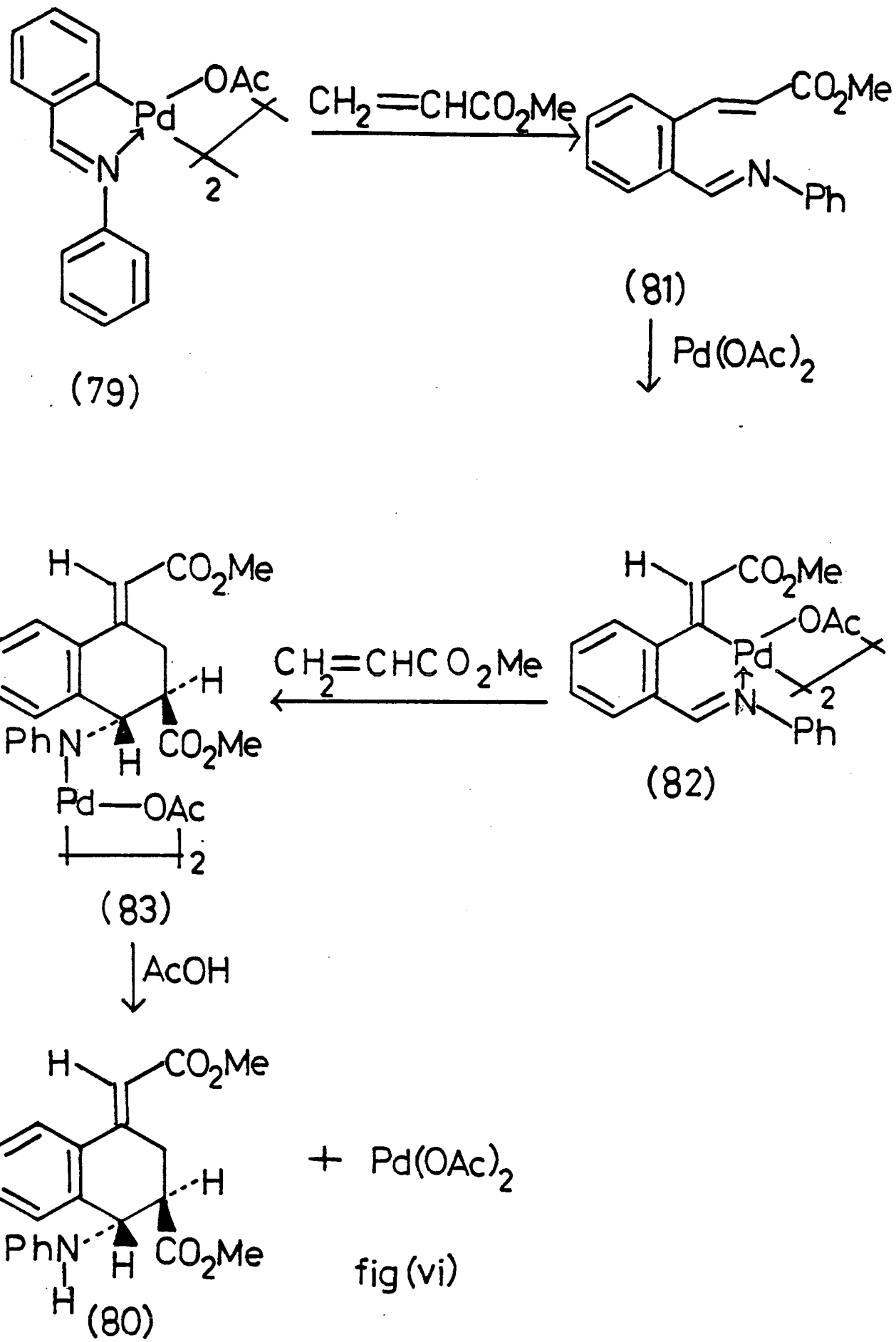

OAc
Pd
N
2
CH2=CHCO2Me
CO2Me
N
Ph
(79)
(81)
Pd(OAc)2
H
CO2Me
H
PhN
H
CO2Me
Pd—OAc
2
CH2=CHCO2Me
OAc
Pd
N
2
Ph
(83)
(82)
AcOH
H
CO2Me
H
PhN
H
H
CO2Me
(80)
+ Pd(OAc)2

fig (vi)

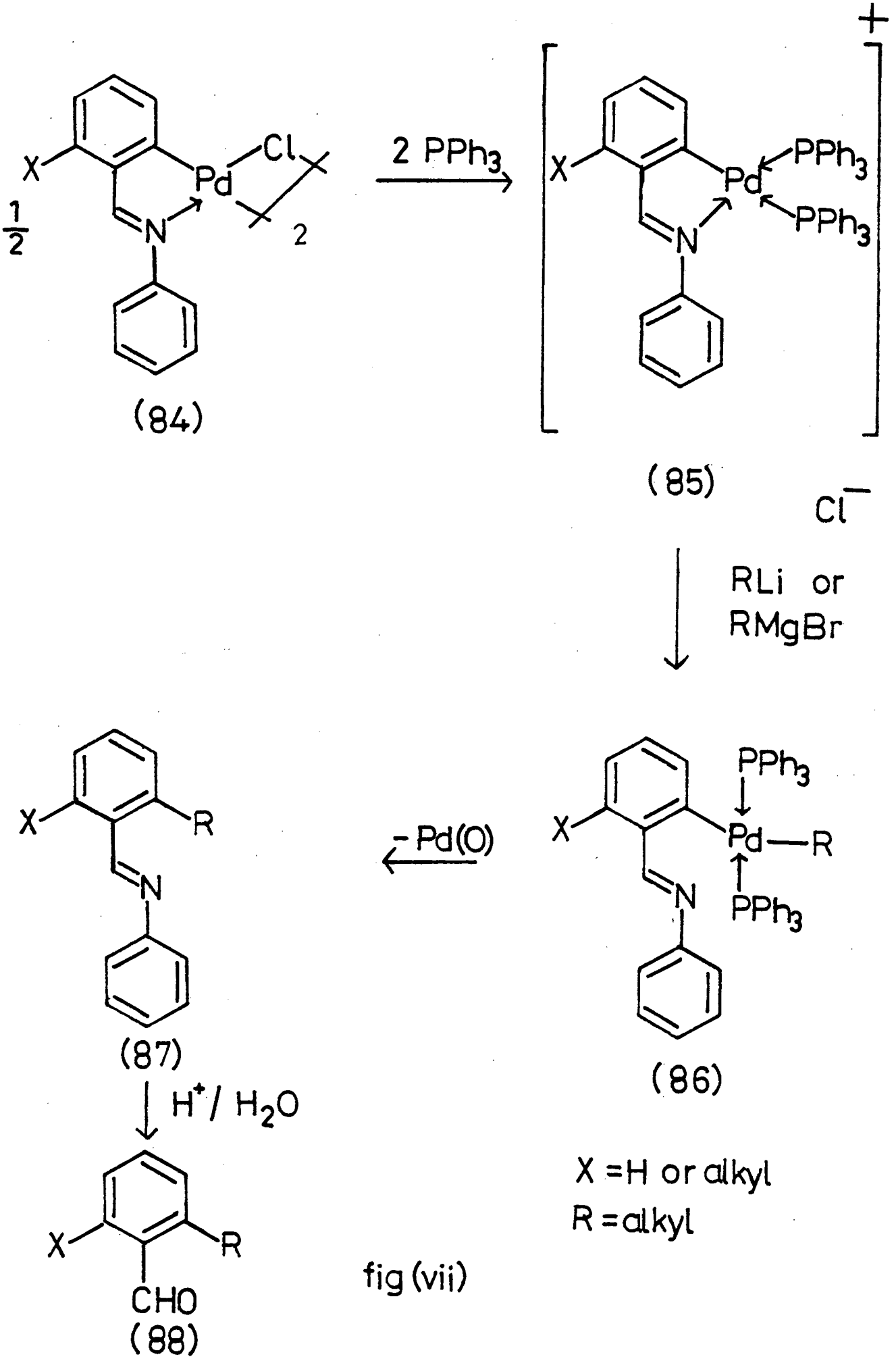
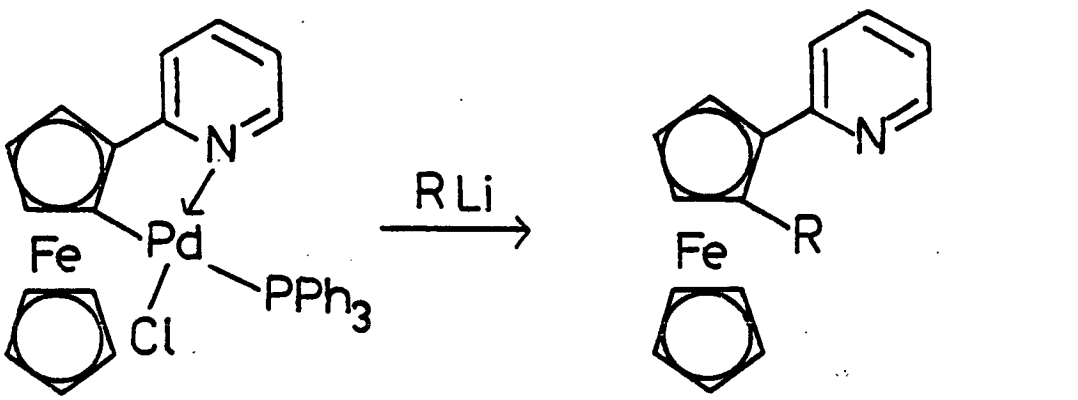

X
Pd
Cl
2
1/2
N
(84)
2 PPh3
PPh3
PPh3
(85)
Cl−
RLi or
RMgBr
PPh3
Pd—R
(86)
X =H or alkyl
R =alkyl
- Pd(0)
R
(87)
H+/ H2O
CHO
(88)

fig (vii)

presumably via the intermediate complex (86) which undergoes reductive elimination.

For (84), (X= H) this process can be performed twice thus forming (87), (X= alkyl), which upon hydrolysis, affords a 2,6-dialkyl substituted benzaldehyde (88), (X= alkyl), which is not accessible by other routes. Azobenzene and benzylamine complexes also underwent alkylation forming products analogous to (87) in high yields.

Kasahara[40] has reported similar reactions of the 2-pyridylferrocene complex (67), with butyl-lithium and phenyl-lithium, yielding 2-butyl-(89) and 2-phenyl-1-(2-pyridyl) ferrocene (90) respectively.



(67) (89, R= n-C_4H_9)

(90, R= Ph)

(5.5) CARBONYLATION

One of the earliest applications of cyclopalladated complexes in heterocyclic synthesis was reported by Takahashi and Tsuji[15] in 1967. A series of substituted azobenzene complexes (91) were carbonylated in alcohol or water forming 2-aryl-3-indazolinones (92) in high yield. The general reaction is illustrated in figure (VIII). The proposed mechanism involves firstly the co-ordination of carbon monoxide and the splitting of the chloride bridges forming (93). A molecule of carbon monoxide is then inserted at the

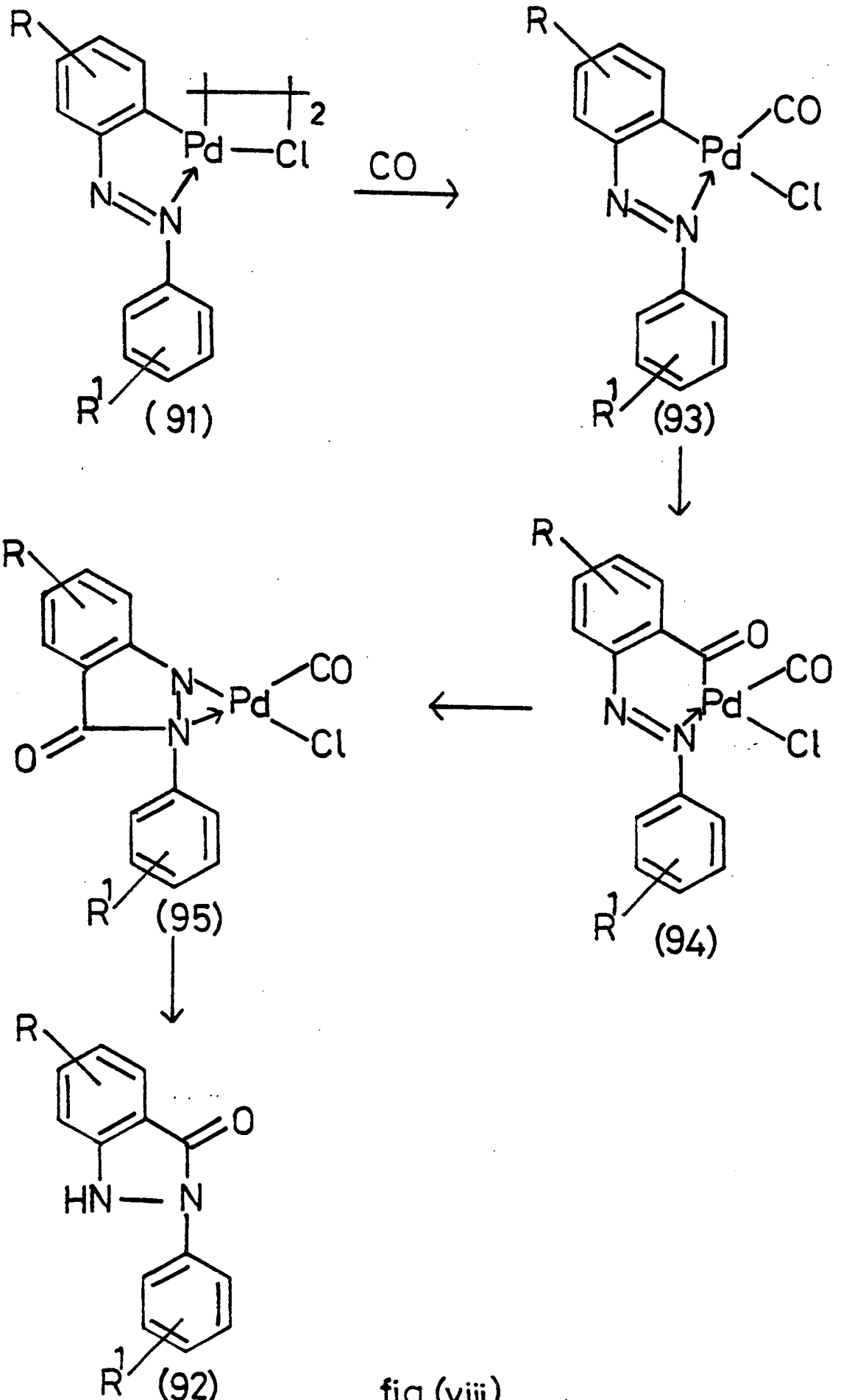


fig (viii)

palladium-carbon σ -bond forming an acyl palladium bond (94). The final step is the insertion of the nitrogen-nitrogen double bond into the palladium acyl bond forming (95) which then undergoes hydrogenolysis to give the indazolinone (92). Indazolinones were previously reported to be formed in the reaction of azobenzene with dicobalt octacarbonyl[56]. It is likely that this reaction also proceeds via a cyclometallated complex intermediate.

Heck and Thomson[57] extended this reaction to the acetate bridged complex (96). Carbonylation in chlorobenzene at 100° gave a mixture of the indazolinone (92), (R= R'= H) and the lactone (97). The postulated reaction pathway leading to the formation of the lactone is illustrated in figure (IX). Initial insertion of carbon monoxide leading to (98) is followed by addition of the acylpalladium moiety across the nitrogen-nitrogen double bond forming (99). Cyclopalladation forms the complex (100) which then undergoes a hydrogen shift from palladium to nitrogen and inserts carbon monoxide forming (101). Cyclisation then occurs by internal addition of the acylpalladium group to the amide carbonyl forming (102) which yields the product (97) by a 1,4-hydridopalladium acetate elimination. It is noteworthy that (97) is also the reaction product from the high temperature reaction of azobenzene with nickel tetracarbonyl.[58]

Heck also extended the carbonylation reaction to a series of cyclopalladated Schiff bases (16). A summary of these reactions is shown in figure (X). The complex (16) was carbonylated in xylene at 100°. The reaction products were thought to be derived from the intermediates (103) and (105). (16a) and (16b) reacted under these conditions to yield the phthalimidines (106). In contrast,

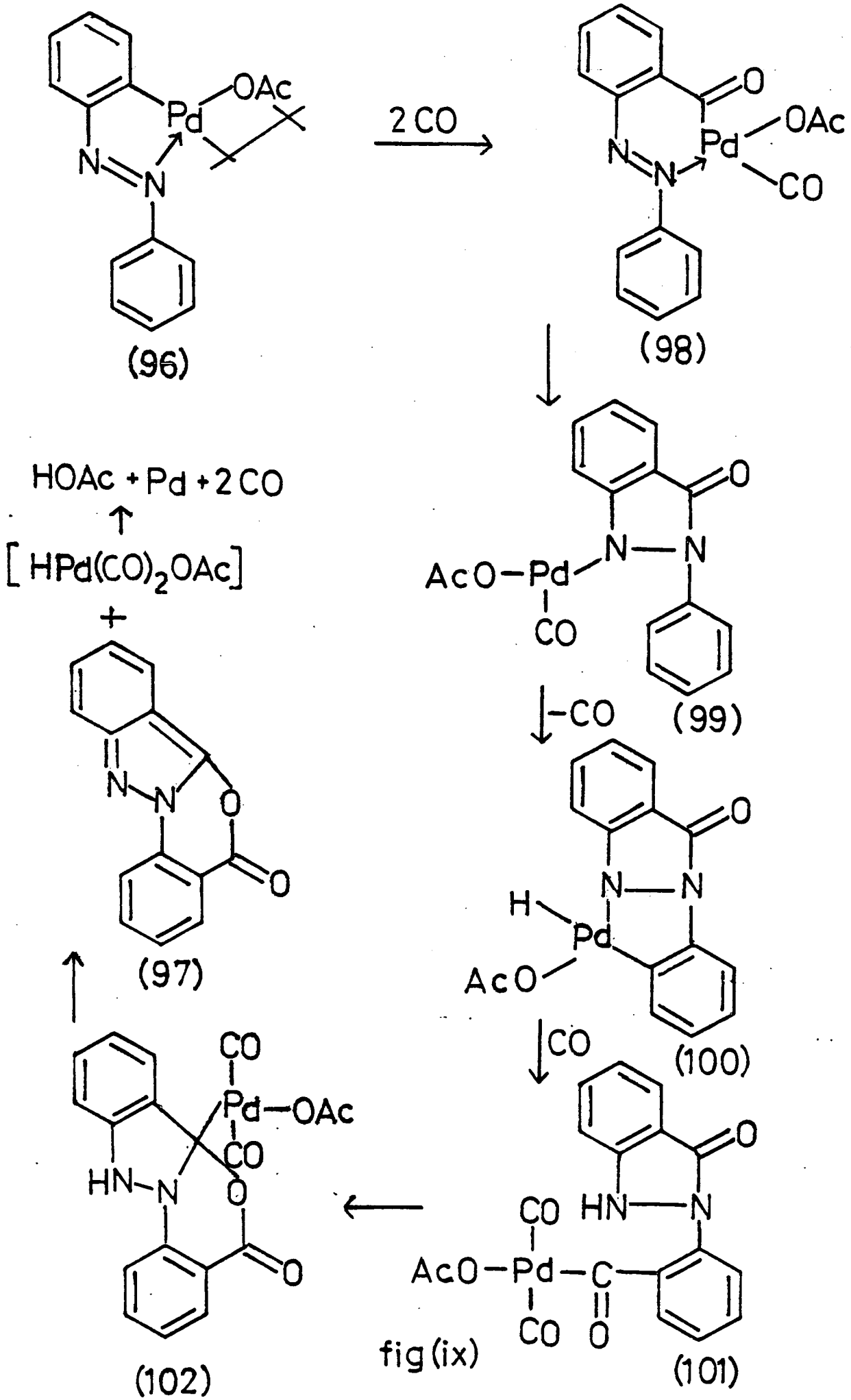
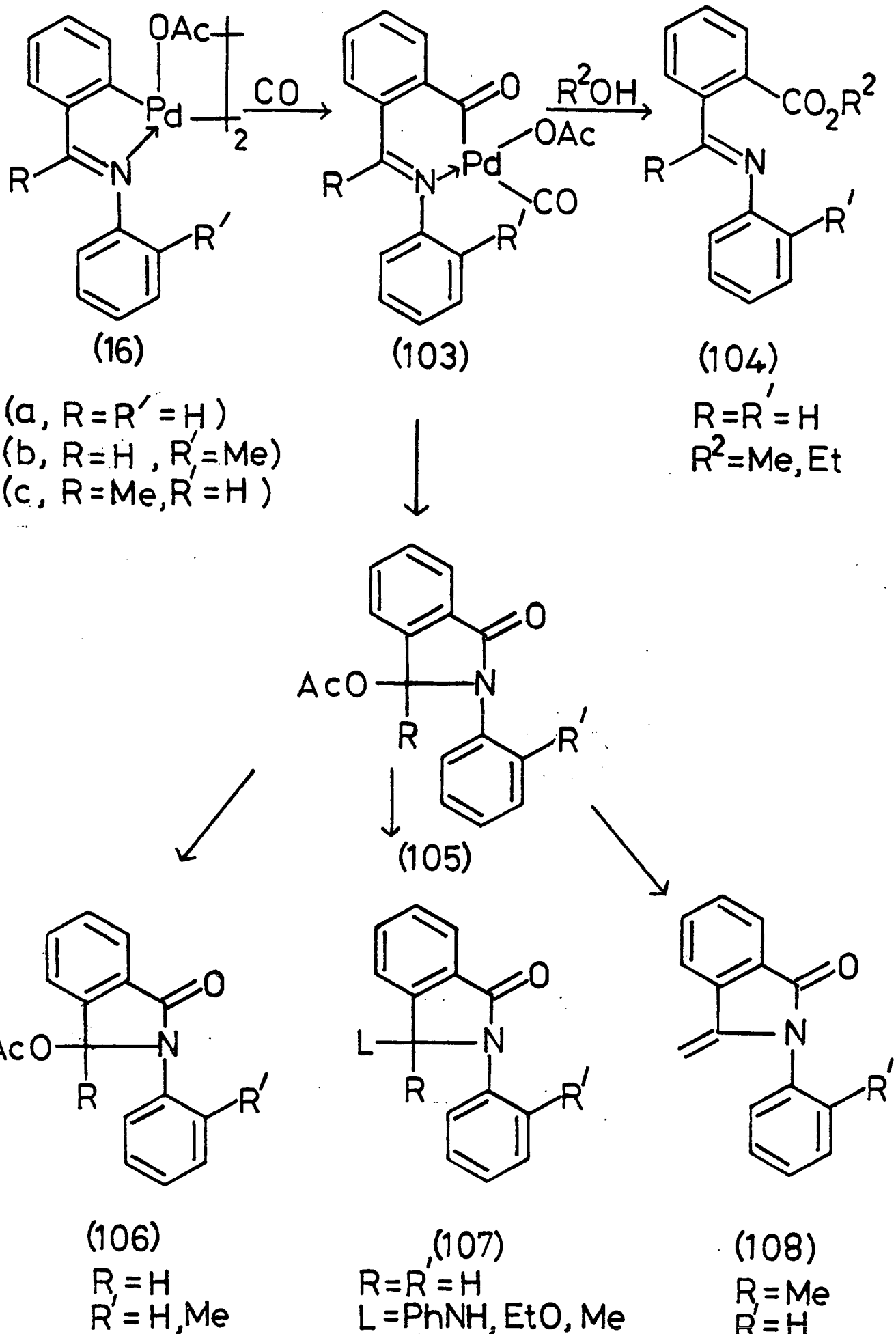

OAc
Pd
N
N
(96)
2 CO
O
OAc
Pd
CO
N
N
(98)
O
N — N
AcO — Pd
CO
(99)
-CO
O
N — N
H
Pd
AcO
(100)
CO
O
HN — N
CO
AcO — Pd — C
CO
O
(101)
CO
Pd — OAc
CO
HN — N
O
O
(102)
HOAc + Pd + 2 CO
[HPd(CO)2OAc]
+
N
N
O
O
(97)

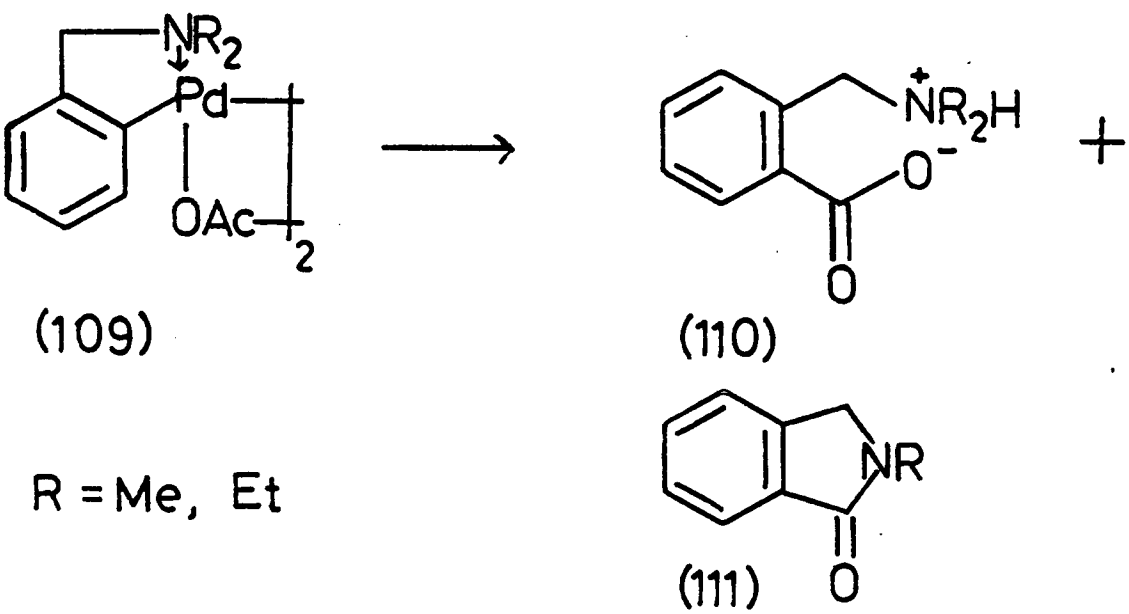
fig (ix)


OAc
Pd
2
CO
O
OAc
Pd
CO
R^2OH
CO_2R^2
R
N
R′
(16)
(103)
(104)
(a, R=R′=H)
(b, R=H, R′=Me)
(c, R=Me, R′=H)
R=R′=H
R^2=Me, Et
AcO
L
(105)
(106)
R=H
R′=H, Me
(107)
R=R′=H
L=PhNH, EtO, Me
(108)
R=Me
R′=H

fig(x)

(16c) yielded the methylenephthalimidine (108). (16a) and (16b) also reacted in the presence of nucleophilic solvents such as methanol, ethanol and aniline yielding the phthalimidines (107). In the presence of the alcohols the uncyclised Schiff base esters (104) were also formed.

A different type of reaction was observed in the carbonylation of the dialkylbenzylamine complex (109). Two products were obtained, one of which, (110) was probably formed via hydrolysis of an initially formed mixed anhydride, and the other, (111) more interestingly, was formed by cyclisation with the loss of an alkyl group.



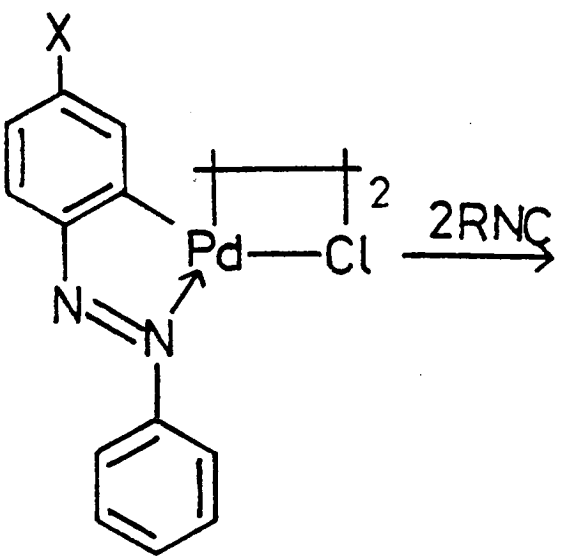
(109) (110)

R = Me, Et

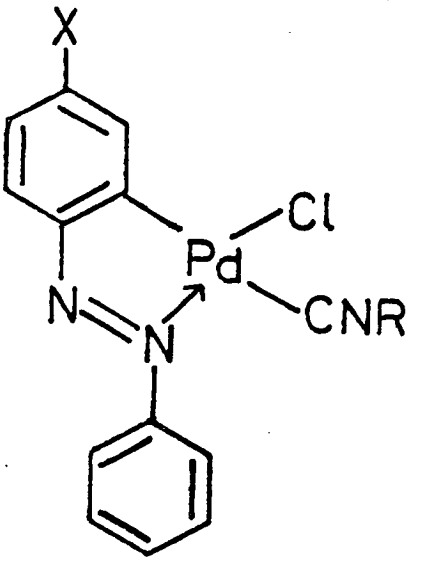
(111)

Heck also reported carbonylation reactions of azine, hydrazone and benzylamine Schiff base complexes but these reactions will not be discussed since they do not differ in principle from the preceding reactions.

Other carbonylation reactions of cyclopalladated complexes, reported by Kasahara[26] and Sokolov,[35,54] have led in all cases, to the formation of uncyclised esters.

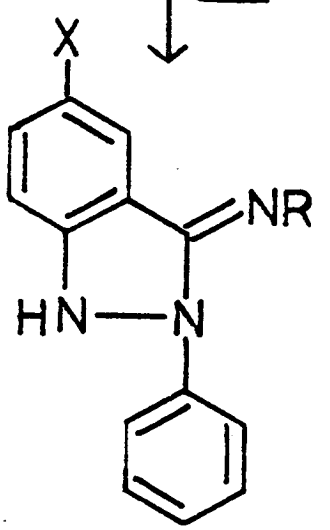


(112a-e)



(113a-e)

	X	R
(a)	H	$^{t}C_4H_9$
(b)	H	c-C_6H_{11}
(c)	MeO	$^{t}C_4H_9$
(d)	MeO	c-C_6H_{11}
(e)	MeO	o-MeC_6H_4



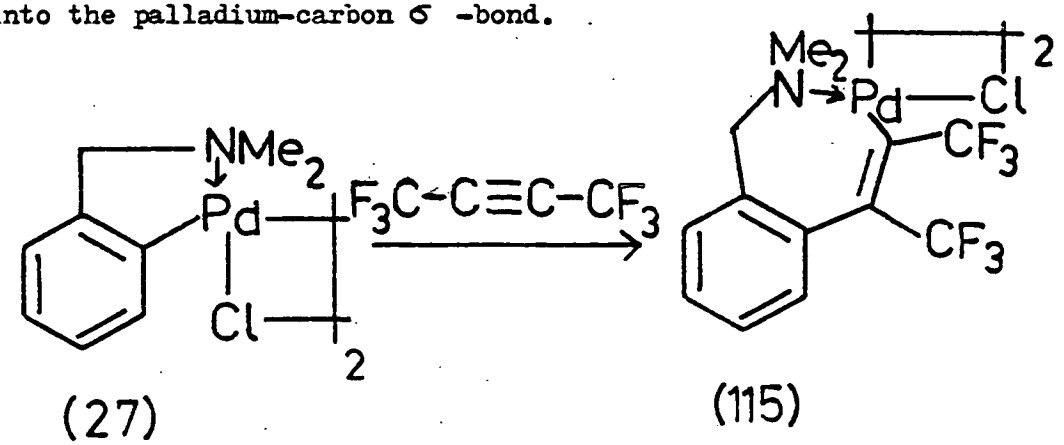
(114a-e)

fig(xi)

(5.6) INSERTION OF MOLECULES OTHER THAN CARBON MONOXIDE

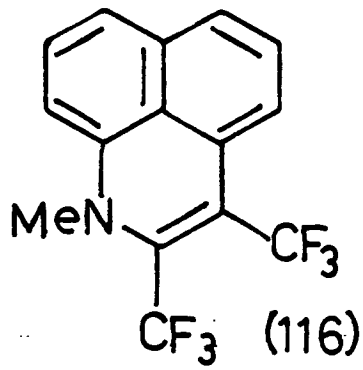
Analogous to the insertion of carbon monoxide is the insertion of isocyanides reported by Yamamoto and Yamazaki[59]. Reaction of the azobenzene complexes (112 a - e) with two equivalents of an isocyanide yielded the monomeric complexes (113 a - e) which were converted, in toluene at 100-130°, into the 3-imino-2-phenylindazolines (114) by insertion of isocyanide and elimination of palladium. The indazolines were also obtained directly from the reaction of (112) in toluene in the presence of 2 molar equivalents of isocyanide. The reaction sequence is illustrated in figure (XI).

Dehand et al[60] have studied the reactions of various cyclopalladated complexes with acetylenes. The dimethylbenzylamine complex (27) reacted with hexafluorobut-2-yne in dichloromethane at 60° yielding a new type of complex (115) formed by insertion of the alkyne into the palladium-carbon σ -bond.



(27) (115)

The cyclopalladated complexes of 8-methylquinoline and benzo [h] quinoline reacted analogously. However, the cyclopalladated N,N-dimethyl-1-napthylamine complex (28) reacted with hexafluorobut-2-yne yielding the heterocyclic compound (116).

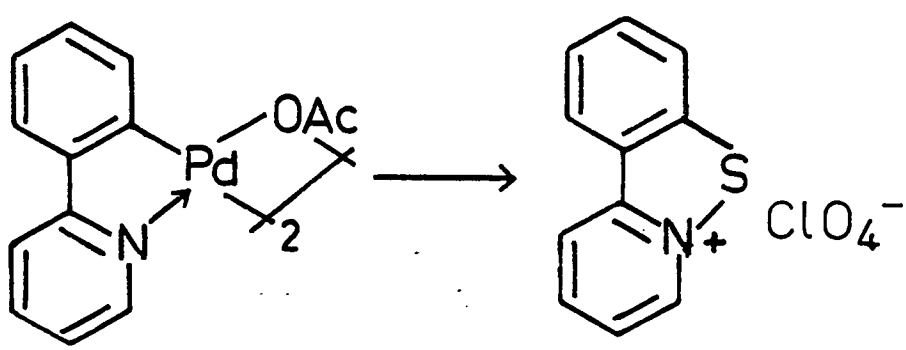


(116)

The formation of this compound is interesting in that cyclisation has occurred with the loss of one N-methyl group. This behaviour is analogous to that of the dimethylbenzylamine complex (27) during carbonylation[57].

(5.7) THIOCYANATION

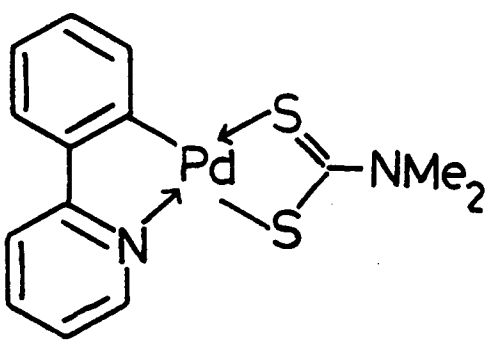
Davis[44] and Grinter[47] have both reported studies on the applications of cyclopalladated complexes in heterocyclic synthesis. Davis studied the feasility of incorporation of sulphur into the palladium-carbon σ-bond of cyclopalladated complexes, as illustrated by the overall conversion of the complex (117) to the isothiazolium salt (118).



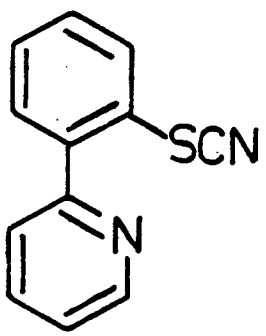
(117) (118)

Davis found that dimeric complexes such as (117), possibly on account of their low solubility, did not react cleanly with reagents which were thought likely to effect this transformation. To overcome

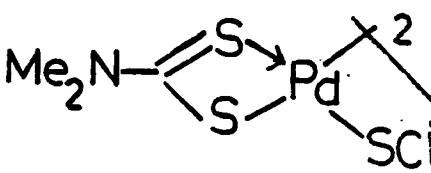
this difficulty, Davis converted the dimeric complexes to the corresponding soluble, monomeric dimethyldithiocarbamate complexes such as (119), prior to the treatment with various sulphurisation reagents. Of the various reagents examined by Davis, only thiocyanogen effected sulphur transfer. Davis reported that treatment of the complex (119) with thiocyanogen in chloroform yielded 2-(2-thiocyanatophenyl) pyridine (120) and di-μ-thiocyanato-bis (N,N-dimethyldithiocarbamato) palladium (II) (121). The chloroform-soluble thiocyanate (120) was easily separated from the insoluble complex (121).



(119)

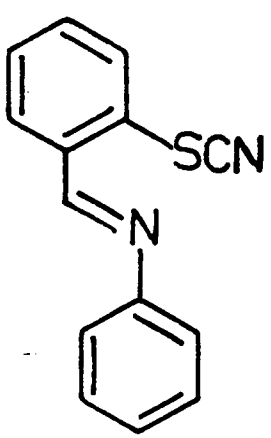


(120)

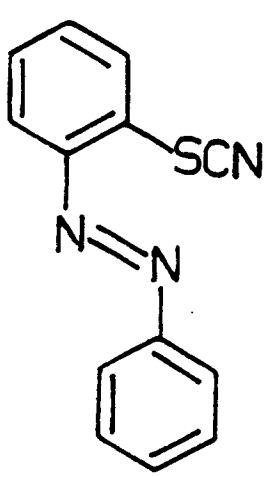


(121)

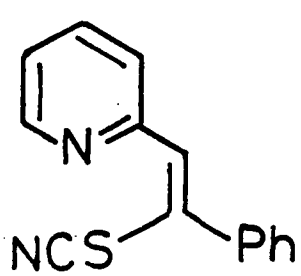
Davis extended this reaction to the preparation of 2-(N-phenylformimidoyl)phenyl thiocyanate (122), 2-thiocyanatoazobenzene (123) and 2-(2-phenyl-2-thiocyanatovinyl) pyridine (124) from the corresponding dithiocarbamate complexes.



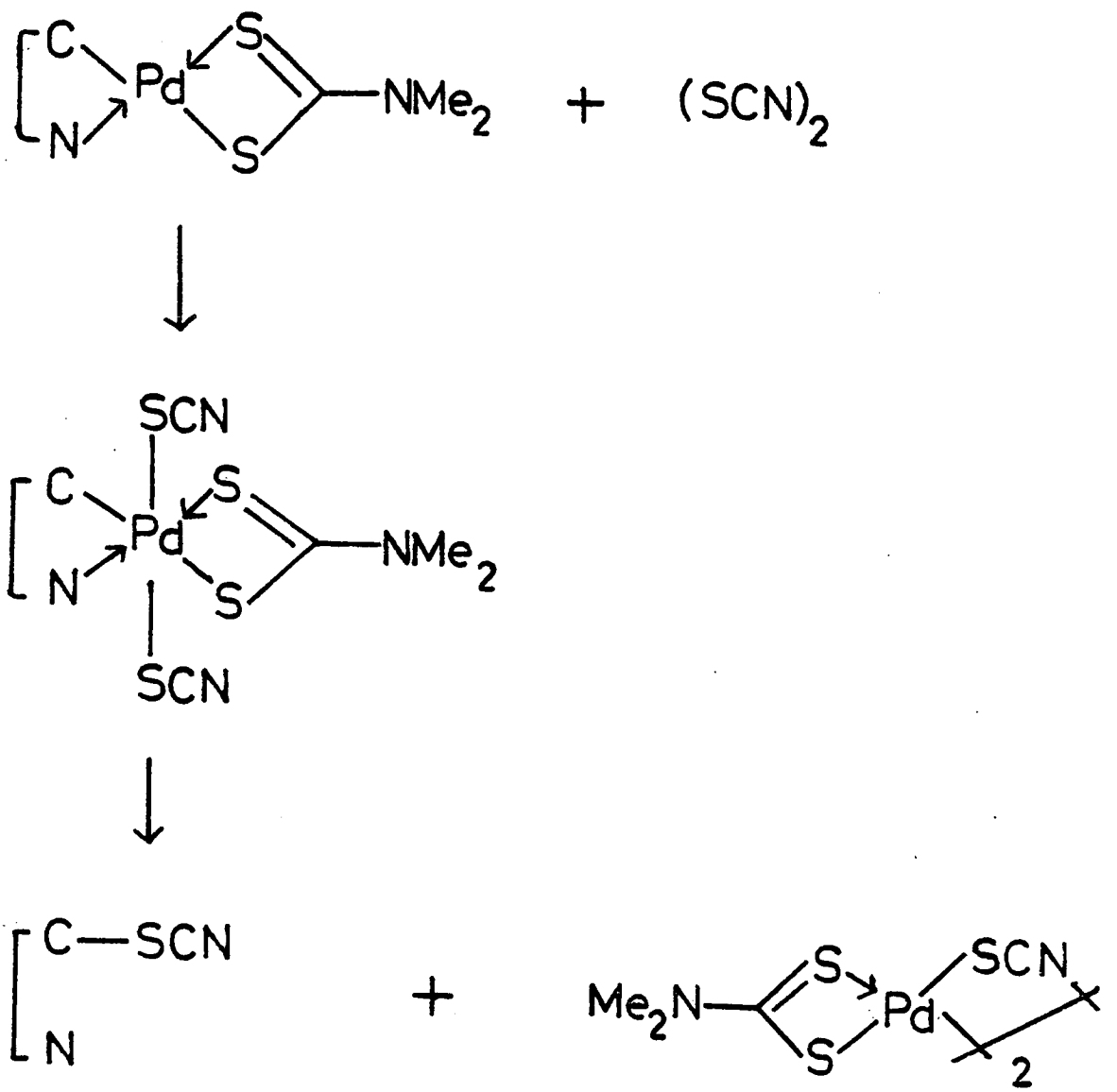
(122)



(123)



(124)



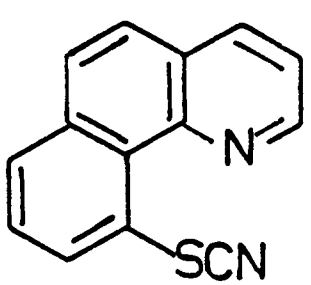
C
N = nitrogen donor ligand

fig (xii)

The thiocyanate (120)cyclised on treatment with bromine and then with perchloric acid to the novel heterocycle [1,2] benzo[15]thiazolo- [2,3 - a] pyridinium perchlorate (118).

The observation that addition of thiocyanogen to a chloroform solution of a dithiocarbamate complex resulted in the immediate formation of a deep red solution which then slowly lightened in colour with the precipitation of the dimeric complex (121) led Davis to postulate a reaction mechanism for the conversion of a dithiocarbamate to an isothiazolium salt. Firstly oxidative addition of thiocyanogen led to an unstable six-co-ordinate Pd^{IV} intermediate complex. In the second step the intermediate complex underwent reductive elimination yielding the products. This mechanism is illustrated in figure (XII).

Davis's work was extended by Grinter, who by analogy, synthesised 10-thiocyanatobenzo [h] quinoline (125), 2-thiocyanatoazoxybenzene (126) and 1-(2-thiocyanatophenyl) pyrazole (127). However, only the thiocyanate (125)cyclised to the corresponding isothiazolium salt on treatment with perchloric acid.



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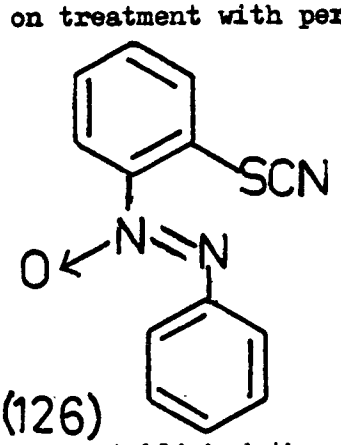
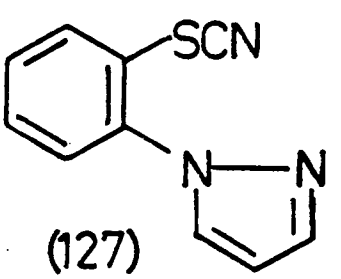
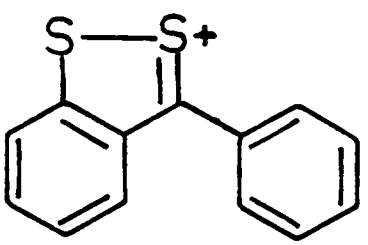


(126)



(127)

Grinter also established the utility of thiocyanogen in the synthesis of the dithiolium salts (128 - 130) from the corresponding sulphur donor dithiocarbamate complexes. However, the dithiolium salt (130) could not be obtained pure by this method.



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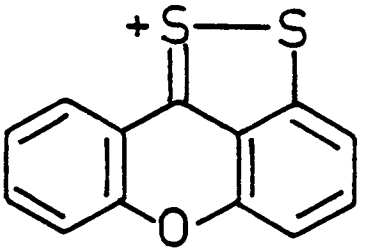

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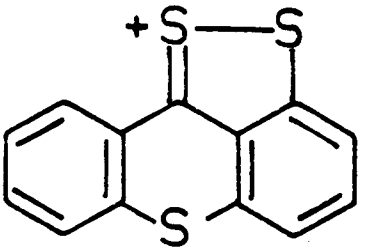
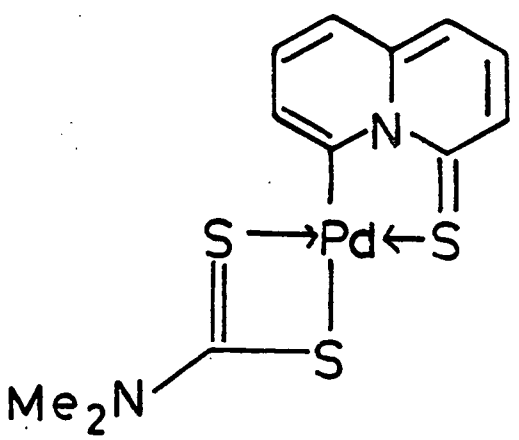


(130)

The thioamides quinolizine-4-thione and 1,2-dihydro-2-methylisoquinoline-1-thione were cyclopalladated but their respective dithiocarbamate complexes (131) and (132) did not react with thiocyanogen to yield the desired thiocyanato compounds.



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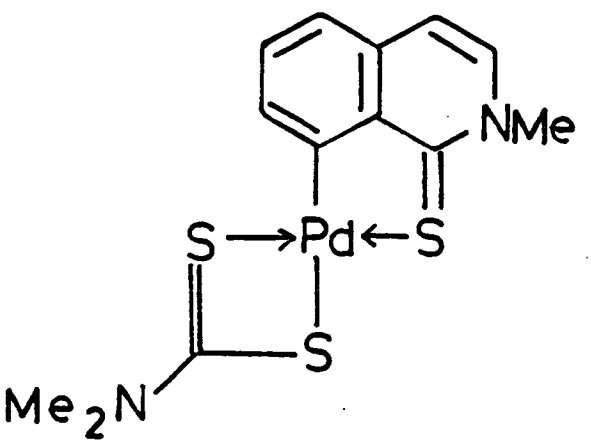


(132)

D I S C U S S I O N

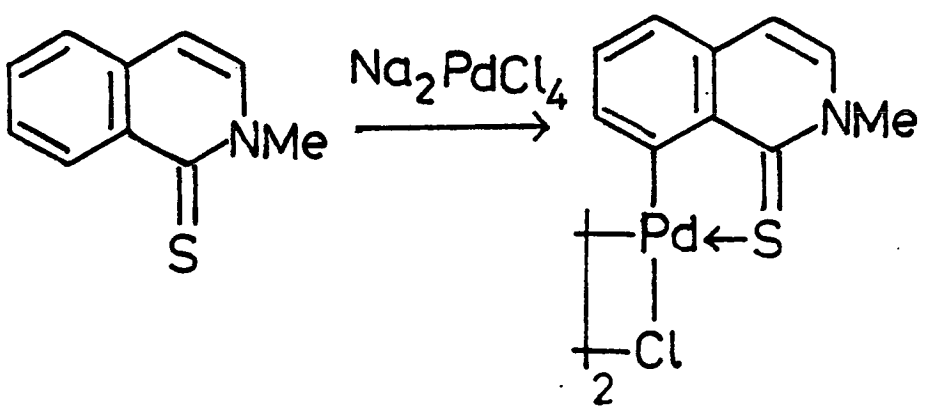
AIMS OF RESEARCH

The aim of this research was to synthesise novel heterocyclic ring systems by extension of the work carried out recently by Davis[44] and by Grinter.[47] A series of cyclopalladated sulphur-and nitrogen-donor ligand complexes were synthesised and their reactions with sulphur transfer reagents were investigated with a view to synthesising the respective 1,2-dithiolium and isothiazolium ring systems.

During the course of this study it was necessary to reinvestigate some areas of the work carried out by Davis[44] and by Grinter.[47] Of particular importance in this context was the limitation of thiocyanogen in the synthesis of novel ring systems from cyclopalladated complexes as reported by Grinter. The participation of N-methyl groups in the cyclopalladation of thiobenzamides as reported by Grinter was also reinvestigated with a view to confirming the nature of the cyclopalladated ligands. Further investigations were carried out into the cyclopalladation of quinolizine-4-thione, a reaction which Davis reported was difficult to effect.

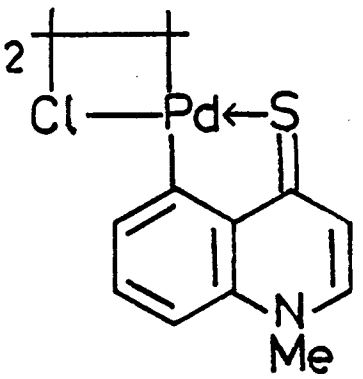
(1.1) THE SYNTHESIS OF CYCLOPALLADATED COMPLEXES OF 2-METHYLISOQUINOLINE-1-THIONE, 7-CHLORO-1-METHYLQUINOLINE-4-THIONE, 10-METHYLACRIDINE-9-THIONE, QUINOLIZINE-4-THIONE AND QUINOLIZINE-4-SELONE

2-methylisoquinoline-1-thione (133) was reported by Grinter[47] to react with methanolic sodium tetrachloropalladate to yield the orange-brown cyclopalladated complex (134). Upon repetition of this reaction a brown precipitate was formed initially (presumably a co-ordination complex) and this became yellow in colour upon heating the reaction mixture under reflux for one hour. The elemental analysis of this compound was in accord with that of the cyclopalladated complex (134). The product isolated by Grinter after a shorter period of reflux gave less satisfactory analytical results and presumably contained a proportion of the non-cyclopalladated complex.

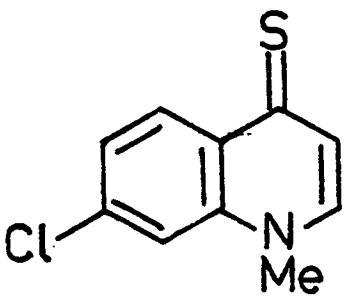


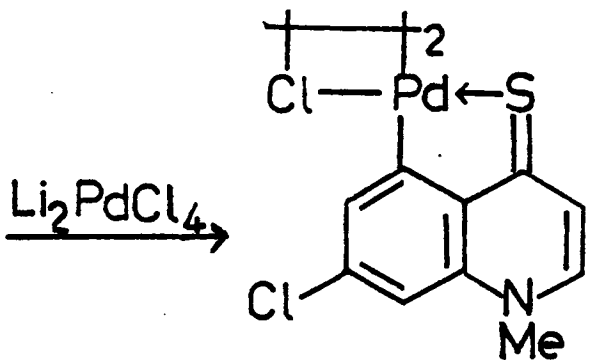
(133) (134)

Grinter obtained a product from the reaction of 1-methylquinoline-4-thione with sodium tetrachloropalladate, the elemental analysis of which was not in accord with that of the cyclopalladated complex (135). Rather than to reinvestigate this reaction, the cyclopalladation of the more accessible 7-chloro-1-methylquinoline-4-thione (136) was attempted. In this case cyclopalladation in

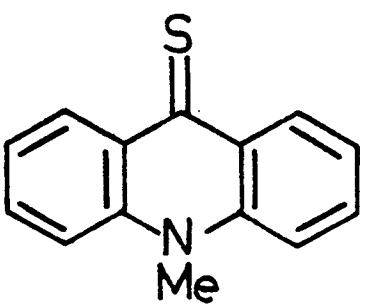


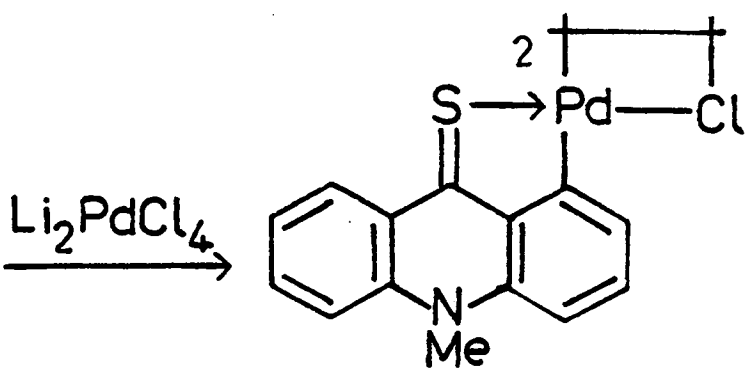
(135)





(136) (137)





(138) (139)

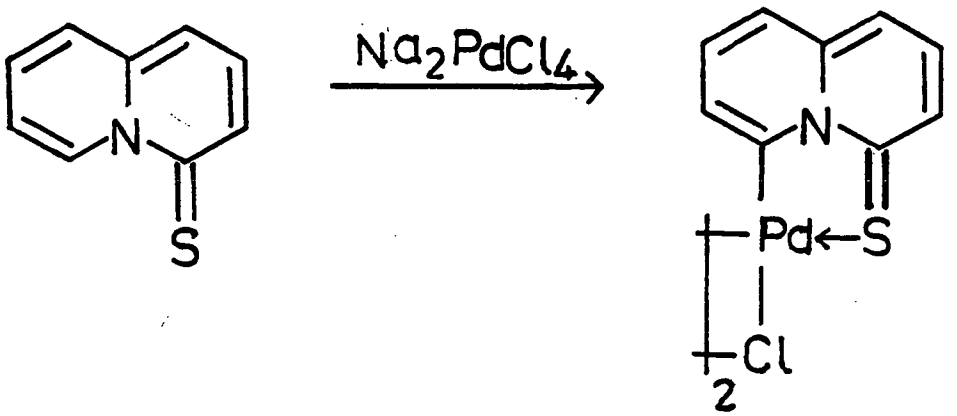
methanolic solution was inappropriate on account of the low solubility of the thione in this solvent. This problem was overcome by dissolving the thione in dichloromethane, in which it is moderately soluble, and then treating this solution with methanolic lithium tetrachloropalladate. Admixture of the two solutions produced a brown precipitate. Subsequent removal of dichloromethane by fractionation and boiling of the residual methanolic suspension for 8 hours yielded the yellow-orange cyclopalladated complex (137).

A similar solubility problem was encountered with 10-methylacridine-9-thione (138). Attempted reaction in methanol-2-methoxyethanol yielded 10-methylacridin-9-one. This behaviour is analogous to the desulphurisation of thiones upon attempted cyclopalladation which has been reported by Alper.[46] However, cyclopalladation was effected in dichloromethane-methanol to yield the red complex (139).

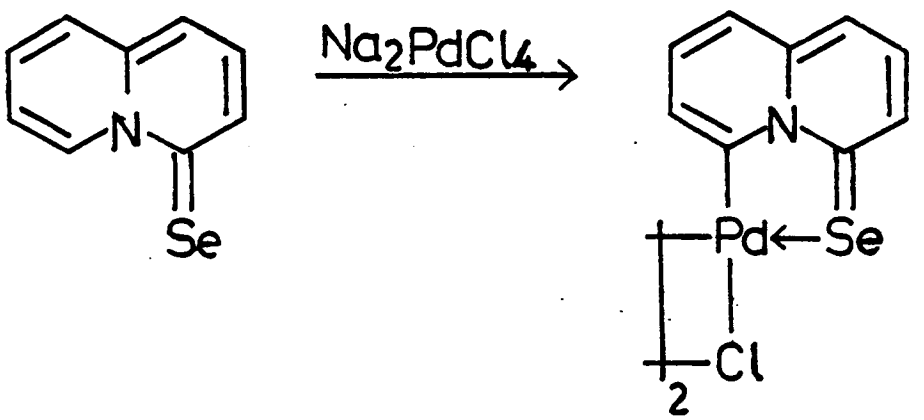
Davis[44] reported that quinolizine-4-thione (140) reacted with methanolic sodium tetrachloropalladate to yield the dark orange complex (141). However, this reaction failed to yield the cyclopalladated complex (141) in subsequent preparations.

Grinter[47] later reported conditions under which the cyclopalladation of quinolizine-4-thione was effected. Both Davis and Grinter confirmed the nature of the cyclopalladated thione by conversion to the monomeric triethylphosphine complex.

In this work, quinolizine-4-thione was treated with methanolic solium tetrachloropalladate under conditions identical with those reported by Grinter to yield only orange co-ordination complexes which could not be characterised on account of their insolubility and involatility. After a thorough investigation it was found that



(140) (141)

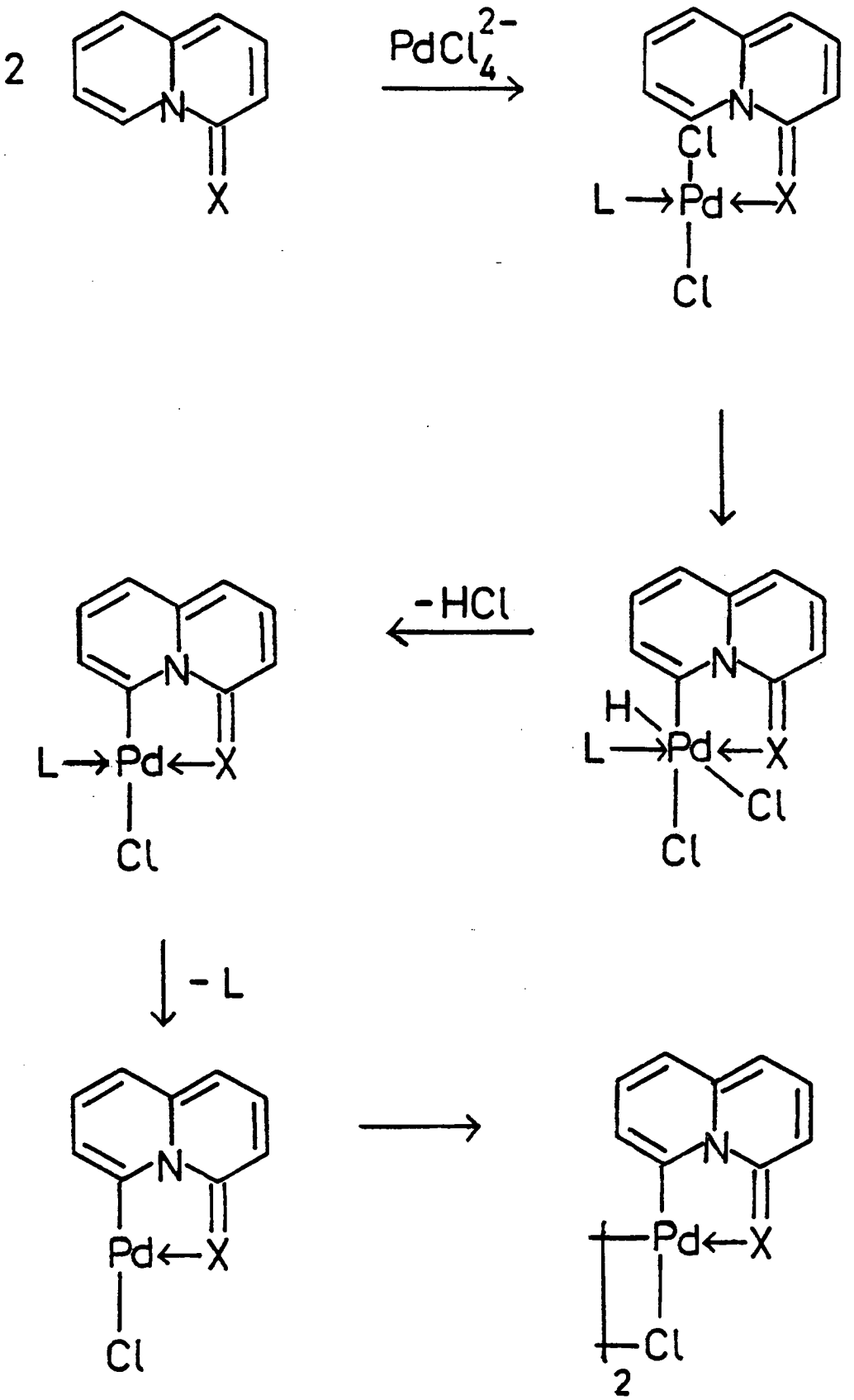


(142) (143)

cyclopalladation was effected in solutions more dilute (ca.0.015 mol dm^{-3}) than those used by Grinter (ca.0.04 mol dm^{-3}). Under these conditions an orange-brown solid was formed initially and this became yellow-orange upon heating the reaction mixture under reflux for several hours. The nature of the yellow-orange solid was established as the cyclopalladated complex by its elemental analysis and conversion to the corresponding monomeric N,N-diisopropyl-dithiocarbamate complex. It may be the case that in more dilute solution an insoluble co-ordination complex remains in solution long enough to undergo further reaction leading to the cyclopalladated complex. It is noteworthy that the product obtained from this reaction by Grinter was not completely cyclopalladated as shown by its brownish colour, poor elemental analysis and additional infrared absorptions compared with the yellow-orange complex obtained from reaction in dilute solution.

Although there have been several reports of cyclopalladated sulphur-donor ligands,[9,44,46,47] there has been no report of the selenium analogues. With a view to synthesising the first cyclopalladated selenium-donor complex, quinolizine-4-selone (142), prepared by reaction of 4-chloroquinolizinium perchlorate with sodium hydrogen selenide, was treated with methanolic sodium tetrachloropalladate under nitrogen. This reaction followed a parallel course to that of quinolizine-4-thione, a brown solid being formed initially, which then became orange-brown upon heating of the reaction mixture under reflux for several hours. The identity of this compound was established as the cyclopalladated complex (143) by its elemental analysis and conversion to the corresponding monomeric triethylphosphine and N,N-diisopropyldithiocarbamate complexes.

The observation that both quinolizine-4-thione and-selone

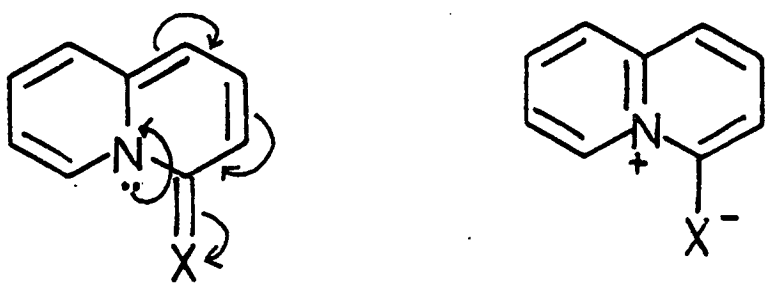


L = quinolizine-4-thione or selone

X = S or Se

fig (xiii)

undergo cyclopalladation is interesting from a mechanistic point of view. Although much evidence has been presented in support of an electrophilic mechanism for cyclopalladation,[15,16,17,22] this reaction pathway would be unfavourable in the cyclopalladation of the quinolizine ring. In this system the carbon at which carbon-palladium σ-bond formation occurs (C - 6) is deactivated towards electrophilic attack owing to electron withdrawal from this centre by the heteroatom at C - 4. This results in a resonance contribution from the canonical structure (144) in which both rings are quaternary pyridinoid.

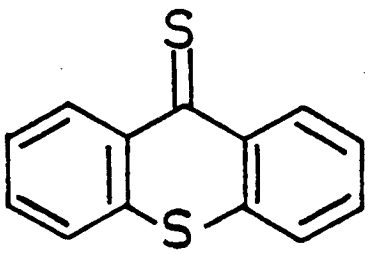


(144)

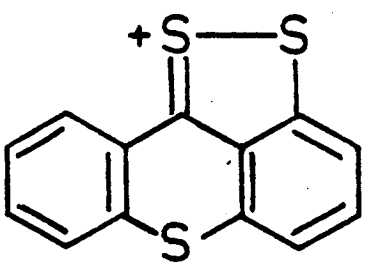
X = S , Se

A plausible mechanism for the cyclopalladation of these ligands which does not involve an electrophilic species is presented here, the essential features of which, are illustrated in figure (XIII).

The first step is the rapid co-ordination of two substrate ligands onto palladium. The second, and perhaps the most difficult step is essentially an oxidative addition as a result of insertion of palladium into the carbon-hydrogen bond at C - 6.



(145)



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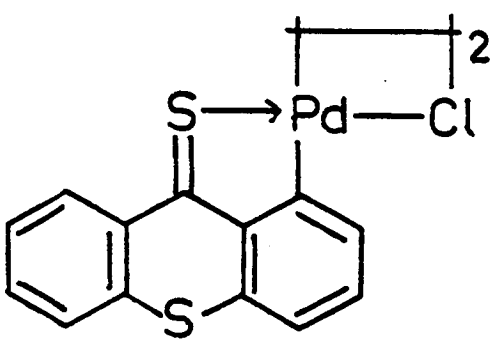
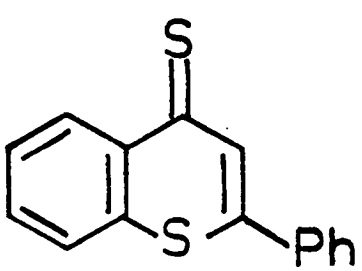
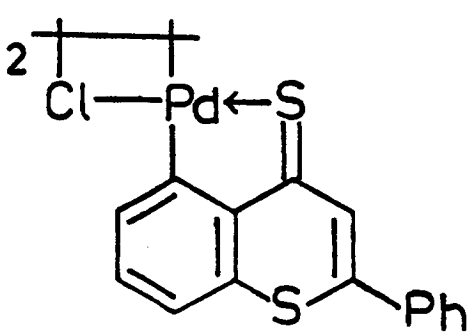


(146)



(147)



(148)

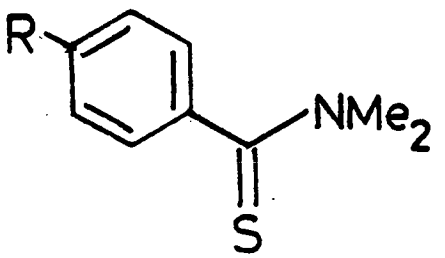
Reductive elimination of hydrogen chloride is then followed by the loss of a substrate ligand. The resulting co-ordinately unsaturated [L Pd Cl] species then dimerises. Alternatively, dimer formation might occur during the initial co-ordination step to give a complex of the type $[L\ Pd\ Cl_2]_2$.

(1.2) THE SYNTHESIS OF CYCLOPALLADATED COMPLEXES OF THIOXANTHENE-9-THIONE AND 2-PHENYLTHIOCHROMENE-4-THIONE

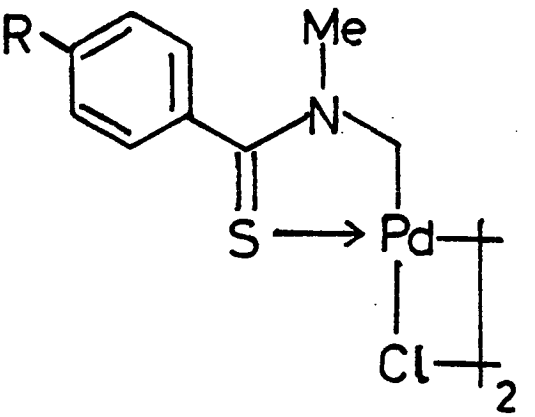
Despite being able to effect the cyclopalladation of thioxanthene-9-thione (145), Grinter[47] was unable to synthesise the novel [1,2] dithiolo [3,4,5-kl] thioxanthylium ring system (130) by replacement of palladium by sulphur. The product was obtained in an impure form and could not be purified upon recrystallisation. The unsatisfactory nature of this reaction prompted further investigations in this field, the first of which was the cyclopalladation of thioxanthene-9-thione.

The reaction of the thione with methanolic sodium tetrachloropalladate was carried out under conditions similar to those reported by Grinter, with the exception that the reaction mixture was heated under reflux for a longer period of time (1 hour as opposed to 10 minutes). Under these modified conditions the cyclopalladated complex (146) was obtained analytically pure, whereas the shorter reaction time used by Grinter led to a product, the elemental analysis of which was in poor agreement with this structure.

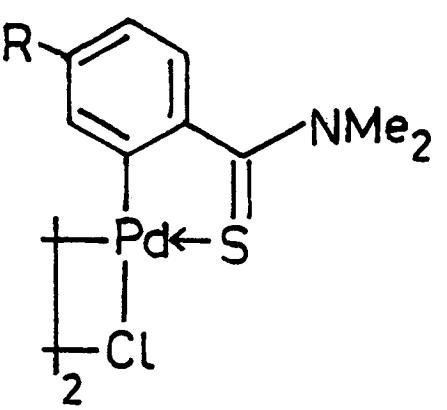
In order to extend the study of cyclopalladated sulphur-donor ligands of this type, the structurally similar 2-phenylthiochromen-4-thione (147) was treated with methanolic sodium tetrachloropalladate to yield the cyclopalladated complex (148), the elemental analysis of which was in accord with this structure.



(149)



(150)



(151)

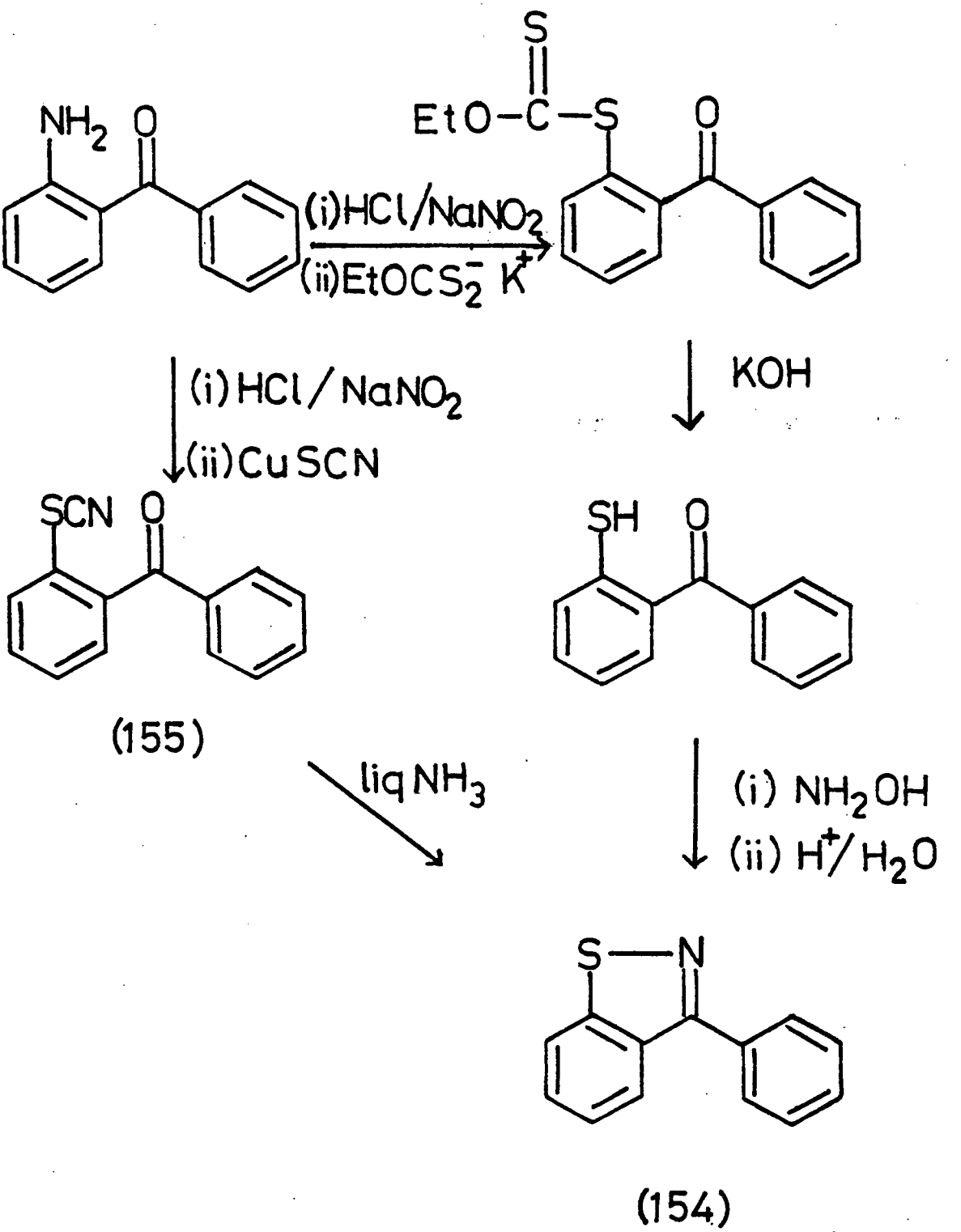
(a, R = H)

(b, R = Me)

(1.3) THE SYNTHESIS OF CYCLOPALLADATED COMPLEXES OF THIOBENZAMIDES

A novel type of cyclopalladated complex in which the site of palladation was at an N-methyl group was reported by Grinter.[47] Upon treatment with methanolic sodium tetrachloropalladate, N,N-dimethylthiobenzamide (149a) and its p-methyl derivative (149b) were reported to yield the brown complexes (150a) and (150b) respectively, and not the expected products (151a) and (151b) in which the site of palladation is at a phenyl ring. On account of their unsatisfactory elemental analyses, these complexes were converted to monomeric triethylphosphine derivatives to facilitate their characterisation. Despite the fact that the phosphine complexes yielded satisfactory elemental analyses, they were far from being pure. It can be assumed that this anomaly, which will be discussed in more detail later, is a consequence of the formation and subsequent reaction of incompletely cyclopalladated complexes. Investigations were therefore carried out to establish conclusively the nature of the cyclopalladated ligands formed in these reactions.

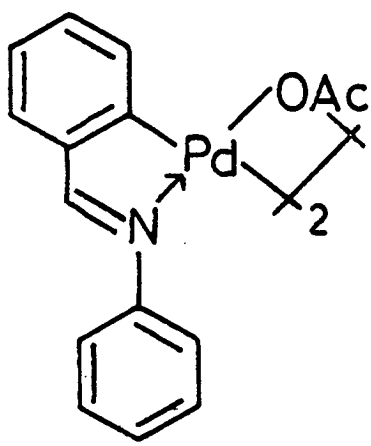
The cyclopalladation of these thiobenzamides was carried out under conditions similar to those reported by Grinter with the exception that the reaction mixture was heated under reflux for a longer period of time (5 hours as opposed to 20 minutes). Under these modified conditions (150a) and (150b) were obtained as pale yellow and grey solids respectively, both of which yielded elemental analyses in accord with the cyclopalladated structures. The difference in purity of these complexes compared with those formed upon shorter reaction times was also reflected in their melting points, the former melting at some 60-90° higher than the latter.


NH2
O
(i)HCl/NaNO2
(ii)EtOCS2 K+
EtO–C–S
S
O
(i) HCl / NaNO2
(ii) CuSCN
KOH
SCN
O
SH
O
(155)
liq NH3
(i) NH2OH
(ii) H+/H2O
S—N
(154)

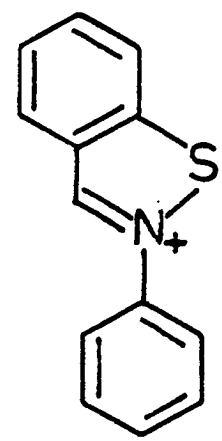
Scheme (ii)

(1.4) THE SYNTHESIS OF CYCLOPALLADATED COMPLEXES OF BENZYLIDENEANILINE, 3-PHENYL-1,2-BENZISOTHIAZOLE, AZOBENZENE AND 2-PHENYLPYRIDINE

Di-μ-acetato-bis [2-(N-phenylformimidoyl) phenyl] dipalladium (II) (152) was synthesised from benzylideneaniline by the method of Onoue and Moritani[7] and was used in subsequent reactions with a view to synthesising the 2-phenyl-1,2-benzisothiazolium ring system (153) by replacement of palladium by sulphur.



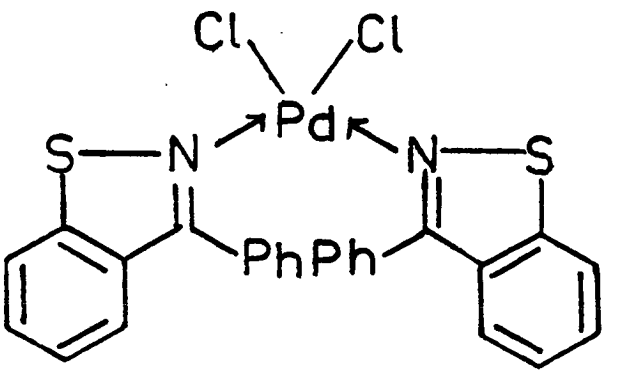
(152)



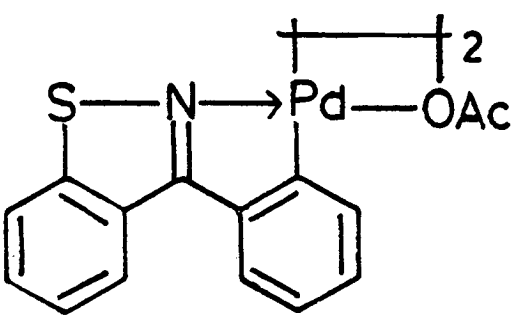
(153)

3-phenyl-1,2-benzisothiazole (154) was synthesised for further studies on the cyclopalladation of nitrogen donor ligands. The synthesis of this compound according to known procedures would involve the preparation of 2-mercaptobenzophenone from 2-aminobenzophenone via diazotisation, treatment with potassium ethyl xanthate, and subsequent hydrolysis of the xanthate[61] (Scheme (II)). Treatment of the mercaptan with hydroxylamine and subsequent dehydration would then form the isothiazole (154).

The disadvantages of this reaction scheme are two-fold. Firstly, the yield of 2-mercaptobenzophenone is low, and secondly,



(156)



(157)

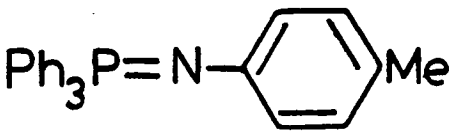
the reaction of the diazonium salt with potassium ethyl xanthate can lead to explosions.

In the light of the reported synthesis of isothiazole from cis 3-thiocyanatopropenal, upon treatment with liquid ammonia,[62] it was thought that a more simple synthesis of 3-phenyl-1,2-benzisothiazole might be achieved by a similar treatment of 2-thiocyanatobenzophenone (155). In practice the benzisothiazole was obtained by this route, but the overall yield was poor. The poor yield was attributed to the reaction of diazotised 2-aminobenzophenone with cuprous thiocyanate. This reaction did not proceed cleanly and no pure thiocyanato - product could be obtained. During the writing of this thesis, a much simpler general synthesis of 1,2-benzisothiazoles from chloro-substituted aldehydes and ketones was reported by Markert and Hagen.[63]

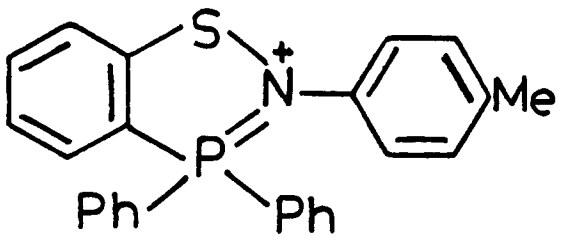
The cyclopalladation of 3-phenyl-1,2-benzisothiazole was attempted initially by treatment with methanolic sodium tetrachloropalladate. However, under these conditions a complex was formed, the elemental analysis of which, was in accord with that of bis (3-phenyl-1,2-benzisothiazole) palladium (II) dichloride (156). Reaction of the isothiazole with palladium acetate in acetic acid under reflux effected cyclopalladation, although the resulting acetate-bridged complex (157) was formed in somewhat low yield.

The ^{1}H n.m.r. spectrum of (157) showed a doublet ($J = 7$ Hz) to low field of the main aromatic region at δ 7.96 and this was assigned to the proton ortho to palladium in the cyclopalladated ring. The remaining aromatic protons appeared as a multiplet and the acetate methyl protons as a singlet at δ 2.28.

Cyclopalladated complexes of azobenzene[4] and 2-phenylpyridine[36] were also prepared in order that further investigations into the replacement of palladium in these complexes by sulphur could be carried out.



(158)



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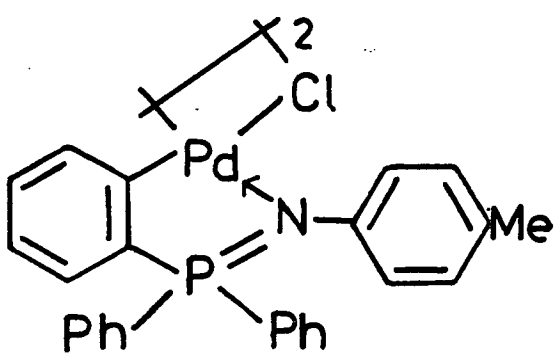


(26a)

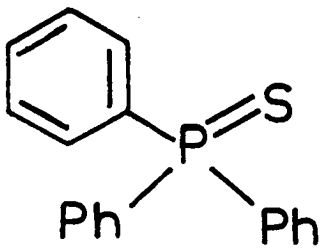
(1.5) THE ATTEMPTED SYNTHESIS OF CYCLOPALLADATED COMPLEXES OF TRIPHENYLPHOSPHINE-N-*p*-TOLYLIMIDE AND TRIPHENYLPHOSPHINE SULPHIDE

The cyclopalladation of triphenylphosphine-N-*p*-tolylimide (158) in methanolic sodium tetrachloropalladate was attempted under conditions identical to those reported by Alper,[30] with a view to synthesising the novel ring system (159). However, despite several attempts, the reaction failed to yield the cyclopalladated complex (26a) obtained by Alper. Instead, a brown solid was formed, the elemental analysis of which was in accord with that of a co-ordination complex of the type $[L\ Pd\ Cl_2]_2$, where L = triphenylphosphine-N-*p*-tolylimide.

The cyclopalladation of triphenylphosphine sulphide (160) was attempted with a view to synthesising the 1,2,3-dithiaphospholium ring system (161). However, the reaction of (160) in methanolic sodium tetrachloropalladate did not yield the desired cyclopalladated complex (162), but a complex, which on the basis of its elemental analysis, was thought to be bis (triphenylphosphine sulphide) palladium (II) dichloride (163).

(2) THE SYNTHESIS OF MONOMERIC PHOSPHINE COMPLEXES

Bridge-splitting reactions have been employed by many workers to facilitate the characterisation of dimeric cyclometallated complexes. In this work the bridge splitting reaction by means of phosphines was used to a lesser extent for several reasons, the two most important of which being that (i) in all cases satisfactory elemental analyses were obtained for dimeric complexes and (ii) monomeric dithiocarbamate complexes were synthesised from the dimeric complexes and yielded spectroscopic and analytical information



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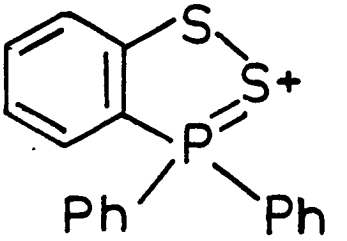

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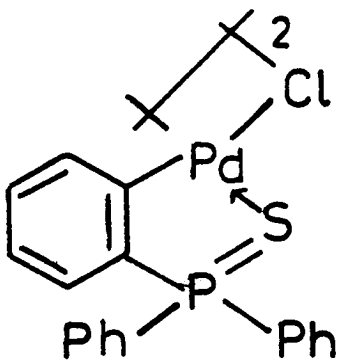

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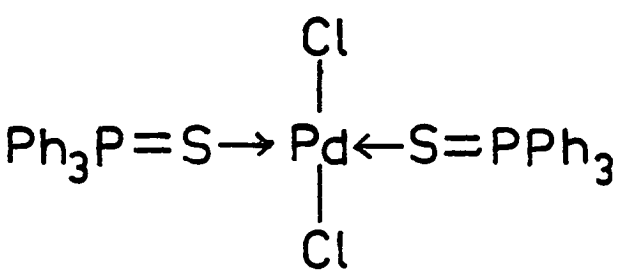


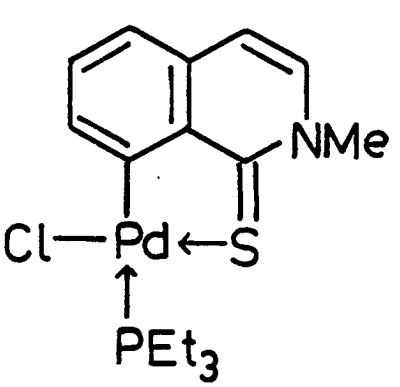
(163)

complimentary to that obtained from phosphine complexes.

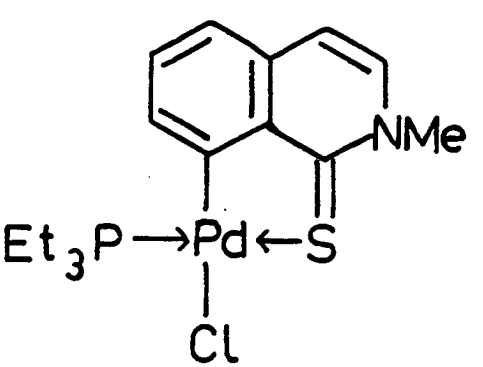
As a consequence of the square planar geometry around the palladium in these phosphine complexes, there exists the possibility of geometric isomerism. In this context, the terms cis and trans will be used to denote the position of the phosphine ligand in relation to the palladium-carbon σ-bond.

The chloride-bridged 2-methylisoquinoline-1-thione complex (134) was reported by Grinter[47] to yield a yellow-orange solid, m.p. 198-200° C, upon treatment with two molar equivalents of triethylphosphine. However, the spectroscopic and analytical information obtained for this compound was not consistent with that expected for the monomeric complex (164) and thus the structure of this compound remained uncertain.

Upon repeating this reaction in this study, a pale yellow solid, m.p. 175-7°C, was obtained, the structure of which was established conclusively as the monomeric phosphine complex by n.m.r. studies. Several features of the n.m.r. spectra were consistent with the presence of two stereoisomers (164a) and (164b) in approximately equal proportions.



(164a)



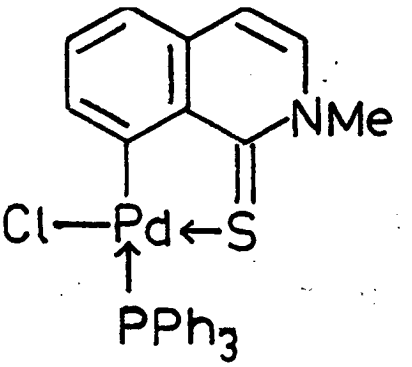
(164b)

The aromatic region of the ^{1}H n.m.r. spectrum showed a triplet (ca. 0.5 H) at δ 8.60, a multiplet at δ 7.6 - 7.2 (ca. 3.5 H) and a doublet at δ 6.95 (1 H). The triplet was assigned to H - 7 in the trans-isomer (164a), its downfield shift being attributed to long-range deshielding by the chlorine-palladium bond. The doublet was assigned to H - 4 in both isomers.

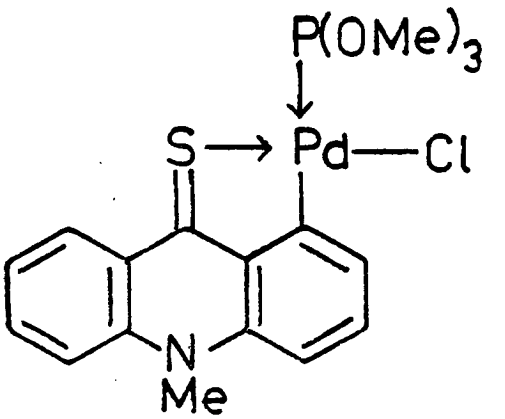
The N-methyl protons appeared as two singlets, each of approximate integrated intensity 1.5 H at δ 4.07 and 3.99 and the phosphine protons as multiplets at δ 1.97 (6 H) and δ 1.18 (9 H).

The presence of two N-methyl signals in addition to the low field triplet was further evidence for the presence of cis and trans isomers. The proton-decoupled ^{31}P n.m.r. spectrum was confirmatory, showing two singlets at 11.5 and 23.3 p.p.m. Hetero-nuclear decoupling experiments were carried out with a view to observing the effect of ^{31}P decoupling on the low field proton signal. Irradiation at the lower ^{31}P frequency collapsed the H - 7 triplet into a doublet ($J = 7$ Hz) and affected the intensities of the phosphine signals. The observed residual splitting of H - 7 was obviously due to coupling with H - 6. Irradiation at the higher ^{31}P frequency did not affect the triplet, only the intensities of the phosphine signals. These results are entirely consistent with the assignment of the triplet to H - 7 in (164a), the trans-configuration being responsible for the relatively large (ca.7 Hz) four-bond P - H coupling.

The triphenylphosphine complex (165) was synthesised from the dimeric complex (134) by an analogous method. Chromatography on alumina of the worked-up reaction mixture yielded two pale yellow solids which, despite appearing to be separable by this method, were found to be identical by spectroscopic and analytical methods. It



(165)



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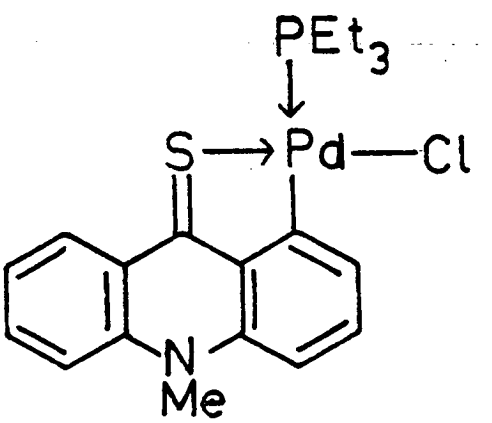


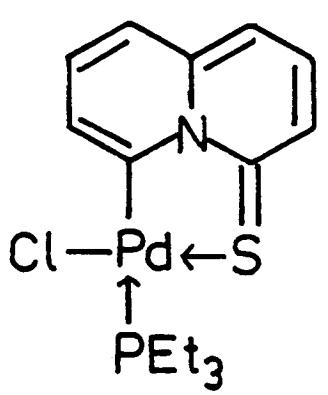
(167)

was thought likely that these compounds were mixtures of *cis* and *trans* isomers which possibly equilibrated in solution. The ^{1}H n.m.r. spectrum of these complexes clearly demonstrated the existence of geometric isomerism, there being two N-methyl signals at δ 4.05 (*ca.* 2H) and δ 3.80 (*ca.* 1H). Confirmatory evidence was obtained by ^{31}P n.m.r. studies, two singlets being observed at 16.8 and 37.4 p.p.m.

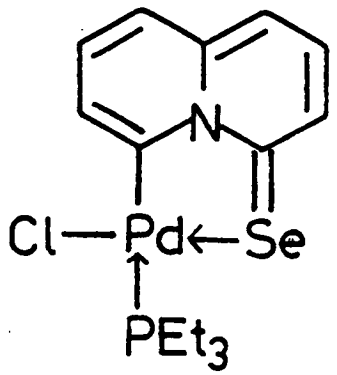
The 10-methylacridine-9-thione complex (139) was treated with trimethylphosphite to yield a complex, the elemental analysis of which was in accord with the structure (166). However, on account of its low solubility, the complex was not amenable to n.m.r. studies. Reaction of (139) with triethylphosphine yielded the analogous phosphine complex (167). The ^{1}H n.m.r. of this complex showed two signals downfield of the main aromatic region. A multiplet at δ 8.7 (1H) was assigned to H-8 and a triplet at δ 8.36 (1H) was assigned to H-2. The multiplicity of the latter signal is thought to arise from coupling to H-3 and to phosphorus, as for the low-field triplet observed in the ^{1}H n.m.r. spectrum of the 2-methylisoquinoline-1-thione complex (164). The N-methyl protons appeared as a singlet at δ 4.10. Although these features pointed towards the presence of only one isomeric form, the ^{31}P n.m.r. spectrum showed two lines at 11.6 and 21.4 p.p.m. (relative intensities *ca.*3 : 1). This observation could not be explained although it did not cast any doubt as to the structure of the dimeric complex (139) as will be shown later.

It has been shown by n.m.r. studies that the quinolizine-4-thione complex (168) exists as a mixture of *cis* and *trans* isomers.[47] A comparative study was therefore carried out with the analogous selone complex (169) which was synthesised by reation of (143) with

triethylphosphine. Further n.m.r. studies on (169) were possible since it contains an additional magnetic nucleus (^{77}Se).



(168)



(169)

The site of palladation in the quinolizine ring was confirmed by the absence of a signal due to H-6, which in quinolizine-4-selone, occurs at δ 10.75. Two signals were observed downfield of the main aromatic region. A multiplet at δ 9.25 (1H) was assigned to H-7 and another multiplet at δ 7.85 (1H) was tentatively assigned to H-3. The existence of only one isomer was clearly demonstrated by ^{13}C n.m.r. which showed nine aromatic carbons, the resonance at lowest field (145.6 p.p.m.) being assigned to either C-4 or C-6. The ^{31}P n.m.r. spectrum showed a single resonance at 14.7 p.p.m. with ^{77}Se satellites ($^{2}J_{PSe} = 10Hz$). The ^{77}Se n.m.r. showed a doublet ($^{2}J_{SeP} = 10Hz$) at 359.3 p.p.m. to low field of dimethyl selenide. In the light of previously reported values (Table 1) for $^{2}J_{Se(M)P}$ coupling constants,[64,65] the observed value of J points to a complex in which the phosphine ligand is <u>cis</u> to the selenium atom.

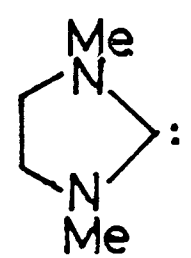
The white complexes (170a), m.p. 178-9° [lit.,[47] yellow-orange; m.p. 150-1°] and (170b), m.p. 200-1° [lit.,[47] red-brown; m.p. 157-8°] were prepared by treatment of the respective dimeric complexes (150a) and (150b) with triethylphosphine. The differences

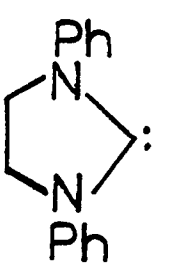
Table 1

Complex	$^2J_{Se(M)P}$ (Hz) cis	trans
$Pd(Se_2CN^iBu_2)PPh_3Cl$	0	104
$Pt(Se_2CNEt_2)PPh_3Cl$	10	100

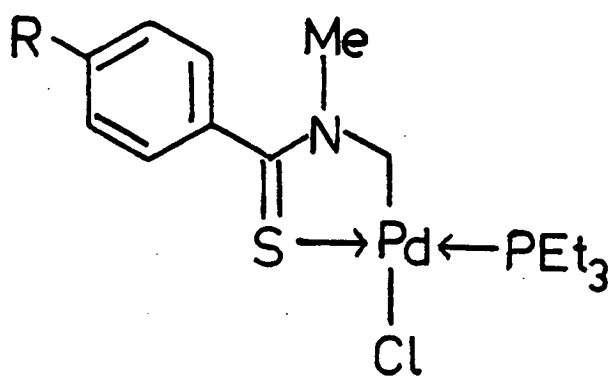
Table 2

Complex	$^2J_{PC}$ (Hz) cis	trans
$Cl_2PBu^n_3PdL$	2.4	180.5 [+]
$Cl_2PPr^n_3PtL$	7	151

L = 

except [+] L = 

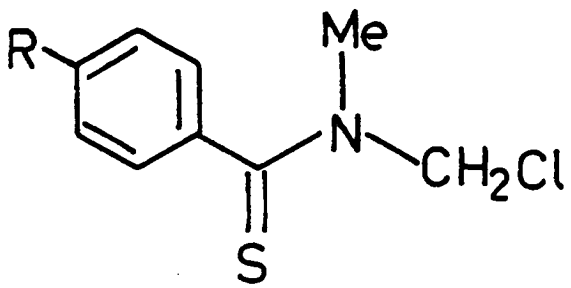
in colour and melting points between these complexes and those previously synthesised is noteworthy. Presumably these differences can be accounted for by the presence of small amounts non-cyclopalladated ligands in the previously reported complexes.



(170a, R = H)
(170b, R = Me)

The ^{1}H and ^{13}C n.m.r. spectra of these complexes were in accord with those reported previously[47]. The key features revealed in these spectra were the NCH_2 group and a non-cyclopalladated phenyl ring. In the light of previously reported[66] values (Table 2) for $^{2}J_{P-M-C}$, the observed value of approximately 4 Hz for $^{2}J_{P-Pd-C}$ points to a cis-configuration, i.e. one in which the phosphine ligand is cis to the CH_2 group.

The mass spectra of these complexes also revealed the presence of the NCH_2 unit in the fragment ion peaks at m/e 201/199 for (170a) and m/e 215/213 for (170b) which were attributed to the formation of the N-methyl-N-chloromethylthiobenzamides (171a) and (171b).



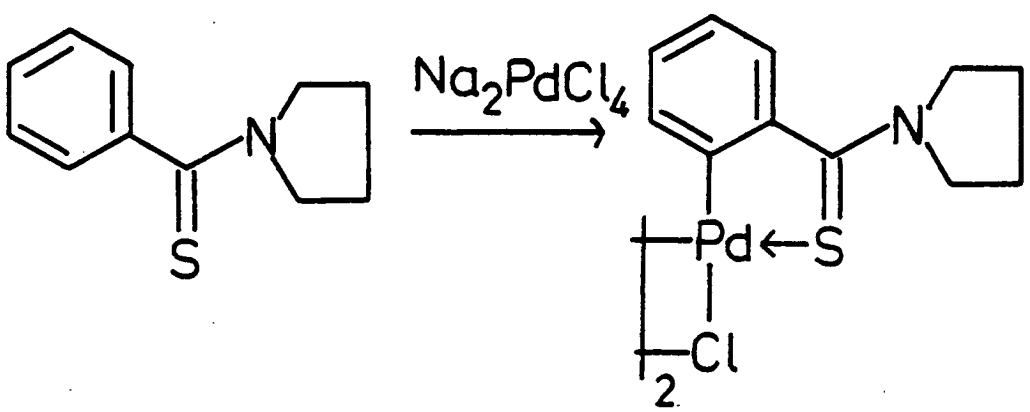
(171 a, R = H)

(171 b, R = Me)

The formation of the dimeric complexes (150a) and (150b) cannot occur by an electrophilic process, and so it is proposed that cyclopalladation of thiobenzamides occurs via the insertion of palladium into the C-H bond. This mechanism is therefore analogous to that proposed for the cyclopalladation of quinolizine-4-thione and selone.

The behaviour of these thiobenzamides in cyclopalladation is in contrast to that of the structurally similar 2-methylisoquinoline-1-thione (133) which undergoes cyclopalladation only in the aromatic ring (C-8). It is proposed that steric interactions during the course of co-ordination of the thiobenzamide sulphur to palladium result in the aryl group rotating out of the plane of the thiocarbonyl group. Cyclopalladation can then occur at an N-methyl group which would be held in the co-ordination plane by the resonance-enforced planarity in the thioamide linkage.

Further investigations in this field have been carried out recently by Leaver and Thomson.[67] In their study, 1-thiobenzoylpyrrolidine (172) was treated with methanolic sodium tetrachloropalladate to yield the cyclopalladated complex (173), the structure of which was established by ^{1}H n.m.r. studies of the corresponding triethylphosphine and N,N-diisopropyldithiocarbamate derivatives.



(172) (173)

The cyclopalladation of (172) at the α-carbons of the pyrrolidine ring would be unfavourable since the hydrogens at these carbon centres cannot lie in the plane of the thioamide group (the co-ordination plane) without considerable distortion of the pyrrolidine ring. The factors governing the course of reaction are thus tipped in favour of cyclopalladation in the aromatic ring despite the freedom of the latter to rotate out of the co-ordination plane.

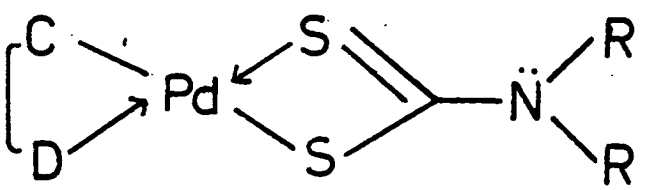
(3) THE SYNTHESIS OF DITHIOCARBAMATE AND RELATED COMPLEXES

Davis[44] found that a prerequisite for the efficient replacement of palladium in cyclopalladated complexes by sulphur was the conversion of highly insoluble dimeric complexes into the more soluble dithiocarbamate complexes. Davis, and later Grinter[47] synthesised a series of N,N-dimethyldithiocarbamate complexes either by treatment of chloride-bridged dimers with sodium, N,N-dimethyldithiocarbamate in dimethylformamide, or by treatment of acetate-bridged dimers with tetraethylammonium N,N-dimethyldithiocarbamate in chloroform. With the larger cyclopalladated ligands, however, the complexes were insufficiently soluble for efficient further reactions even after conversion to the dimethyldithiocarbamato derivatives.

In this work a more pronounced increase in solubility was observed upon conversion of the dimeric complexes to the corresponding N,N-diisopropyldithiocarbamate complexes. In addition, the greater solubility of these complexes facilitated their characterisation by spectroscopic and analytical methods. Dithiocarbamate complexes exhibit several characteristic spectroscopic features, the most important of which, will be briefly discussed here.

(i) ^{1}H n.m.r. spectra

Restricted rotation about the S_2C-N bond of the dithiocarbamate ligand (174) as a consequence of the contribution from the canonical resonance structure (175) results in the non-equivalence of the groups R.



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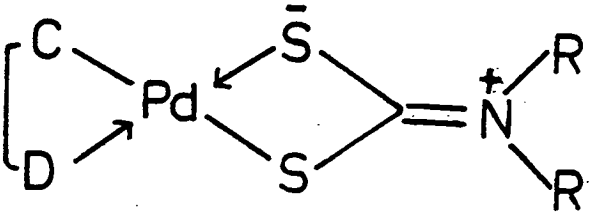


(175)

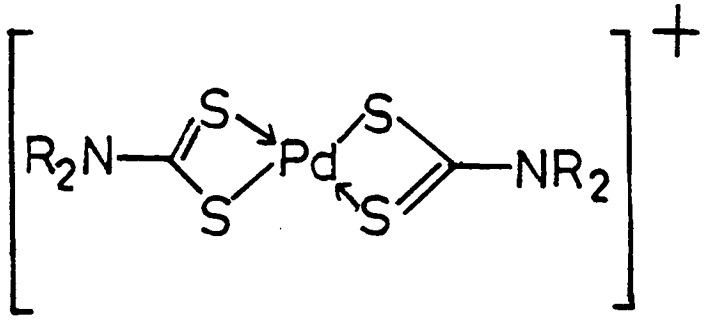
When R = methyl, two methyl signals are observed. However, when R = isopropyl, a more complex spectrum is observed. Two isopropyl methyl signals are observed, each of which is split into a doublet by the methine proton. At ambient temperatures these signals show considerable broadening thus suggesting that coalescence is being approached (i.e. the isopropyl groups are approaching equivalence owing to slow rotation about the thioamide C-N bond). The methine proton appears as a multiplet in the region 4-5 δ.

(ii) Infrared spectra

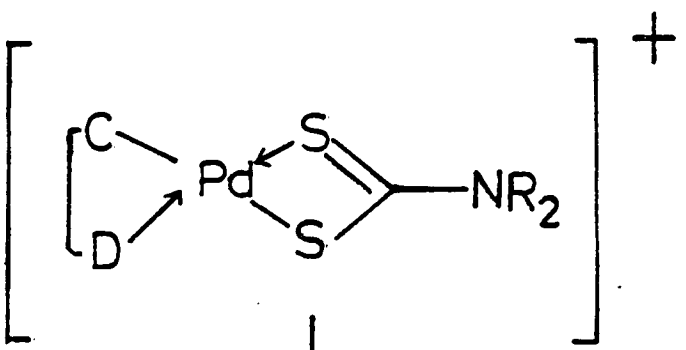
In general the dithiocarbamate ligand exhibits a moderate to strong intensity C=N absorption in the region 1480-1530 $cm.^{-1}$

(iii) Mass spectra

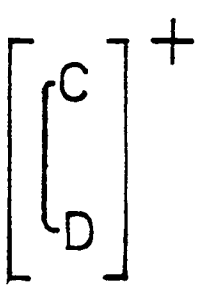
All the dithiocarbamate complexes synthesised in this work exhibited moderate to strong intensity molecular ions. The commonest breakdown fragment ions of these complexes are shown in figure (XIV). Disproportionation reactions in the mass spectro-

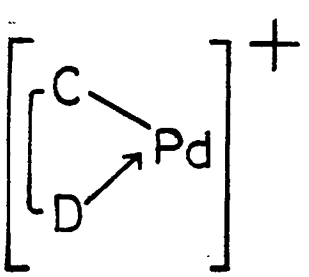


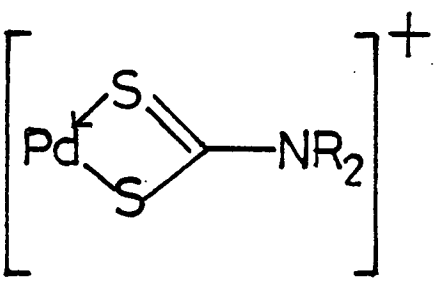
↑ disproportionation



↓ cleavage

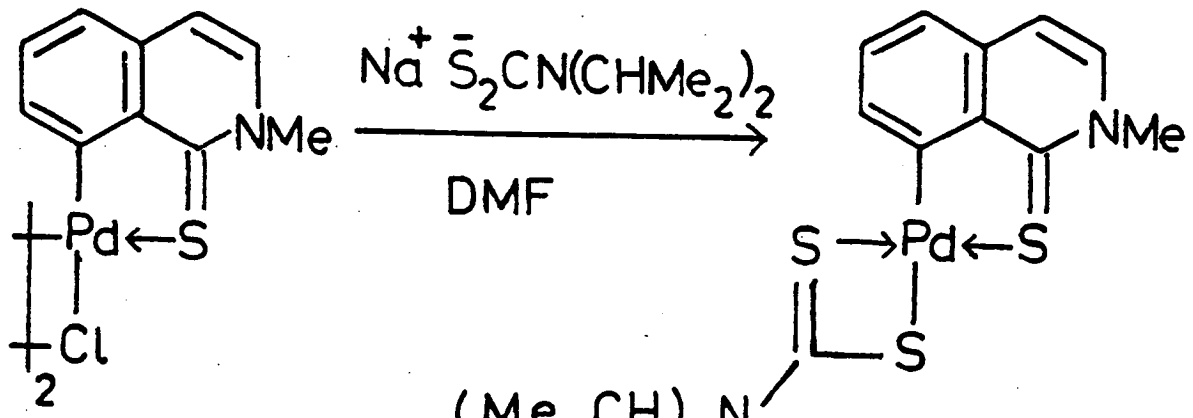




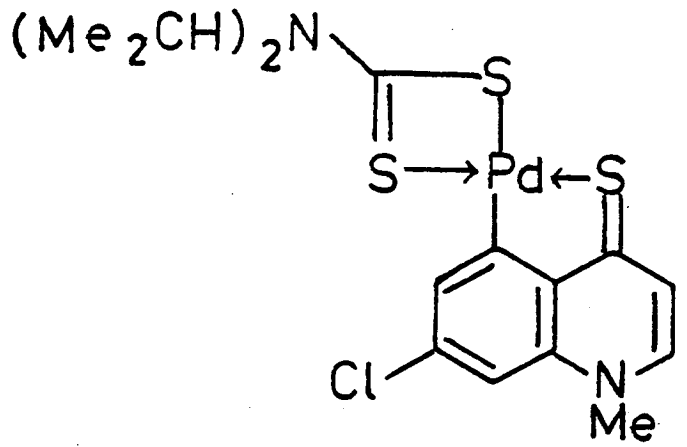


$\begin{bmatrix} C \\ \\ D \end{bmatrix}$ = substrate donor ligand

fig (xiv)



(134) (176)



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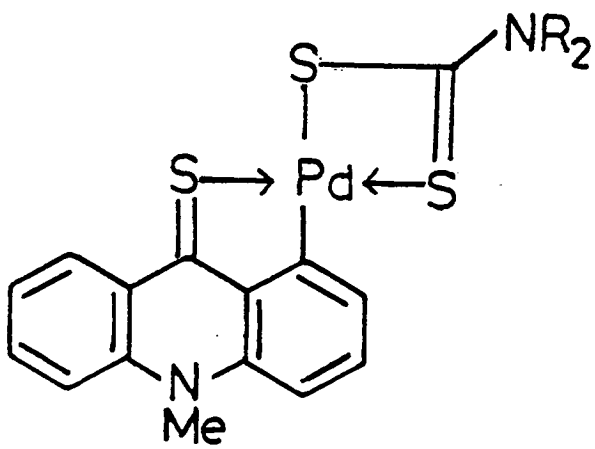


(178a, R=Me)
(178b, R=^{i}Pr)

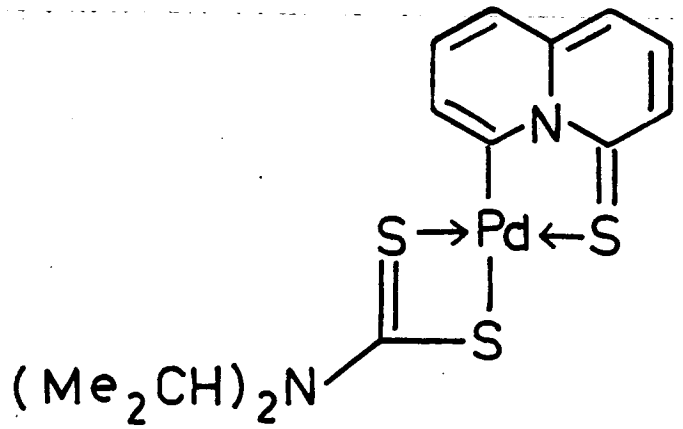
meter yielding bis dithiocarbamate complexes are also observed. The various m/e values quoted for palladium containing ions refer to ^{106}Pd which is the commonest isotope of palladium.

The chloride-bridged 2-methylisoquinoline-1-thione complex (134) was treated with sodium N,N-diisopropyldithiocarbamate in dimethylformamide to yield the complex (176) quantitatively. Similar exchange reactions of the dimeric complexes (137), (139), (141), (143), (146), (148), (2) and (40) gave the respective N,N-diisopropyl-(and in some cases N,N-dimethyl-)dithiocarbamate complexes (177), (178), (179), (180), (181), (182), (183) and (184).

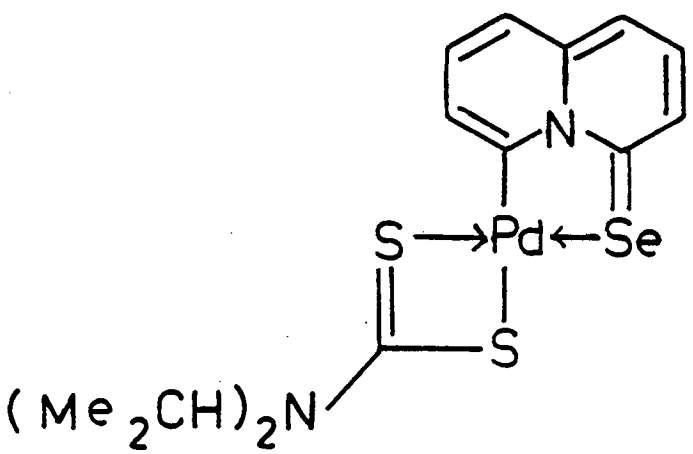
The acetate-bridged isothiazole complex (157) was treated with tetraethylammonium dimethyl- and diisopropyl-dithiocarbamate in chloroform to yield complexes (185a) and (185b) respectively.
The structures of the dithiocarbamate complexes synthesised in this work were most easily established by ^{1}H n.m.r. studies, the key features of which will be described here. Since the signals for the dithiocarbamate ligand protons vary only slightly upon changing the nature of the substrate ligand, the discussion of that particular region of the spectrum will in most cases be omitted. It can be assumed that the features of that region were as described previously for the general case.

The ^{1}H n.m.r. spectrum of the 2-methylisoquinoline-1-thione complex (176) showed a doublet ($J = 7Hz$) at δ 6.88 (1H), upfield of an aromatic multiplet, and this was assigned to H-4. The N-methyl protons appeared as a singlet at δ 4.02.

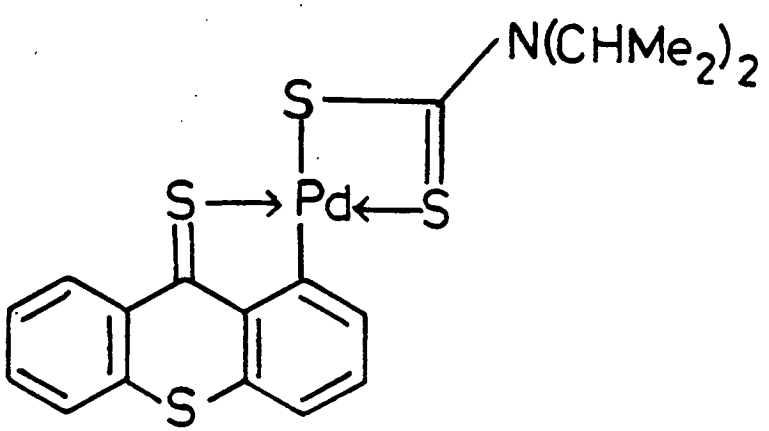
The ^{1}H n.m.r. spectrum of the 7-chloro-1-methylquinoline-4-thione complex (177) showed two <u>ortho</u> coupled doublets ($^{3}J = 7Hz$) at δ 7.40 (1H) and δ 6.90(1H). An unambiguous assignment of these



(179)



(180)

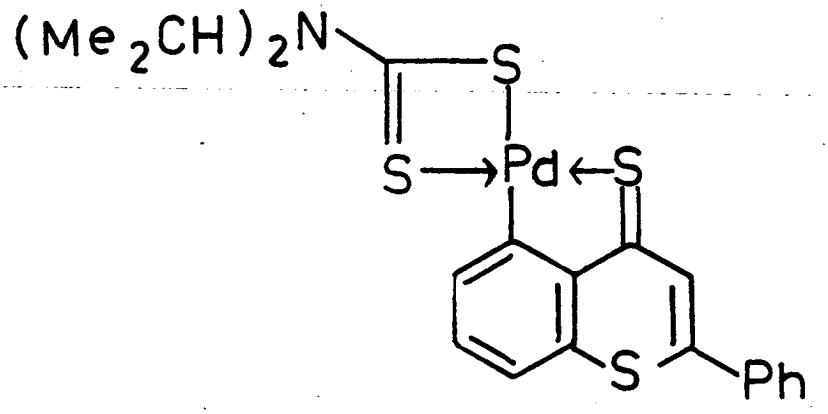


(181)

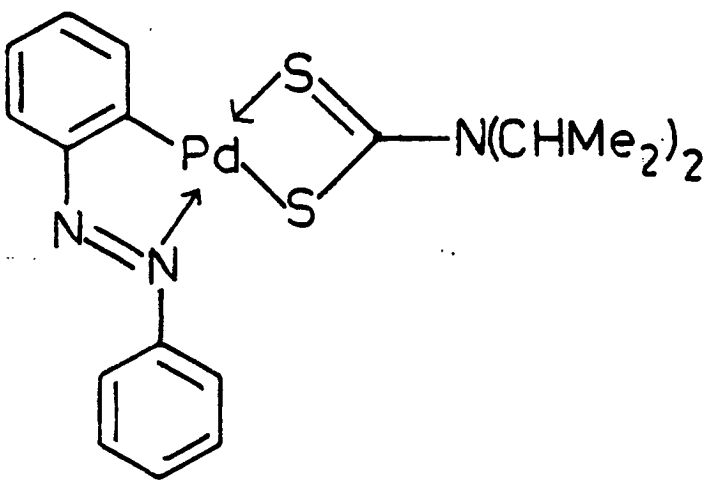
signals to either H-2 or H-3 was not possible though it seems likely that the low-field doublet was due to H-2. A similar problem was encountered in the assignment of the meta-coupled doublets ($^4J = 1.5$Hz) at δ 7.03 (1H) and δ 6.88 (1H) to H-6 or H-8. The N-methyl protons appeared as a singlet at δ 4.00. The absence of a signal due to H-5, which appears at δ 8.80 in the parent thione (136), was strong evidence for palladation having occurred in this position. The 10-methylacridine-9-thione complex (178b) was considerably less soluble than the other dithiocarbamate complexes synthesised in this work and a ^{1}H n.m.r. spectrum could only be obtained by a Fourier Transform technique. The aromatic region of the spectrum consisted of a doublet ($J = 7$Hz) at δ 8.78 (H-8) multiplets at δ 8.3-8.0 (2H), δ 7.8-7.5 (3H) and δ 7.3 (1H).

The N-methyl protons appeared as a singlet at δ 4.25. The corresponding N,N-dimethyldithiocarbamate complex (178a) was also synthesised, but on account of its very low solubility, it was neither amenable to n.m.r. studies nor to further chemical reaction.

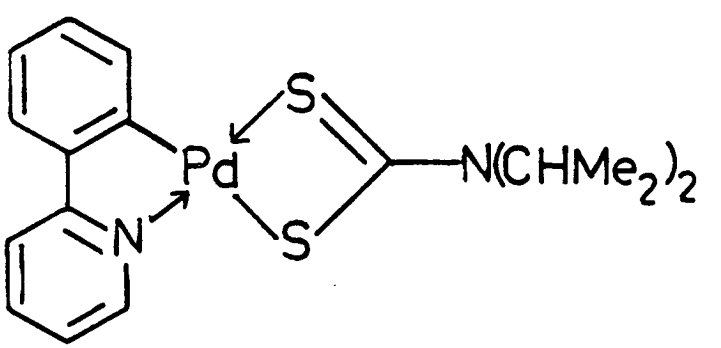
The quinolizine-4-thione complex (179) was shown by analytical and spectroscopic methods to have incorporated 0.5 molar equivalents of benzene upon recrystallisation from this solvent. The ^{1}H n.m.r. spectrum was recorded at 360 MHz. A doublet of doublets ($^3J = 7.96$ Hz, $^4J = 1.33$ Hz) at δ 7.70 was assigned to H-7, the downfield shift of this proton being attributed to the proximity of a Pd-S bond of the dithiocarbamate ligand. A triplet ($J = 7.96$ Hz) at δ 7.57 was tentatively assigned to H-8, although H-2 could also be considered here. A doublet of doublets ($^3J = 8.07$Hz, $^4J = 1.33$Hz) at δ 7.35 was assigned to H-9. The remaining aromatic protons were observed as a multiplet in the region δ 7.53 - 7.46.



(182)



(183)



(184)

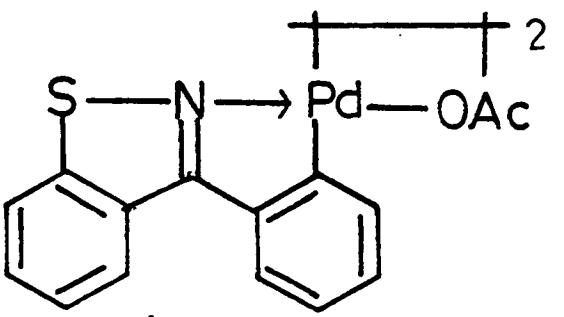
The structurally similar quinolizine-4-selone complex (180) was also shown to have incorporated 0.5 molar equivalents of benzene upon recrystallisation from this solvent. The ^{1}H n.m.r. spectrum of this complex was second order, even at 360 MHz. By analogy with the thione complex (179) a doublet of doublets (^{3}J = 7.09Hz, ^{4}J = 1.93Hz) at δ 7.96 was assigned to H-7. Another doublet of doublets (^{3}J = 6.12 Hz, ^{4}J = 2.80Hz) at δ 7.74 was tentatively assigned to H-3. The remaining aromatic protons appeared as a multiplet in the region δ 7.58-7.48. The absence of a signal due to H-6, which appears at δ 10.75 in the parent selone (142), was strong evidence for palladation having occurred in this position.

The thioxanthene-9-thione complex (181) showed a doublet (J = 8Hz) at δ 9.07 (1H) downfield of an aromatic multiplet which, as in the 10-methylacridine-9- thione complex (178b), was assigned to H-8. The remaining aromatic protons appeared as a multiplet in the region δ 7.7-7.2. It is interesting to note the greater solubility of this complex compared with its, N,N-dimethyldithiocarbamate analogue, for which no ^{1}H n.m.r. spectrum could be obtained.[47]

The 2-phenylthiochromene-4-thione complex (182) showed a singlet at δ 8.08 (H-3), the remaining aromatic protons appearing as a multiplet in the region δ 7.8-7.3. The absence of a signal due to H-5, which appears at δ 9.0 in the parent thione (147), was strong evidence for palladation having occurred in this position.

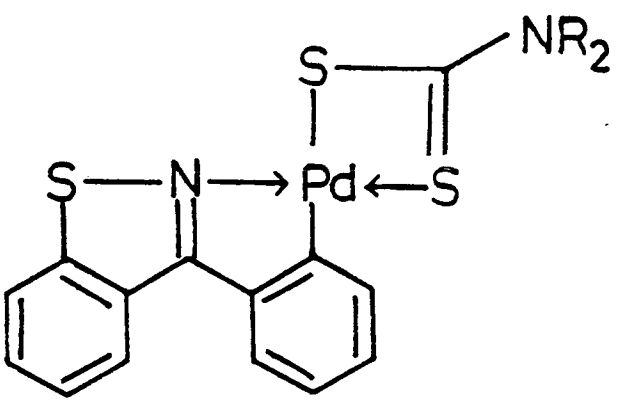
The ^{1}H n.m.r. spectrum of the azobenzene complex (183) was not resolved in the aromatic region when recorded at 100 MHz. The aromatic protons appeared as a multiplet in the region δ 8.1-7.1.

The 2-phenylpyridine complex (184) showed a doublet (J = 6Hz) at δ 8.36(1H) downfield of an aromatic multiplet and this was



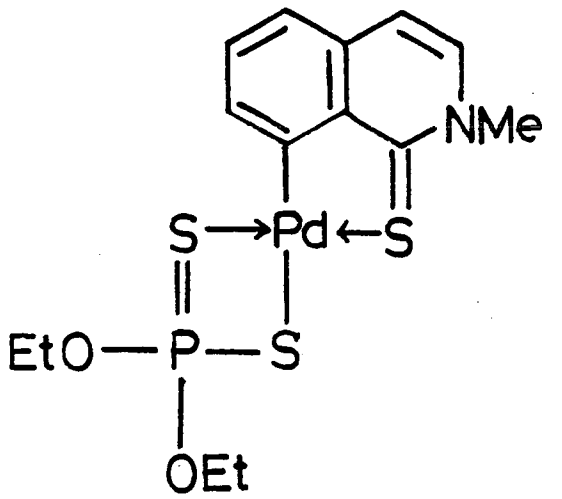
(157)

$Et_4\overset{+}{N}\ \bar{S}_2CNR_2$

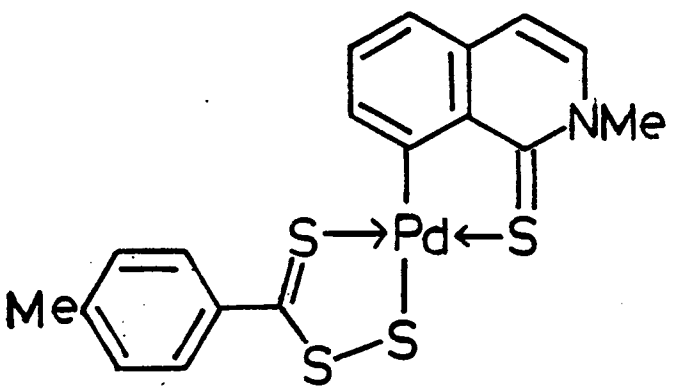


(185a , R = Me)

(185b , R = ^{i}Pr)



(186)



(187)

assigned to the 6 -pyridyl proton. The remaining aromatic protons appeared as a multiplet in the region δ 7.8-7.0.

The ^{1}H n.m.r. spectrum of the isothiazole complex (185a) showed a multiplet at δ 8.7(1H) downfield of an aromatic multiplet in the region δ 8.2-7.2. The low field signal was tentatively assigned to the proton ortho to palladium in the cyclopalladated ring. The N-methyl resonances appeared as two singlets at δ 3.42 and δ 3.39, thus demonstrating their non-equivalence. The aromatic region of the ^{1}H n.m.r. spectrum of the much more soluble N,N-diisopropyldithiocarbamate complex (185b) was very similar to that of (185a).

The complex 1-thioxo-2-methylisoquinolin-8-yl (0,0-diethyldithiophosphato) palladium (II) (186) was prepared by reaction of the dimeric complex (134) with tetraethylammonium 0,0-diethyl-dithiophosphate in dimethylformamide. Its ^{1}H n.m.r. spectrum was recorded at 360 MHz and all five aromatic protons were distinguishable. Interestingly, the lowest field signal, that due to H-7, was observed as a doublet of doublets of doublets at δ 7.64 and showed five-bond phosphorus coupling in addition to ortho and meta - coupling. The relatively large value 1.88Hz for $^5J_{PH}$ is noteworthy. The signals due to H-6 and H-5 were observed as a triplet at δ 7.43 and a doublet of doublets at δ 7.25 respectively. The doublets at δ 7.35 and δ 6.97 were assigned to H-3 and H-4 respectively, the low-field shift of the former signal relative to the latter being attributed to the inductive effect of the α -nitrogen atom. The N-methyl protons were observed as a singlet at δ 4.04 and the ethoxy protons as a multiplet at δ 4.23 (4H) and a triplet at δ 1.38 (6H).

The complex 1-thioxo-2-methylisoquinolin-8-yl (p-

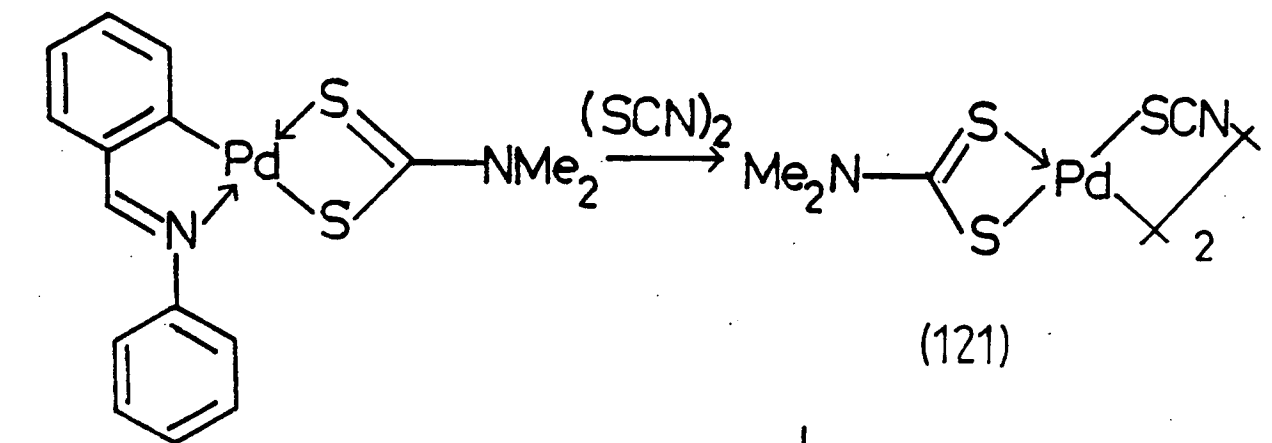
perthiotoluato) palladium (II) (187) was prepared by reaction of the dimeric complex (134) with bis (p-perthiotoluato) zinc (II) in dimethylformamide. The characterisation of this complex was by mass spectroscopic (m/e 479, M^+) and analytical methods as it was not sufficiently soluble for n.m.r. studies.

(4.1) REACTIONS OF DITHIOCARBAMATE AND RELATED COMPLEXES WITH VARIOUS POTENTIAL SULPHUR-TRANSFER REAGENTS

Davis[44] reported the first use of thiocyanogen as a reagent for the replacement of palladium in cyclopalladated complexes by a thiocyanato-group. This work was then extended by Grinter[47] who demonstrated the potential of this reaction in the synthesis of novel isothiazolium and 1,2-dithiolium ring systems.

As a starting point in this investigation, the benzylideneaniline complex (188), was treated with thiocyanogen to yield di-μ-thiocyanato-bis (N,N-dimethyldithiocarbamato) palladium (II) (121) and N-(2-thiocyanatobenzylidene)aniline (122). As reported by Davis, the thiocyanate (122), a yellow oil, could not be crystallised. Treatment of the oil with perchloric acid in acetic acid gave a precipitate of the hitherto unknown 2-phenyl-1,2 benzisothiazolium perchlorate (189).

The ^1H n.m.r. spectrum of (189) showed a sharp, one-proton singlet at δ 9.74 due to H-3 and a narrow, five-proton multiplet at δ 7.7-7.9 due to the phenyl protons. Between these signals were four others which, though quite well resolved, showed second order effects which prevented assignment with complete certainty. Tentatively, two broad doublets at δ 8.55 and 8.31 were assigned to H-4 and H-7, respectively, a triplet of doublets at δ 8.12 to H-6, and a partially obscured signal(probably a distorted triplet of doublets) at δ 7.99 to H-5.



(188)

(121)

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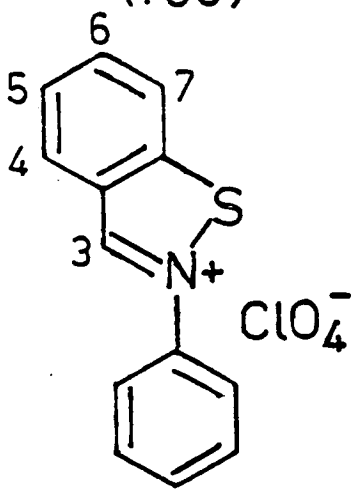
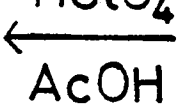
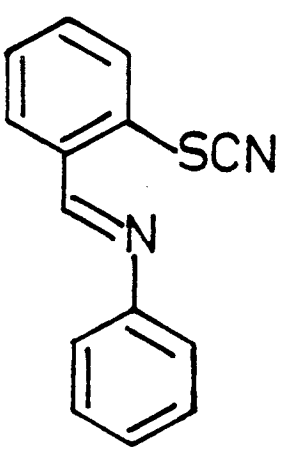


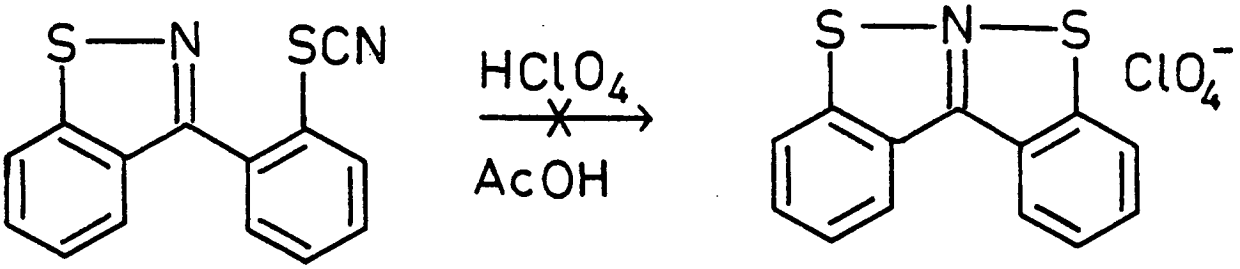




(189)

(122)

Reaction of the isothiazole complex (185a) with thiocyanogen yielded 3(2-thiocyanatophenyl)-1,2-benzisothiazole (190) which was characterised by infrared studies (SCN absorption at 2150 cm^{-1}), mass spectroscopy [M^+ 268 and 242 (M^+ - CN),] and by exact mass measurements of these ion peaks. Its ^1H n.m.r. spectrum was uninformative, showing only a multiplet in the region δ 8.1-7.4. Upon treatment with perchloric acid in acetic acid, no reaction was observed after 24 hours. Warming the reaction mixture caused decomposition to yield an intractable tar. In view of the mass spectrometric loss of CN to give, presumably, the cation of (191), the failure to obtain this ring system by chemical means was unexpected and disappointing. Had the compound (191) been formed, the linkage of two sulphur atoms to the same nitrogen atom would have been a unique and interesting structural feature of this heteroaromatic system.



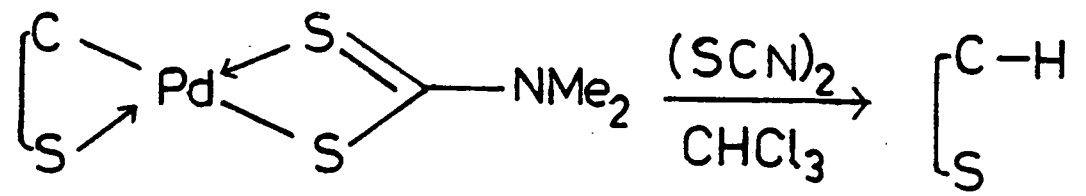
(190) (191)

Limitations in the use of thiocyanogen in these reactions were reported by Grinter[47] who found that reaction of the quinolizine-4-thione and 2-methylisoquinoline-1-thione complexes, (131) and (132) respectively, with thiocyanogen failed to yield the expected palladium-free thiocyanato-compounds. In both these the parent thiones and di-μ-thiocyanato-bis (N,N-dimethyldithiocarbamato) palladium (II) (121) were formed (figure (XV)).

To account for these observations Grinter suggested that the electron-donating thioamide group in these complexes stabilised the electron-deficient $Pd^{(IV)}$ complex which has been proposed as an intermediate in these reactions.[44] The stabilised intermediate might then decompose via a homolytic process to yield a 4-thioxo-quinolizin-6-yl (or 1-thioxo-2-methylisoquinolin-8-yl) radical which could abstract hydrogen from the solvent (chloroform) to yield the parent thiones.

The more soluble 2-methylisoquinoline-1-thione N,N-diisopropyldithiocarbamate complex (176) synthesised in this work was therefore treated with thiocyanogen under similar conditions in the hope that a different reaction course would be followed. Upon admixture of the reactants, a deep red solution formed immediately and then became lighter in colour with the simultaneous precipitation of a yellow solid. On the basis of its elemental analysis and infrared SCN absorptions, this solid was thought to be di-μ-thiocyanato-bis (1-thioxo-2-methylisoquinolin-8-yl) dipalladium (II) (192). Chromatography of the soluble portion of the reaction mixture yielded a small amount of bis (N,N-diisopropyldithiocarbamato) palladium (II) and other unidentified material.

The possibility that reaction might occur in the desired



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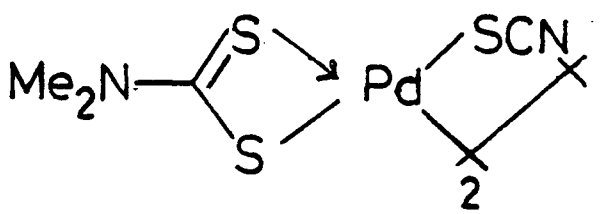
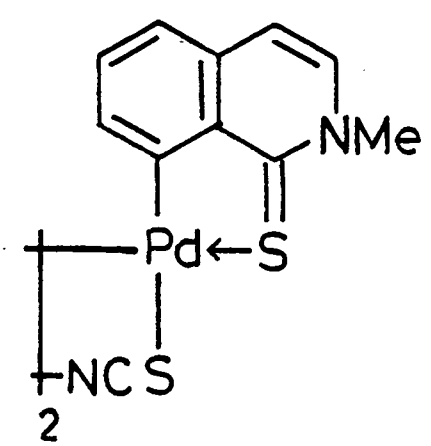


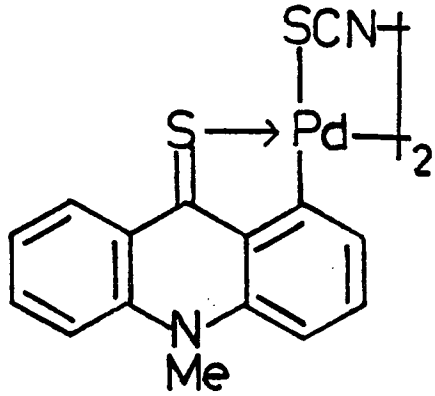
(121)

$\left[\begin{matrix} C \\ \\ S \end{matrix}\right.$ = substrate sulphur donor ligand

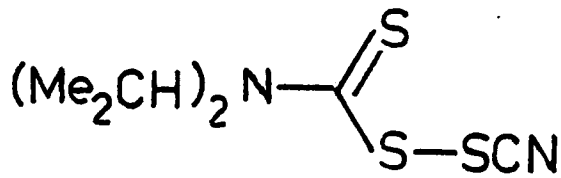
fig (xv)



(192)



(193)



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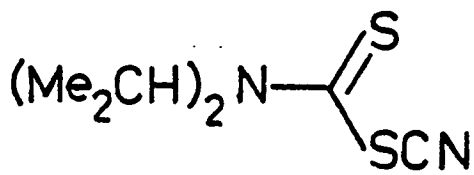


(195)

manner by use of a complex which contained a ligand other than a dithiocarbamate was examined. For this purpose the O,O-diethyl dithiophosphate complex (186) was treated with thiocyanogen but the result was analogous to that of the previous reaction; the thiocyanate-bridged complex(192) was isolated in addition to a small amount of bis (O,O-diethyl dithiophosphato)palladium (II).

The reaction of the 10-methylacridine-9-thione complex (178b) with thiocyanogen also followed a parallel course. Di-μ-thiocyanato-bis (9-thioxo-10-methylacridin-1-yl) dipalladium (II) (193) was obtained upon filtration of the reaction mixture and was characterised by its elemental analysis and infrared spectrum. A mass spectrum of material recovered from the filtrate showed, in addition to ion peaks at m/e 458 and 282 corresponding to bis (N,N-diisopropyldithiocarbamato) palladium (II), two other ion peaks at m/e 234 and 202. These peaks were thought to correspond to N,N-diisopropylthiocarbamoylsulphenyl thiocyanate (194) and N,N-diisopropyl-thiocarbamoyl thiocyanate (195) respectively, the latter being probably a mass spectral breakdown fragment of the former.

To account for these observations, the following mechanism is proposed and is illustrated in figure (XVI). The initial step is the oxidative addition of thiocyanogen to yield a $Pd^{(IV)}$ intermediate complex. Reductive elimination then occurs, one thiocyanate unit remaining bound to palladium to form the thiocyanate-bridged dimer, the other being transferred to the dithiocarbamate ligand to yield the sulphenyl thiocyanate. The sulphenyl thiocyanate was never isolated from these reactions but it is probable that such a reactive molecule would decompose upon chromatography of the reaction mixture.

The products isolated from these reactions were different from those reported by Grinter,[47] but it would seem unlikely that such

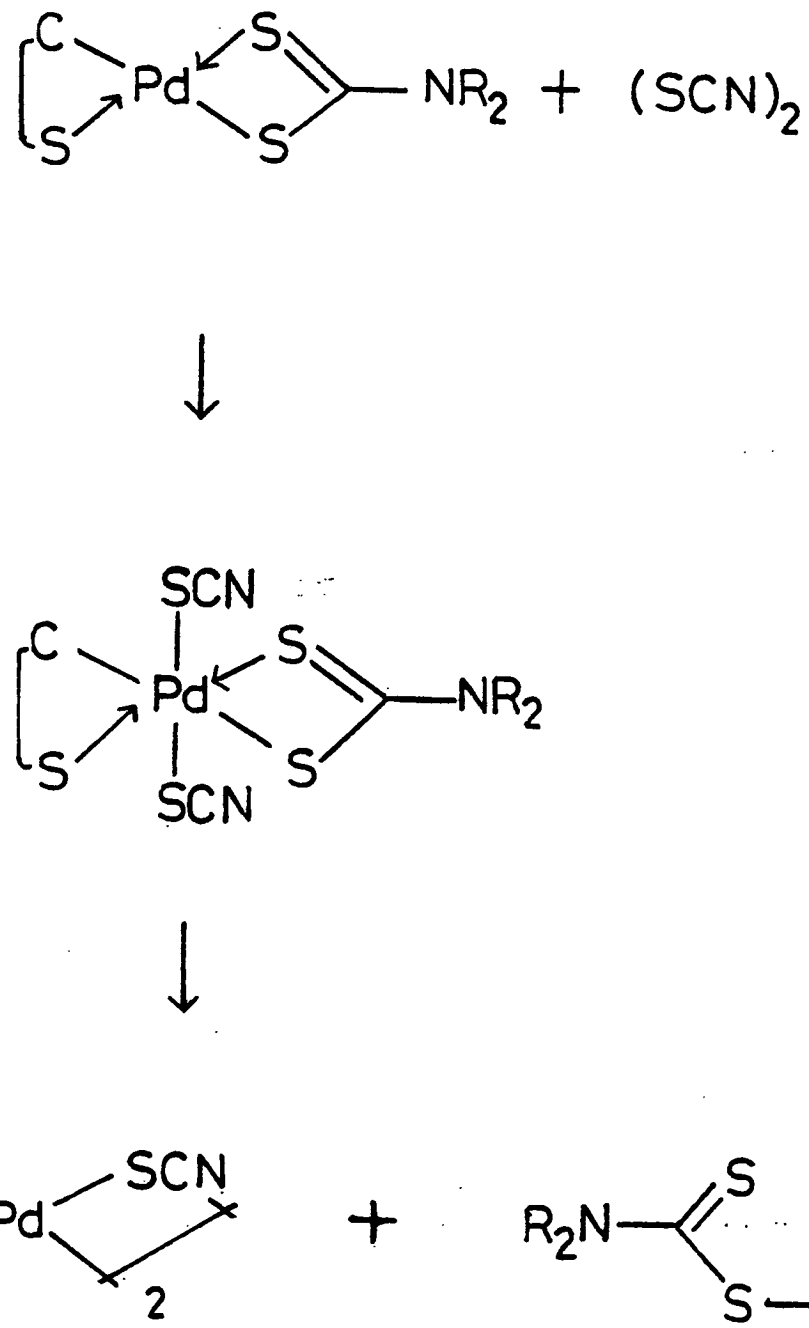


fig (xvi)

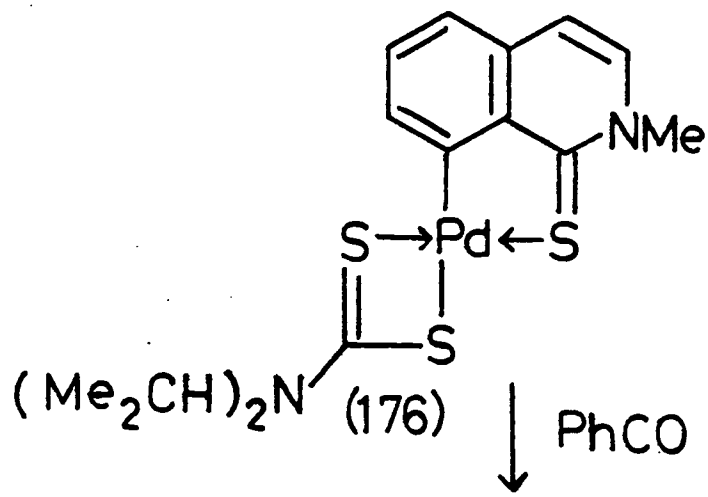
differences could arise as a result of the change in dithio ligands (dimethyl to diisopropyldithiocarbamates). The reason for this anomaly therefore remains obscure.

The failure of the thiocyanogen method led to a search for alternative methods to bring about the replacement of palladium in cyclopalladated thioamide complexes by sulphur. Only the 2-methylisoquinoline-1-thione complex (176) was used in these investigations as its behaviour towards potential sulphur-transfer reagents was likely to be typical of other cyclopalladated thioamide complexes.

Reaction of (176) with dibenzoyl disulphide was attempted with a view to synthesising the thioester (196), hydrolysis of which to the corresponding thiol, and subsequent oxidation would yield the dithioloisoquinolinium salt (197) (Scheme (III)). It was thought that this electronegatively substituted disulphide, like thiocyanogen, would be a sufficiently strong oxidant to form the Pd^{IV} intermediate complex (198), and that the subsequent reductive elimination of (196) should be favoured by chelation of the thiobenzoyl ligand to palladium to yield (199).

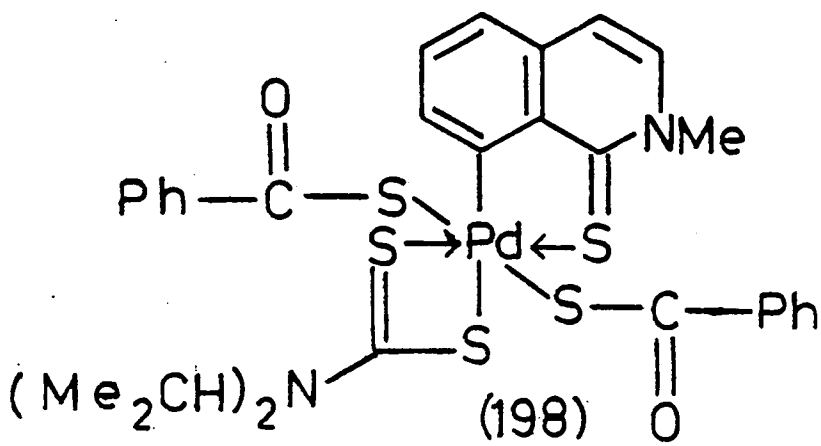
In practice, however, it was found that no reaction occurred either in boiling chloroform or in boiling 1,1,2-trichloroethane. In the latter solvent, decomposition of the disulphide occurred, the palladium complex (176) being recovered after chromatography on alumina.

Another approach to the dithioloisoquinolinium ring system (197) involving the use of sulphur transfer reagents [S] was investigated. It was envisaged that treatment of complex (176) with such a reagent would yield the complex (200) via insertion of a sulphur atom into

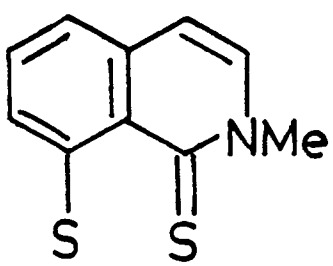


(176)

PhCO S-S COPh



(198)



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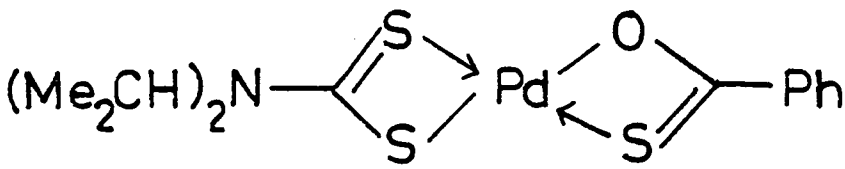
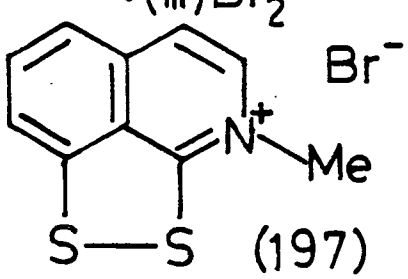


(199)

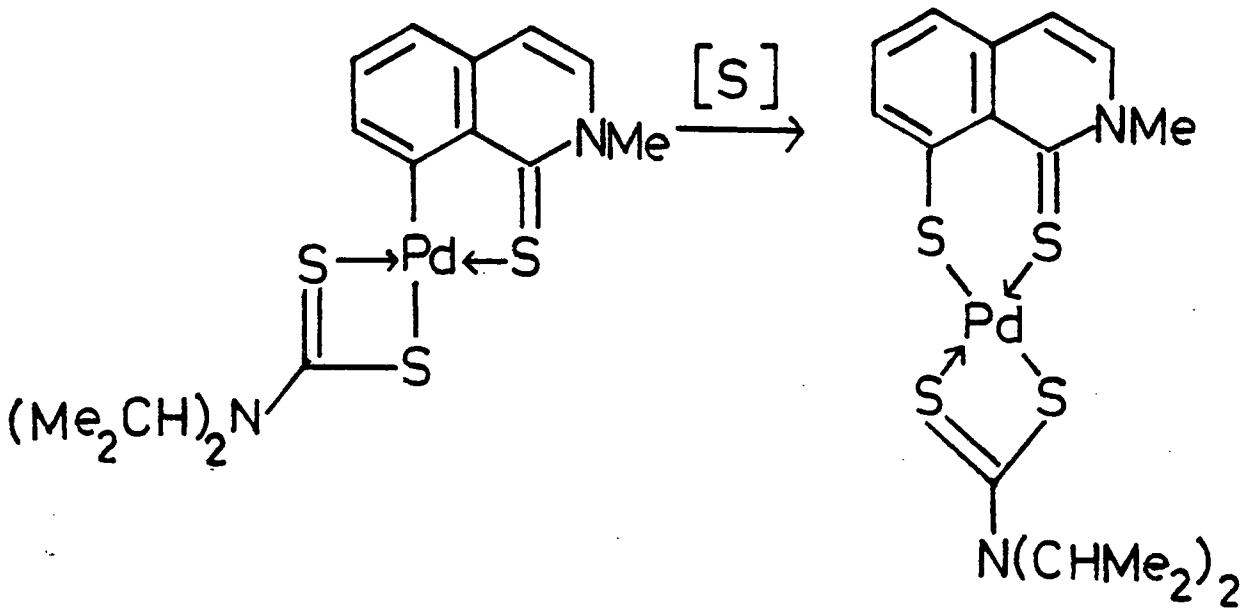
CO.Ph (196)

(i) H^+/ H_2O
(ii) H_2O_2
(iii) Br_2

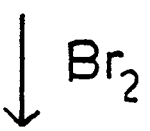


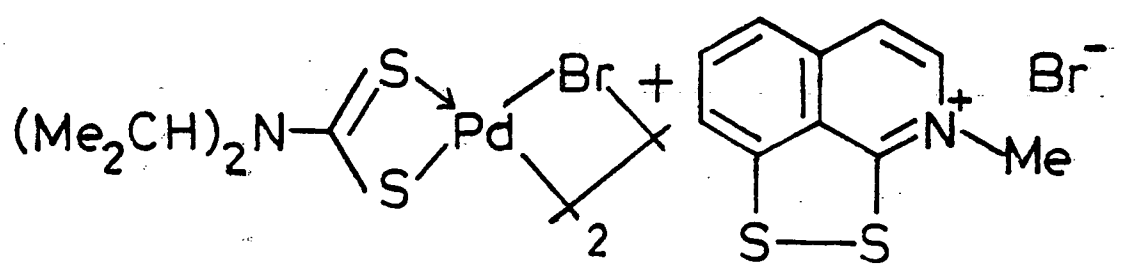
(197)

Scheme (iii)



(176) (200)



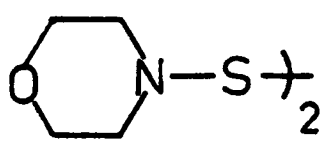


(201) (197)

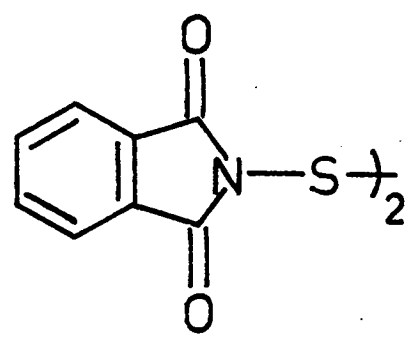
Scheme(iv)

the palladium-carbon σ -bond. Subsequent treatment of this complex with bromine might then yield the dithioloisoquinolinium ring system (197) and the bromide-bridged dithiocarbamate complex (201) (Scheme(IV)).

It was thought that bis (amine) disulphides $(R_2NS)_2$, in the light of their well established role as vulcanisation agents, might effect this conversion. It was recently shown[68] that thiophenes are formed when such disulphides are heated with acetylenes, and it was suggested that this sulphur-transfer reaction involves the intermediacy of thionitroxyl radicals ($R_2NS\cdot$) which are known[69] to be formed, by reversible dissociation, when the disulphides are heated alone.

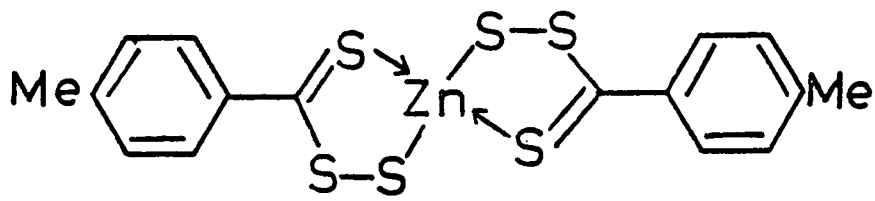


(202)



(203)

Reaction of complex (176) with N,N′-dithiobismorpholine (202) in boiling toluene yielded only starting materials, the recovery of which was effected by chromatography. Under similar conditions, reaction of complex (176) with N,N′-dithiobisphthalimide (203) yielded the palladium complex (176) only, the disulphide decomposing to intractable material.

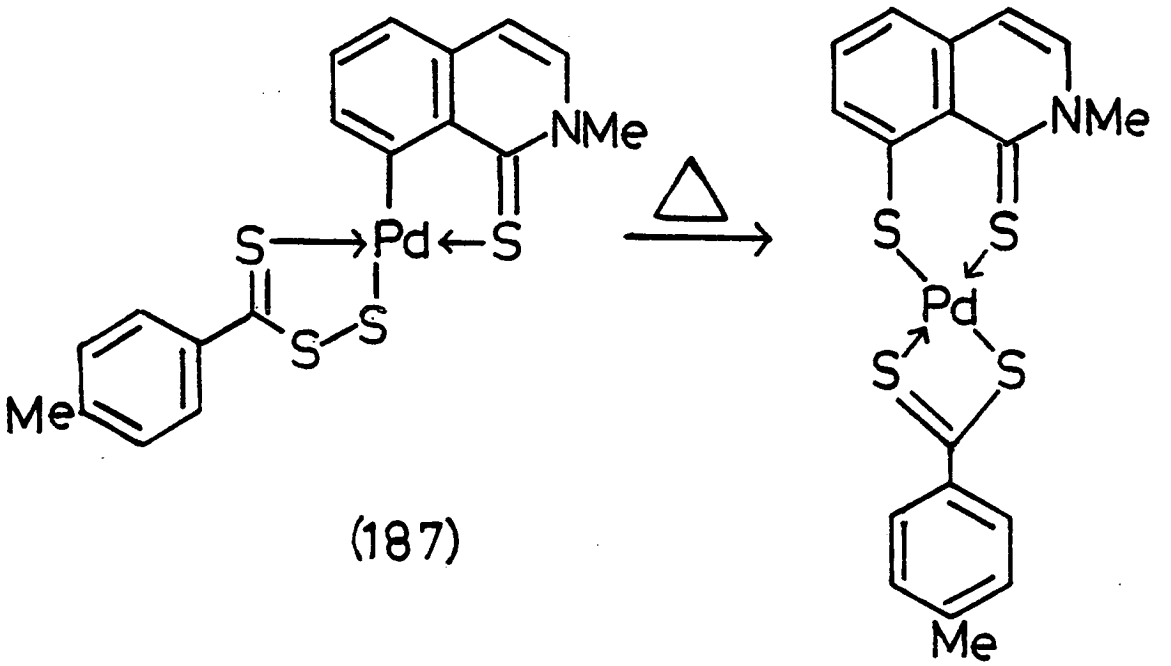


(204)

Reaction of complex (176) with the sulphur-rich complex bis (p-perthiotoluato) zinc (II)[70,71] (204) in boiling dimethylformamide yielded a solid which was thought to be zinc sulphide and a multi-component gum which was not likely to be separable by column chromatography.

In view of the failure of these reactions to effect sulphur transfer by an intermolecular process, the possibility of intramolecular sulphur transfer was therefore examined.

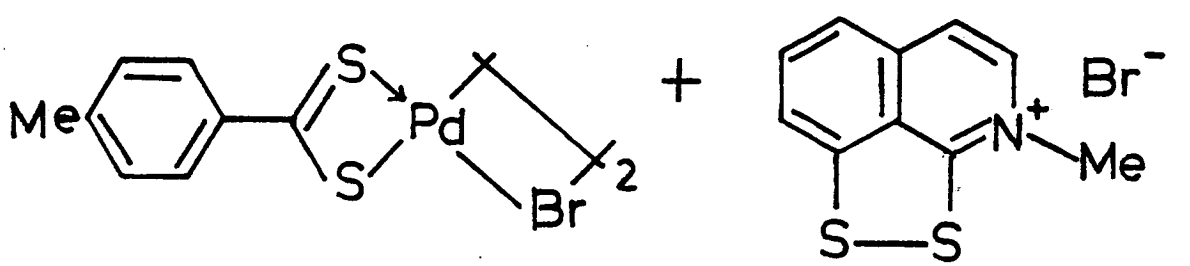
Fackler has demonstrated the exceptional lability of sulphur in perthiocarboxylate zinc complexes[72] as exemplified by the equilibrium (205) $\rightleftharpoons$ (206) in which interligand transfer of sulphur is sufficiently rapid to render the two R groups magnetically equivalent at moderate temperatures.



(187)

(207)

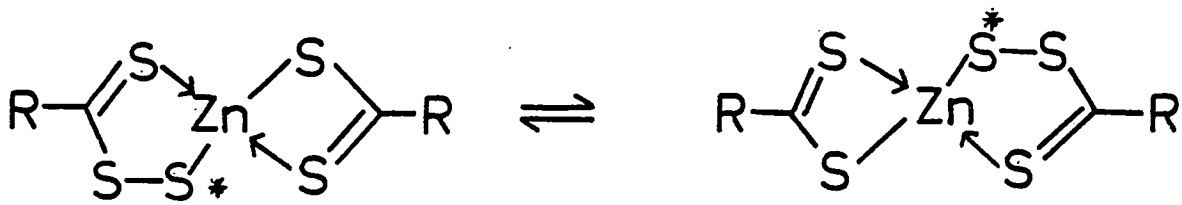
Br_2



(208)

(197)

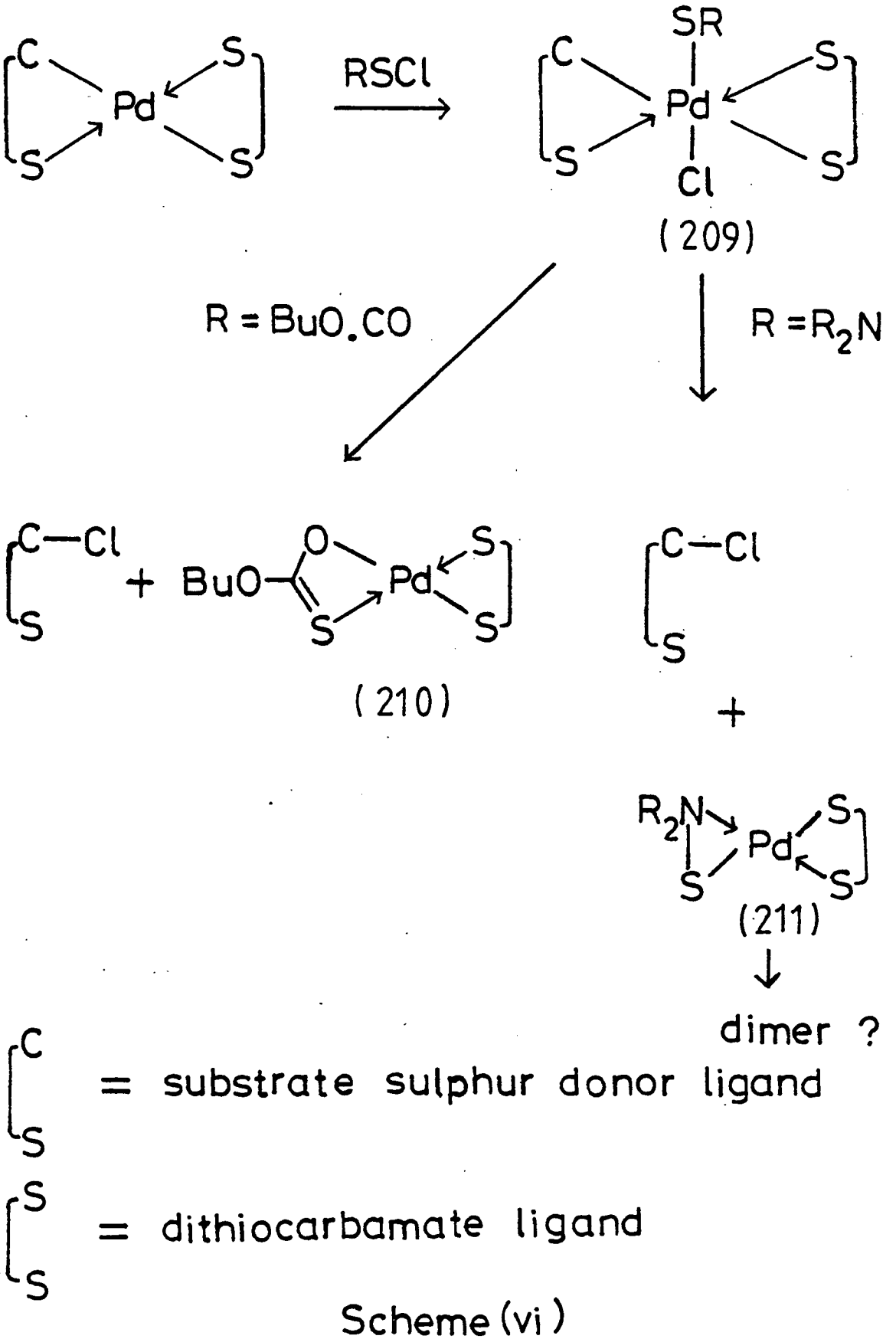
Scheme (v)



(205) (206)

This equilibrium suggested the possibility of a similar interligand transfer in the palladium complex (187), thus generating the complex (207). Such a reaction would probably be irreversible since the latter complex would be more stable than the former on account of its greater number of palladium-sulphur bonds. Upon treatment with bromine, complex (207) might then yield the dithioloisoquinolinium ring system (197) and the bromide-bridged dimeric complex (208) (Scheme (V)). However, in practice it was found that the perthiotoluate complex (206) was stable to thermolysis in boiling 1,1,2-trichloroethane and in 1,2,4-trichlorobenzene at 190°.

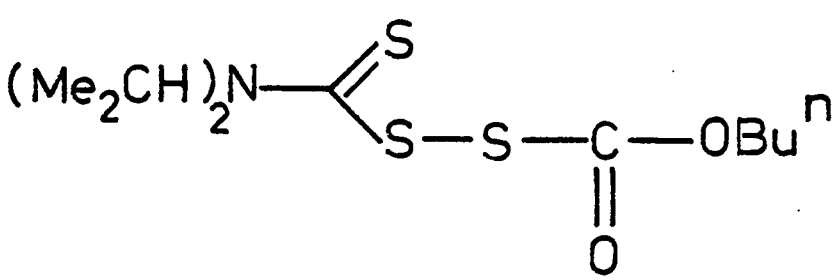
It is convenient at this stage, to discuss the reactions of the palladium complex (176) with certain sulphenyl chlorides (R S Cl). These reactions were originally envisaged as possible methods for the replacement of Pd by Cl (Scheme (VI)) and it was argued that oxidative addition would take place initially, forming the intermediate complex (209), and that the subsequent reductive elimination might be encouraged to proceed in the desired manner if


RSCl
SR
Cl
(209)
R = BuO.CO
R = R2N
BuO
(210)
+
R2N
(211)
dimer ?
= substrate sulphur donor ligand
= dithiocarbamate ligand

Scheme (vi)

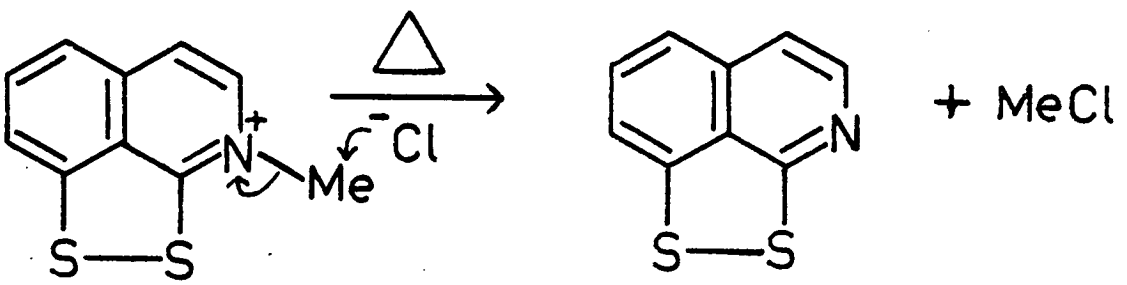
the group R contained a donor atom capable of transforming the group RS from a unidentate to a bidentate ligand. Two known[73] sulphenyl chlorides of appropriate constitution were n-butoxy-carbonylsulphenyl chloride (BuO.CO.SCl) and morpholine-N-sulphenyl chloride (R_2N S Cl), the bidentate ligand complexes they might possibly form, being (210) and (211) respectively. In the event, neither of these reagents gave the proposed products but the second one led to a highly efficient method for the replacement of palladium by sulphur.

Upon reaction of the complex (176) with n-butoxy-carbonylsulphenyl chloride a yellow precipitate formed and was identified as di-μ-chloro-bis (1-thioxo-2-methylisoquinolin-8-yl) dipalladium (II) (134). Chromatography of the soluble portion of the reaction mixture yielded only a small amount of a substance which was thought to contain mainly bis (N,N-diisopropyldithiocarbamato) palladium (II). The formation of (134) in this reaction suggests that oxidative addition had occurred but that the subsequent reductive elimination had not taken the expected course. The fate of the n-butoxycarbonylsulphenyl moiety was not discovered. Stoichiometeric considerations suggest that it ought to have been removed as (212) and it is possible that this compound might have decomposed during attempted chromatography.



(212)

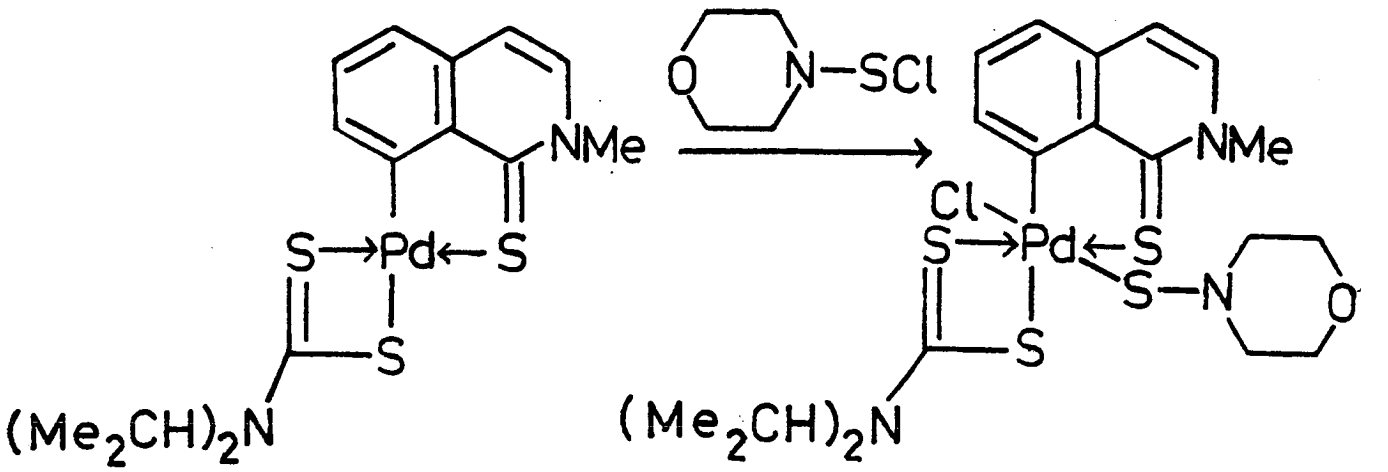
Treatment of the complex (176) with one molar equivalent of morpholine-N-sulphenyl chloride in chloroform produced a yellow precipitate. Infrared studies on this substance suggested that it was a mixture, one component of which, was di-μ-chloro-bis (1-thioxo-2-methylisoquinolin-8-yl) dipalladium (II) (134). Its mass spectrum showed ion peaks at m/e 191 and 52/50 (Cl) and were assigned tentatively to the thermal breakdown fragments of 3-methyl [1,2] dithiolo [3,4,5-ij] isoquinolinium chloride (213), i.e., [1,2] dithiolo [3,4,5-ij]isoquinoline (214) (m/e 191) and methyl chloride (m/e 52/50).



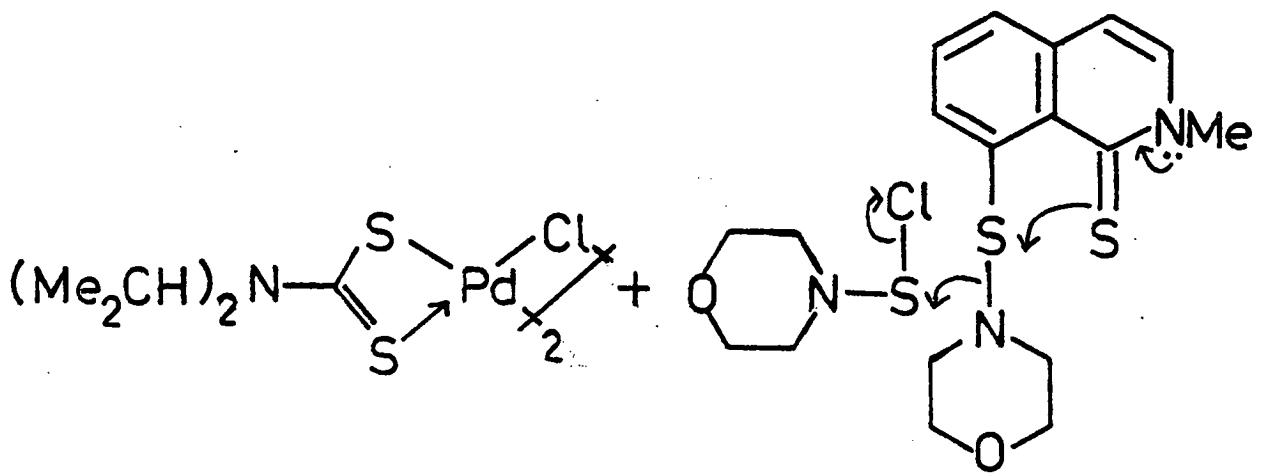
(213) (214)

Chromatography of the soluble portion of the reaction mixture yielded a cream coloured solid, which was identified as N,N'-dimorpholinyl sulphide (215), in addition to bis (N,N-diisopropyl-dithiocarbamato) palladium (II). To account for the formation of these products the following mechanism is proposed and is illustrated in figure (XVII).

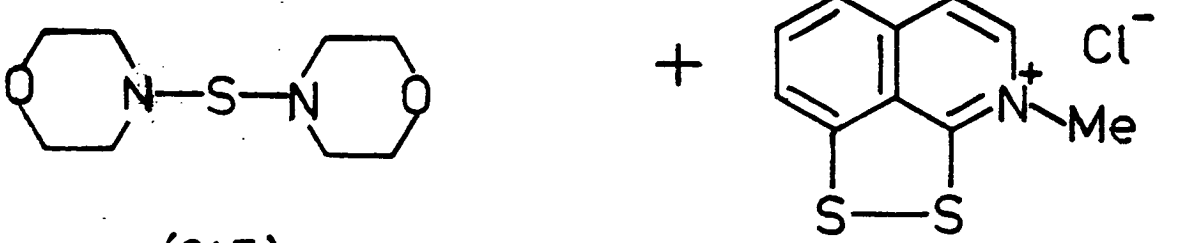
Oxidative addition of morpholine-N-sulphenyl chloride forms the $Pd^{(IV)}$ complex (216) which then undergoes reductive elimination of the sulphenamide (217) to form complex (218).



(176) (216)



(218) (217)



(215) (213)

(176) + (218) ⟶ (134) + $[(Me_2CH)_2NCS_2]_2Pd$

fig (xvii)

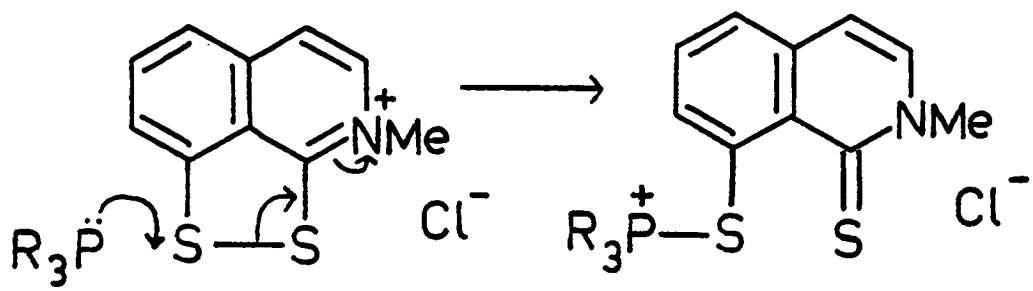
The sulphenamide then reacts with another molecule of morpholine-N-sulphenyl chloride to form the sulphide (215) and the dithiolo-isoquinolinium salt (213). Ligand exchange occurs between (176) and (218) to yield (134) and bis (N,N-diisopropyldithiocarbamato) palladium (II).

Upon consideration of the stoichiometry of this reaction it is obvious that two molar equivalents of morpholine-N-sulphenyl chloride would be required for complete conversion of (176) to (213). The undesirable ligand exchange reaction could be minimised by maintaining an excess of the sulphenyl chloride throughout the course of the reaction. This condition was most easily met by the dropwise addition of a solution of the palladium complex to a solution containing two molar equivalents of sulphenyl chloride. These conditions resulted in the formation of only the dithiolo-isoquinolinium salt (213), the chloride-bridged dithiocarbamate complex (218) and N,N'-dimorpholinyl sulphide (215).

The separation of the highly insoluble compounds (213) and (218) proved difficult initially. Neither compound was amenable to chromatography or preferential solvent extraction. A more likely solution to this problem was thought to lie in the ability of monodenate ligands to react with dimeric complexes such as (218) forming more soluble monomeric derivatives. Separation of the dithiolo-isoquinolinium salt from the monomeric derivative would then be facilitated on account of their different solubilities. The use of phosphines as bridge-splitting agents in this reaction was considered inappropriate since precedent exists for the reaction of phosphines with disulphide bonds.

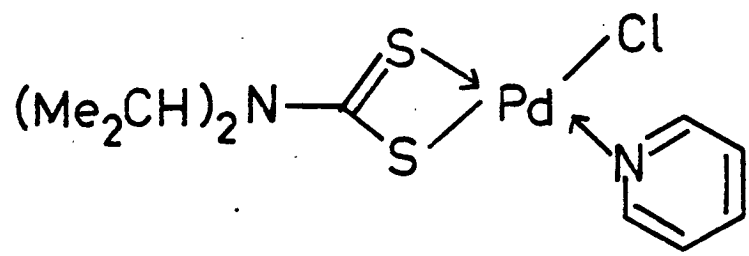
It is known, for example, that triphenylphosphine reacts with acyl, thioacyl, and vinylogous acyl disulphides, via

nucleophic displacement on sulphur to yield the corresponding monosulphide.[74] Reaction of a phosphine with dithioloisoquinolinium salt (213) might conceivably yield the phosphonium salt (219).



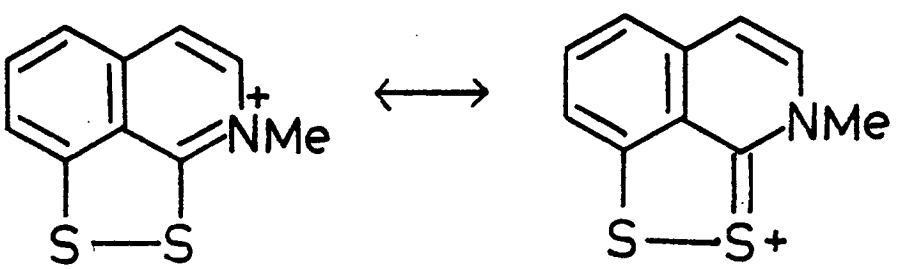
(213) (219)

The choice of the hard base pyridine was considered to be more appropriate in this context on account of its lesser thiophilicity compared with phosphine soft bases. Upon treatment of a dichloromethane suspension of (213) and (218) with an excess of pyridine, the soluble orange complex (220) formed and was easily separated from the insoluble dithioloisoquinolinium salt by filtration.



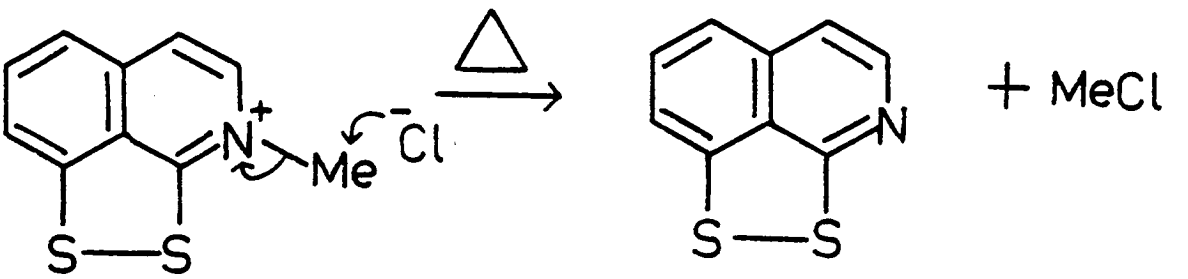
(220)

The salt obtained from this reaction was found to be analytically pure and thus illustrated the effectiveness of the separation. The novel ring system thus prepared was characterised by high field ^{1}H n.m.r. studies, details of which will be discussed later. It may be formulated as an isoquinolinium salt (213) or as a dithiolium salt (213a) and clearly both structures will contribute to the resonance hybrid, though the former is expected to be the more important.



(213) (213a)

In order to test the idea that the formation of [1,2] dithiolo [3,4,5-ij] isoquinoline (214) from the salt (213) in the mass spectrometer was a consequence of thermal reaction rather than of electron impact, the salt (213) was heated at 250°C in a sublimation tube *in vacuo*. An orange sublimate was formed, which upon subsequent chromatography, yielded the yellow dithiole (214) which appeared to be unstable in air. The identity of this product was established by ^{1}H n.m.r. and exact mass measurement of the molecular ion (m/e 191).

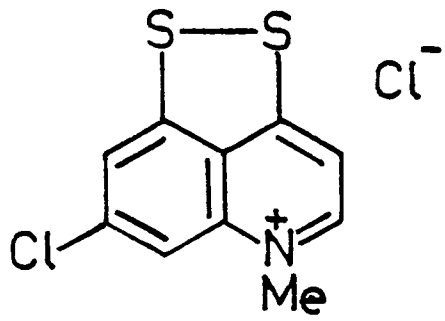


(213) (214)

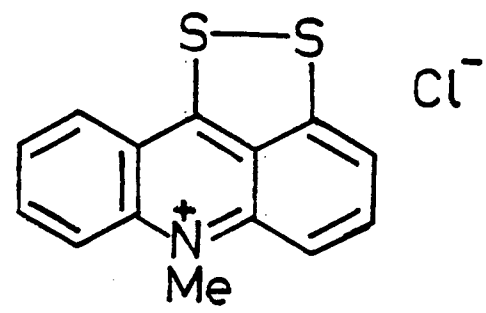
The ^{1}H n.m.r. spectrum of the dithiole showed two doublets ($J = 6Hz$) at δ 8.02 and 7.05, which were assigned to H-4 and H-5 respectively, and a multiplet in the region δ 7.5-7.2, assigned to H-6,7, and 8.

This new synthetic route to 1,2-dithiolium salts was extended to yield several novel 1,2-dithiolium ring systems. Reaction of the dithiocarbamate complex (177) with morpholine-N-sulphenyl chloride yielded 7-chloro-5-methyl [1,2] dithiolo [3,4,5-de] quinolinium chloride (221). The analytically pure product in this case, and in subsequent cases, was obtained by conversion to the perchlorate salt. The dithiocarbamate complex (178) yielded 6-methyl [1,2] dithiolo [3,4,5-kl] acridinium chloride (222) in the same way.

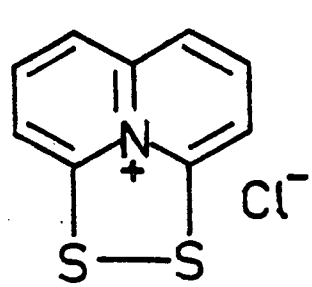
Similarly, [1,2,4] dithiazolo [3,4,5-de] quinolizinylium chloride (223) was synthesised from the dithiocarbamate complex (179). This ring system can be represented by the canonical resonance structures (223a) and 223b), the latter of which is isoelectronic with the 12 π antiaromatic cycl [3,3,3,] azine system (224). In marked



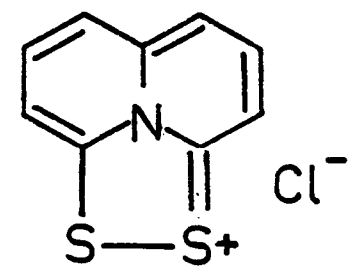
(221)



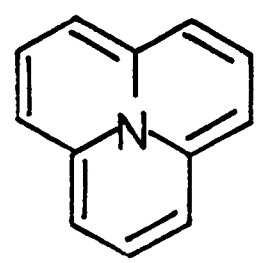
(222)



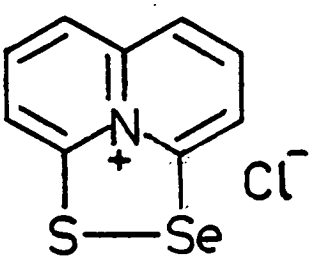
(223a)



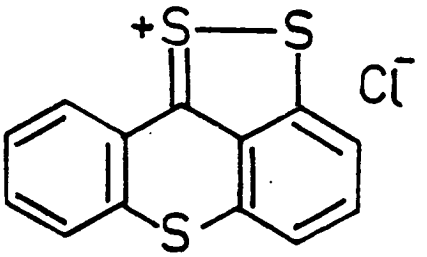
(223b)



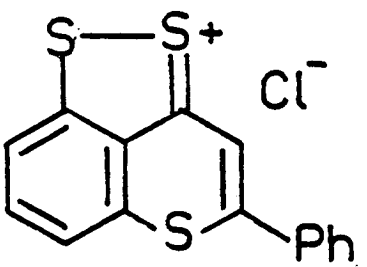
(224)



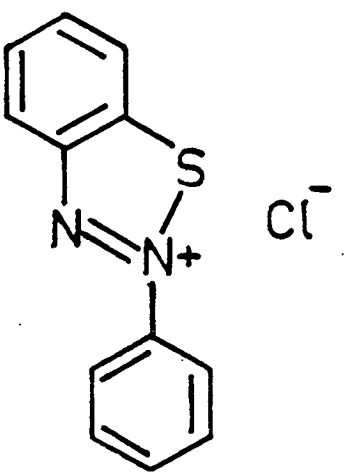
(225)



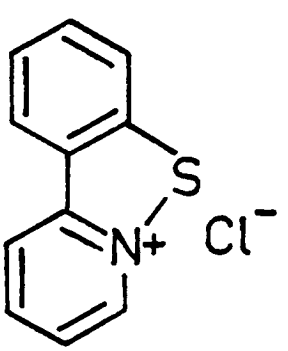
(130)



(226)



(227)



(118)

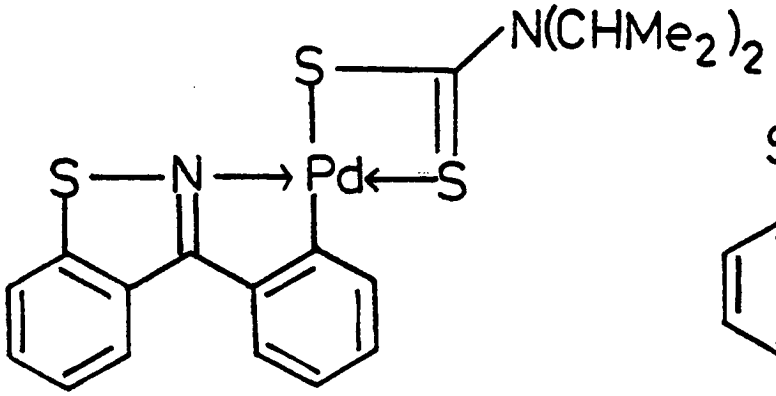
contrast to (224), however, the quinolizinylium salt (223) was indefinitely stable and its ^{1}H n.m.r. spectrum showed chemical shifts which were typically aromatic. It may be concluded, therefore, that canonical structure (a) is much more important than (b).

The related quinolizineselone complex (180) reacted with morpholine-N-sulphenyl chloride to yield [1,2,4] thiaselenazolo [3,4,5-de] quinolizinylium chloride (225). Like the closely related thiadiazolo cation (223), this ring system was aromatic by ^{1}H n.m.r. criteria.

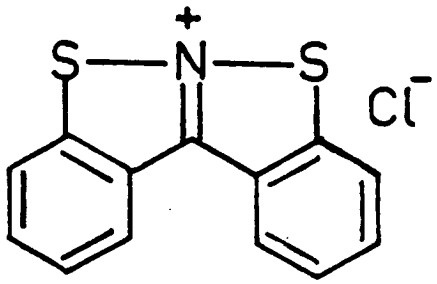
[1,2] Dithiolo [3,4,5-kl] thioxanthylium chloride (130) and 4-phenyl [1,2] dithiolo [3,4,5-de] thiochromylium chloride (226) were also synthesised from their respective dithiocarbamate complexes (181) and (182). It is noteworthy that the thioxanthylium salt could not be synthesised by reaction of the corresponding dithiocarbamate complex with thiocyanogen.[47]

The general utility of morpholine-N-sulphenyl chloride in these reactions was further illustrated by the extension of this method to the synthesis of 2-phenylbenzo [1,2,3] thiadiazolium chloride (227) and [1,2] benzothiazolo [2,3,-a] pyridinium chloride (118) from their respective dithiocarbamate complexes (183) and (184). It is interesting to note that the yield of (118) in these reactions was considerably higher than that synthesised from the dithiocarbamate complex via the thiocyanogen route.[44]

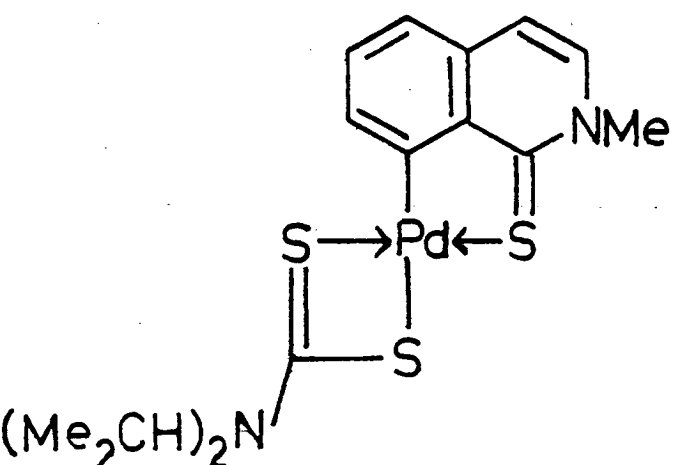
In view of the high efficiency of these reactions with morpholine-N-sulphenyl chloride, it seemed worthwhile to try the same method for the synthesis of the isothiazoloisothiazolium salt (191) which could not be prepared from the thiocyanato-compound (190).



(185b)

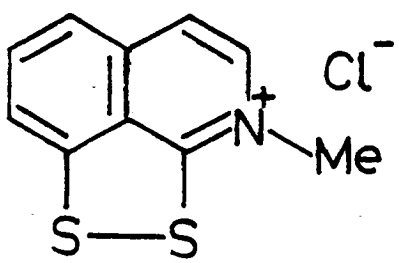


(191)



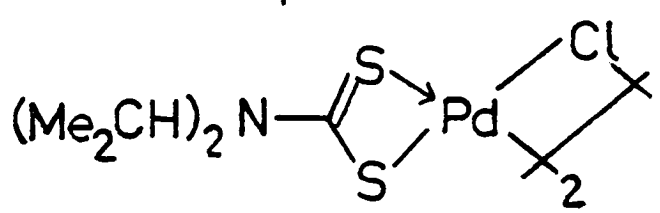
(176)

SCl_2



(213)

+

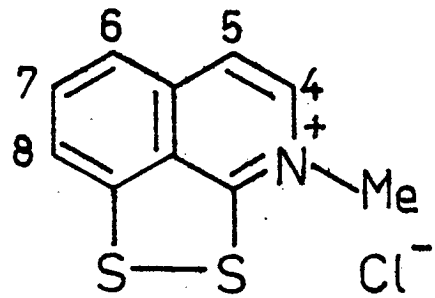


(218)

fig (xviii)

Treatment of the dithiocarbamate complex (185b) with the sulphenyl chloride under the usual conditions gave an orange solution but no salt was precipitated. The evaporated reaction mixture was extracted with ether and the extract was shown to contain N,N'-dimorpholinyl sulphide by mass spectroscopy. Treatment of the ether-insoluble residue with pyridine in dichloromethane yielded morpholine hydrochloride, the filtrate from which was evaporated and treated with perchloric acid in methanol. The resulting solid product could not be identified but infrared, ^{1}H n.m.r. and mass spectroscopic studies showed the presence of isothiazole and diisopropyldithiocarbamate moieties in this substance. The failure of this reaction was unexpected and no explanation could be put forward to account for the products formed in it.

A simplified procedure for the conversion of dithiocarbamate complexes to the corresponding isothiazolium or 1,2-dithiolium salts, using sulphur dichloride instead of morpholine-N-sulphenyl chloride was also investigated (figure (XVIII)). The addition of a chloroform solution of the dithiocarbamate complex (176) to an equimolar amount of sulphur dichloride produced a deep red solution which then became lighter in colour with the precipitation of 3-methyl [1,2] dithiolo [3,4,5-ij] isoquinolinium chloride and di-μ-chloro-bis (N,N-diisopropyldithiocarbamato) palladium (II). The separation of these compounds was effected by the established method using pyridine in dichloromethane. Compared with the analogous reaction of the dithiocarbamate complex with morpholine-N-sulphenyl chloride, this reaction gave a lower yield of less pure dithiolium salt. The less satisfactory nature of this reaction was attributed to the inherent instability of sulphur dichloride, disproportionation of which occurs to yield disulphur dichloride and chlorine.[5]



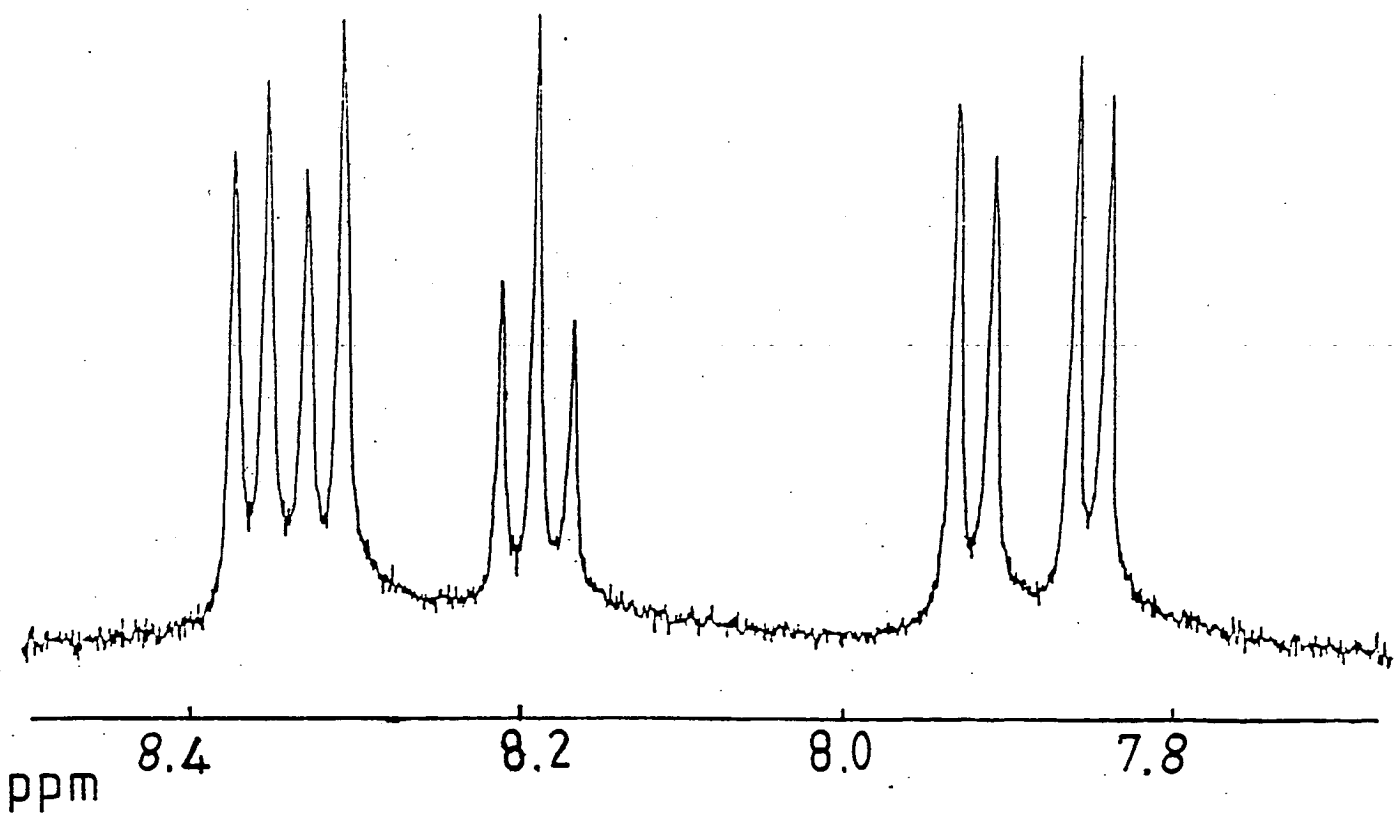


fig (XIX)

Decomposition of morpholine-N-sulphenyl chloride cannot occur in this manner and its use in these reactions is to be preferred to that of sulphur dichloride.

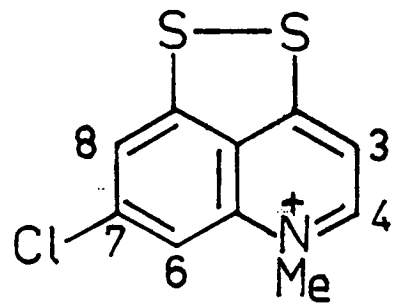
(4.2) ^{1}H.N.m.r. SPECTRA OF THE FUSED-RING 1,2-DITHIOLIUM SALTS

^{1}H.N.m.r. studies provided the most convincing evidence of the polycyclic cations discussed in the previous section. These spectra were recorded at 360 MHz for all the novel dithiolium salts synthesised in this work, with the exception of the 1,2-dithioloquinolinium ring system (221), the spectrum of which was well resolved at 100 MHz. The aromatic region of each spectrum is shown in figures (XIX) to (XXV).

The aromatic region of the ^{1}H n.m.r. spectrum of 3-methyl [1,2] dithiolo [3,4,5-ij] isoquinolinium chloride (213) is shown in figure (XIX); H-4 and H-5 were observed as doublets (J= 7.1 Hz) at δ 8.35 and δ 7.86 respectively. The triplet at δ 8.18 was assigned to H-7. On account of the assumed higher bond order across C-6/C-7 compared with C-7/C-8, $^3J_{6,7}$ is expected to be larger than $^3J_{7,8}$ and this led to the assignment of the doublet (J= 8.25 Hz) at δ 8.30 to H-6 and the doublet (J= 7.9 Hz) at δ 7.92 to H-8. The N-methyl protons were observed as a singlet at δ 4.16.

The ^{1}H n.m.r. spectrum of 7-chloro-5-methyl [1,2] dithiolo [3,4,5-de] quinolinium perchlorate (221) (figure (XX)) showed two doublets (J= 7 Hz) at δ 8.71 and δ 7.82 assigned to H-4 and H-3 respectively. The other pair of doublets (J= 1.5 Hz) at δ 8.10 and 7.86 are clearly due to H-6 and H-8 but individual assignments are not possible in the absence of additional evidence. The N-methyl protons were observed as a singlet at δ 4.09.

The signal at lowest field in the ^{1}H n.m.r. spectrum of



ClO_4^-

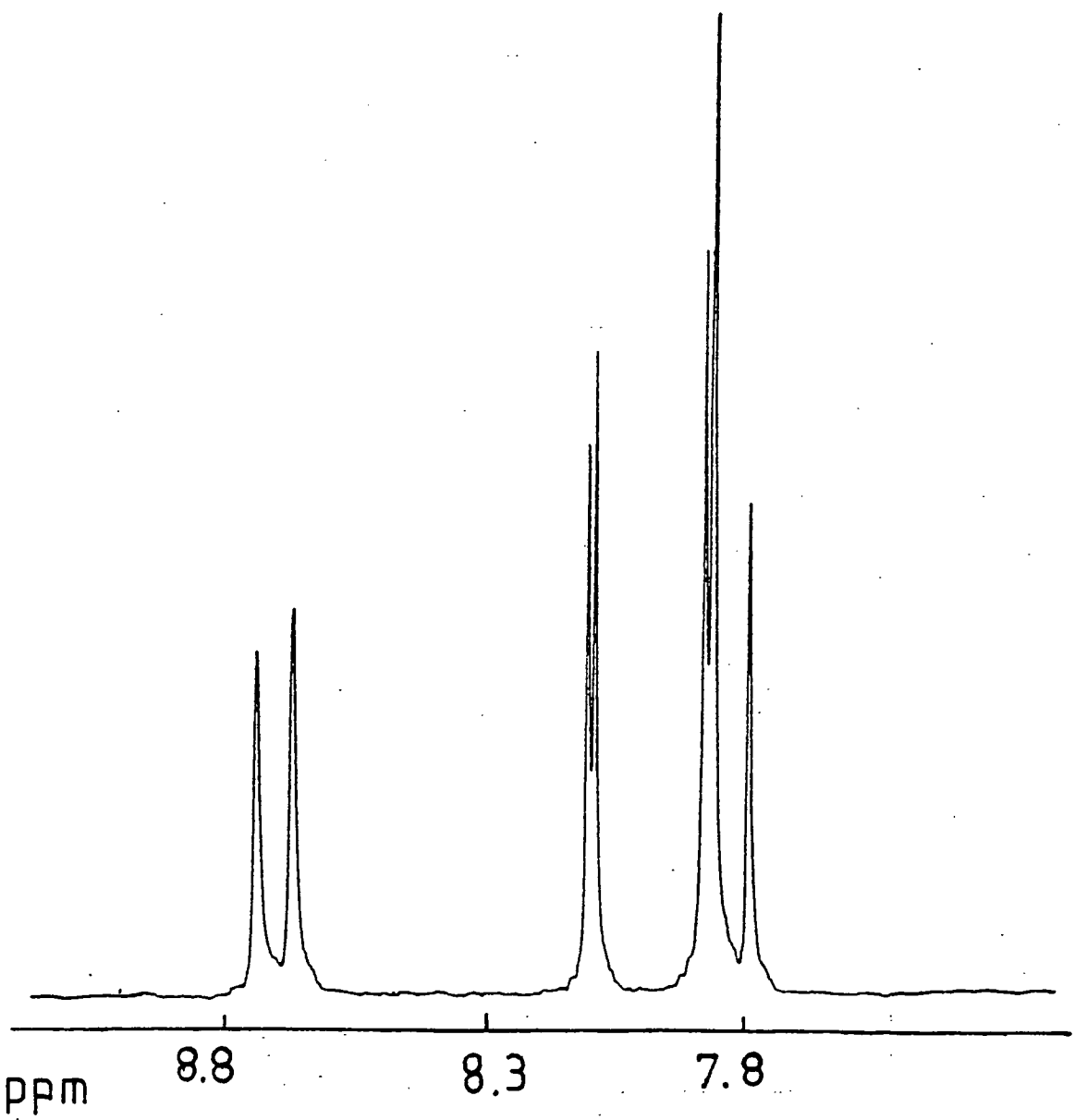
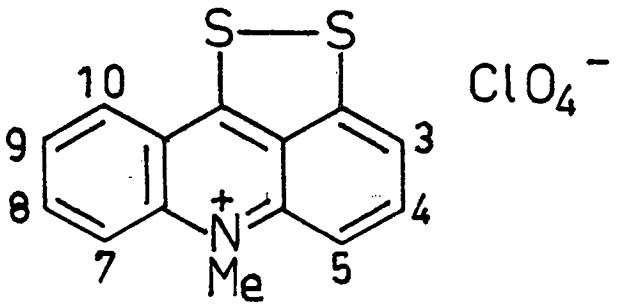


fig (XX)



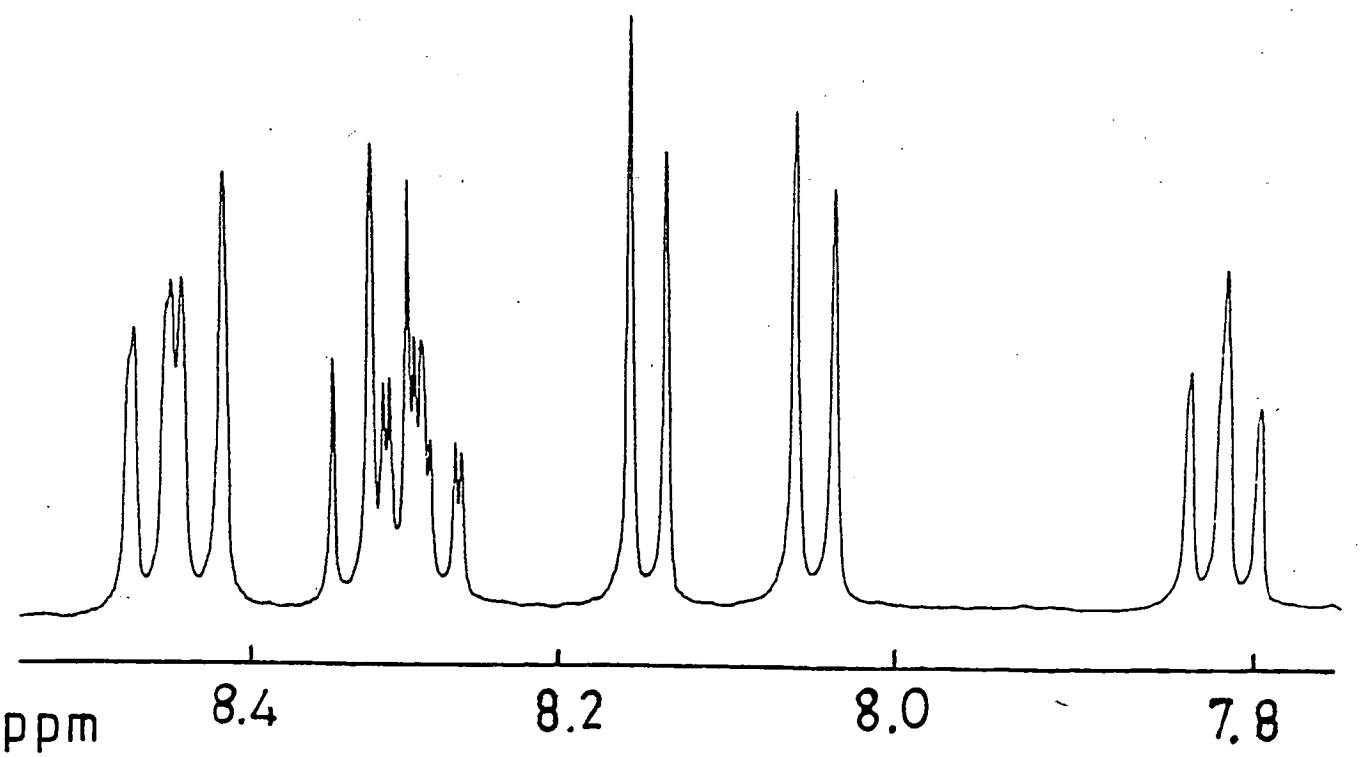
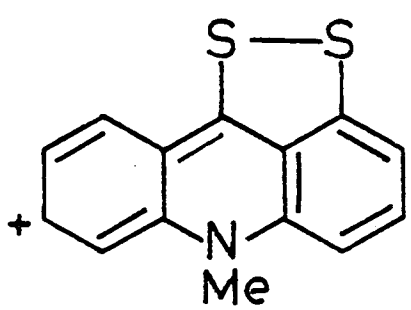
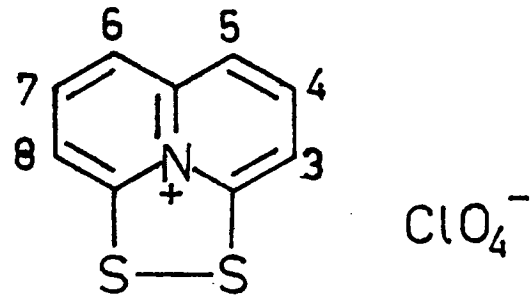


fig (XXI)

6-methyl [1,2] dithiolo [3,4,5-kl] acridinium perchlorate (222) figure (XXI)), a doublet (J= 8.25 Hz) at δ 8.47 was assigned to H-10 which is deshielded by the C_{10b}- S_1 bond (partial C=S character). The sharp triplet at δ 8.34 was assigned to H-4 in preference to H-8 or H-9 on account of the absence of any meta-coupling. Similarly, the signals due to H-3 and H-5 would be expected to be simple doublets. The sharp doublets at δ 8.17 (J = 7.92 Hz) and δ 8.07 (J = 8.58 Hz) were therefore due to H-3 and H-5, though it was not possible to assign them individually. The broad doublet (J = 9.07 Hz) at δ 8.44 was assigned to H-7. The two remaining signals, a triplet of doublets at δ 8.31 and a triplet at δ 7.82 were assigned to H-8 and H-9 respectively. The former signal was assigned to H-8 in preference to H-9 on consideration of the contributing canonical resonance structures of (222), for which a structure bearing a positive charge on C-8, but not on C-9 can be formulated, i.e. (228). The N-methyl protons appeared as a singlet at δ 4.36.



(228)



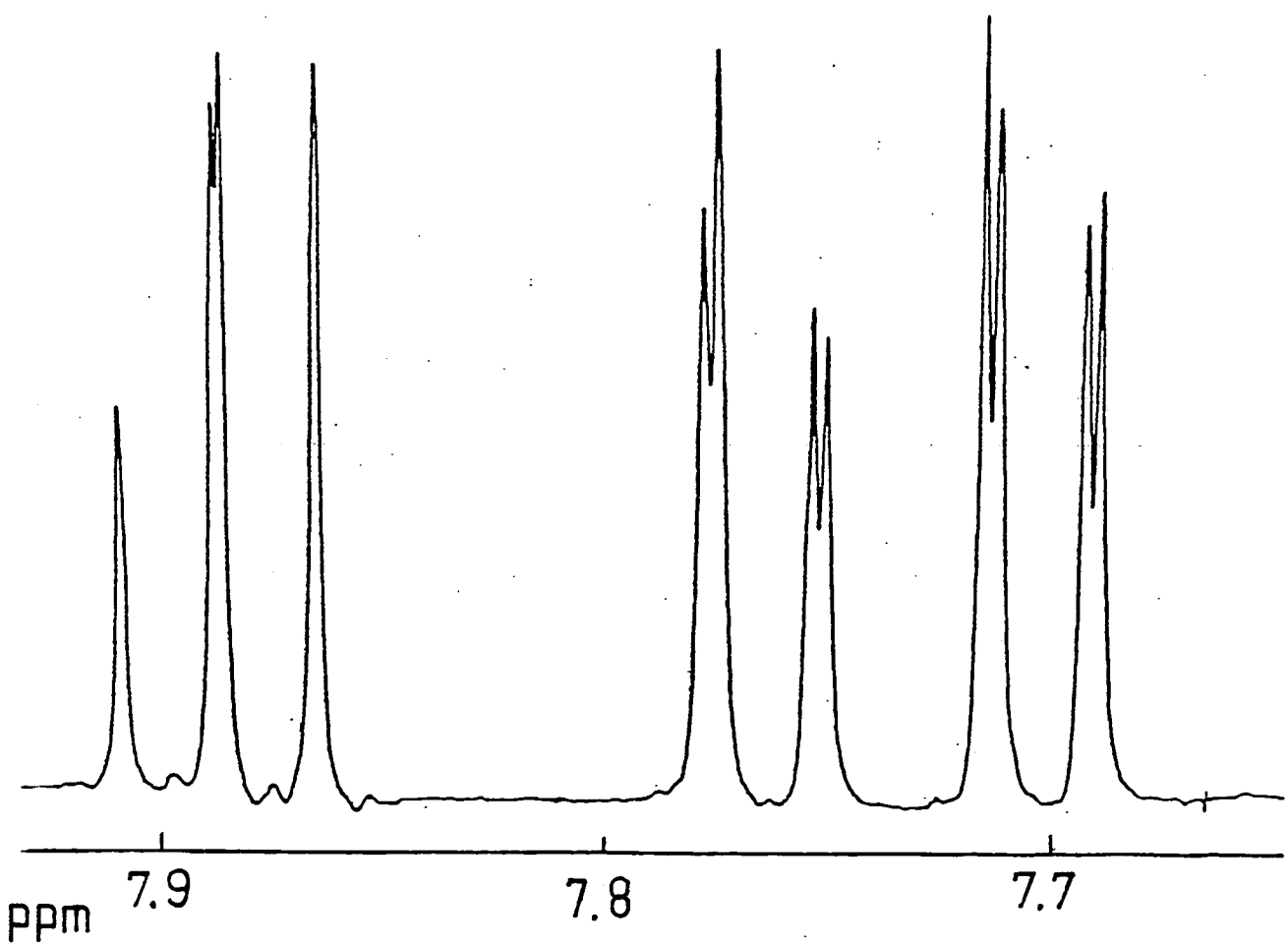
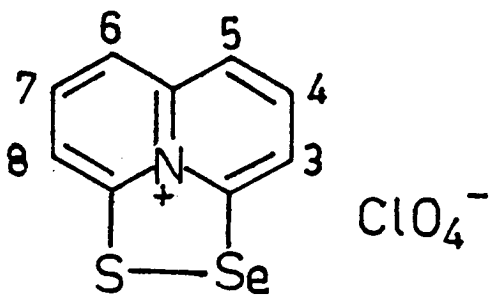


fig (XXII)



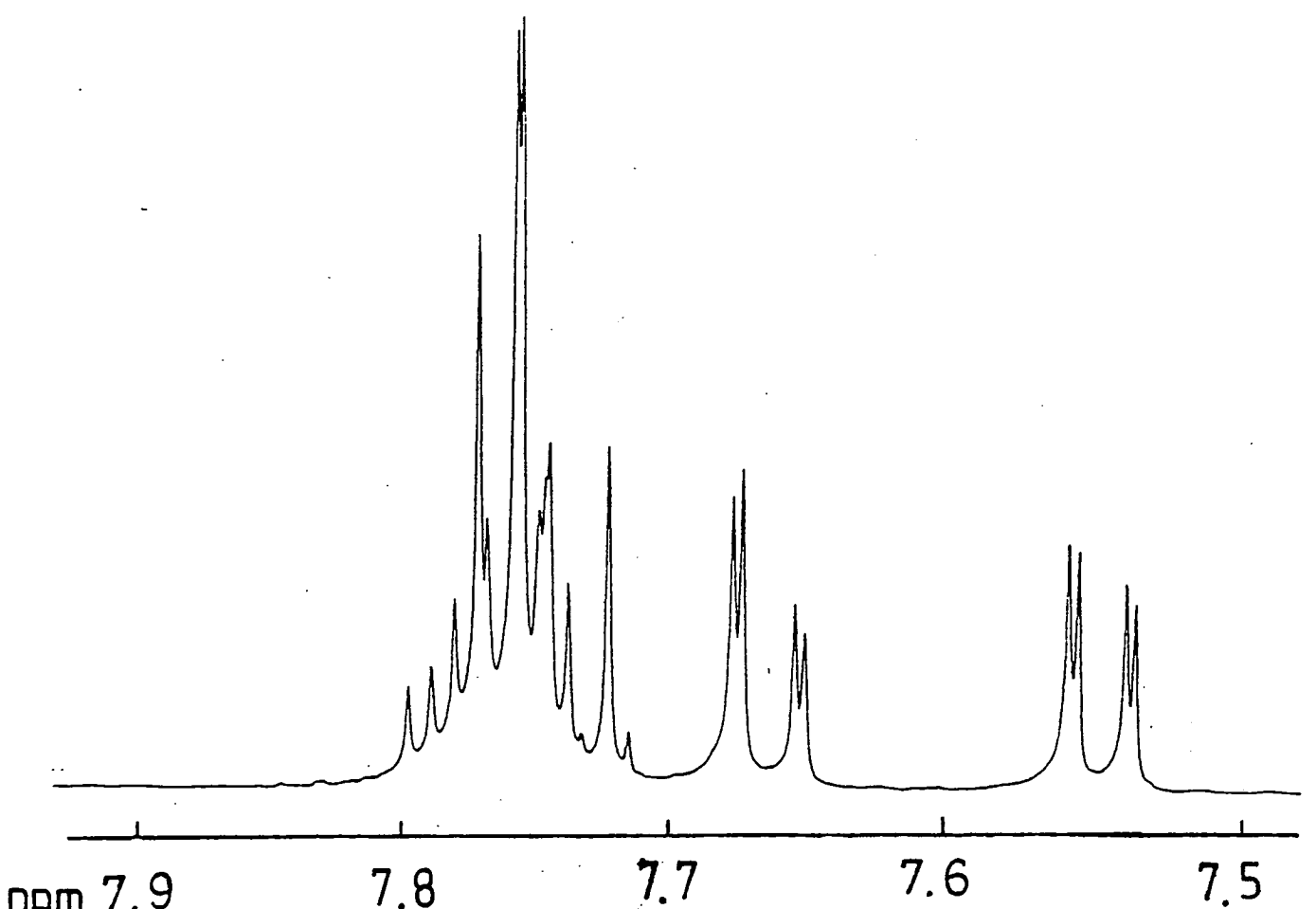


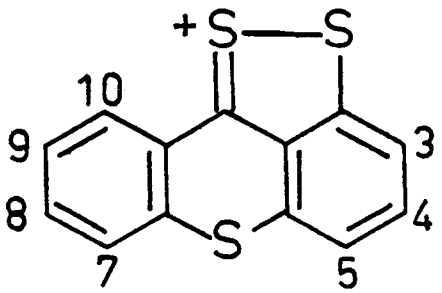
fig (XXIII)

The ^1H n.m.r. spectrum of [1,2,4] dithiazolo [3,4,5-de] quinolizinylium perchlorate (223) (figure (XXII)) showed a distorted triplet at δ 7.88 (H-4 / H-7) and two doublets of doublets at δ 7.76 (^3J = 8.67 Hz; ^4J = 1.10 Hz) and δ 7.70 (^3J = 7.86 Hz; ^4J = 1.10 Hz). The signal at δ 7.76 was assigned to H-5 / H-6 on account of the larger observed value for ^3J which is in accord with the assumed higher bond order across the C_4-C_5 bond compared with the C_3-C_4 bond. The signal at δ 7.70 was therefore assigned to H-3/ H-8.

The ^1H n.m.r. spectrum of the structurally similar [1,2,4] thiaselenazolo [3,4,5-de] quinolizinylium perchlorate (225) (figure (XXIII)) was in marked contrast to that of its dithiazolo analogue. Two doublets of doublets at δ 7.66 (1H) and δ 7.54 (1H) were observed in addition to a complex multiplet in the region δ 7.8 -7.7 (4H). No unambiguous assignments were possible.

The signal at lowest field in the ^1H n.m.r. spectrum of [1,2] dithiolo [3,4,5-kl] thioxanthylium perchlorate (130)(figure (XXIV), a doublet (J = 8.46 Hz) at δ 8.78, was assigned to H-10, as in the corresponding acridinium salt. A doublet (J = 8.82 Hz) was observed at δ 8.56, the sharpness of which led to its assignment to either H-3 or H-5. A broad triplet at δ 8.15 and a triplet of doublets at δ 7.92 were assigned to H-8 and H-9 respectively, for reasons similar to those discussed for the acridinium system. The broadness of the signal at δ 8.15 eliminated H-4. The remaining three protons appeared as a multiplet in the region δ 8.4 - 8.25.

Details of the ^1H n.m.r. spectrum of the closely related xanthylium ring system (129) have been reported by Leaver and Thomson.[67] In contrast to that of the thioxanthylium ring system,



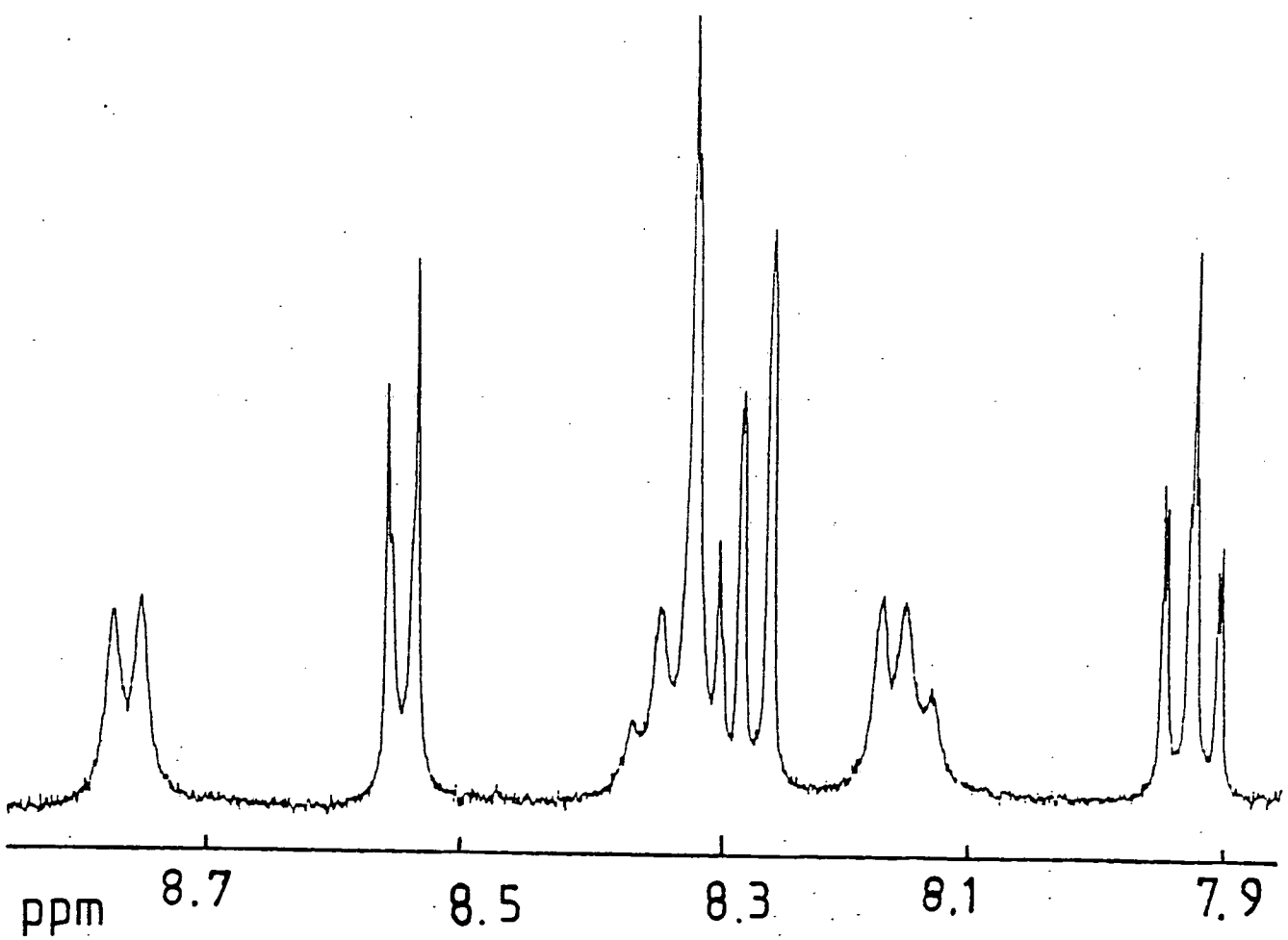
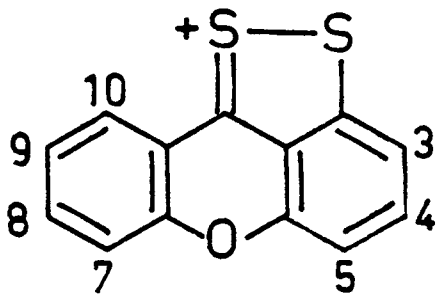


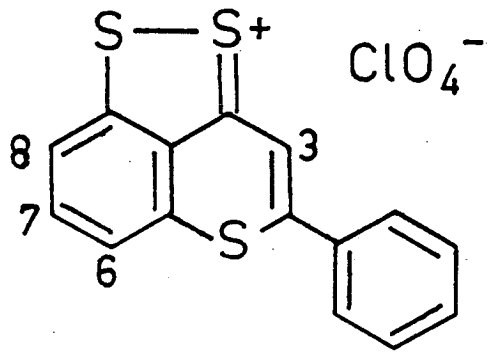
fig (XXIV)

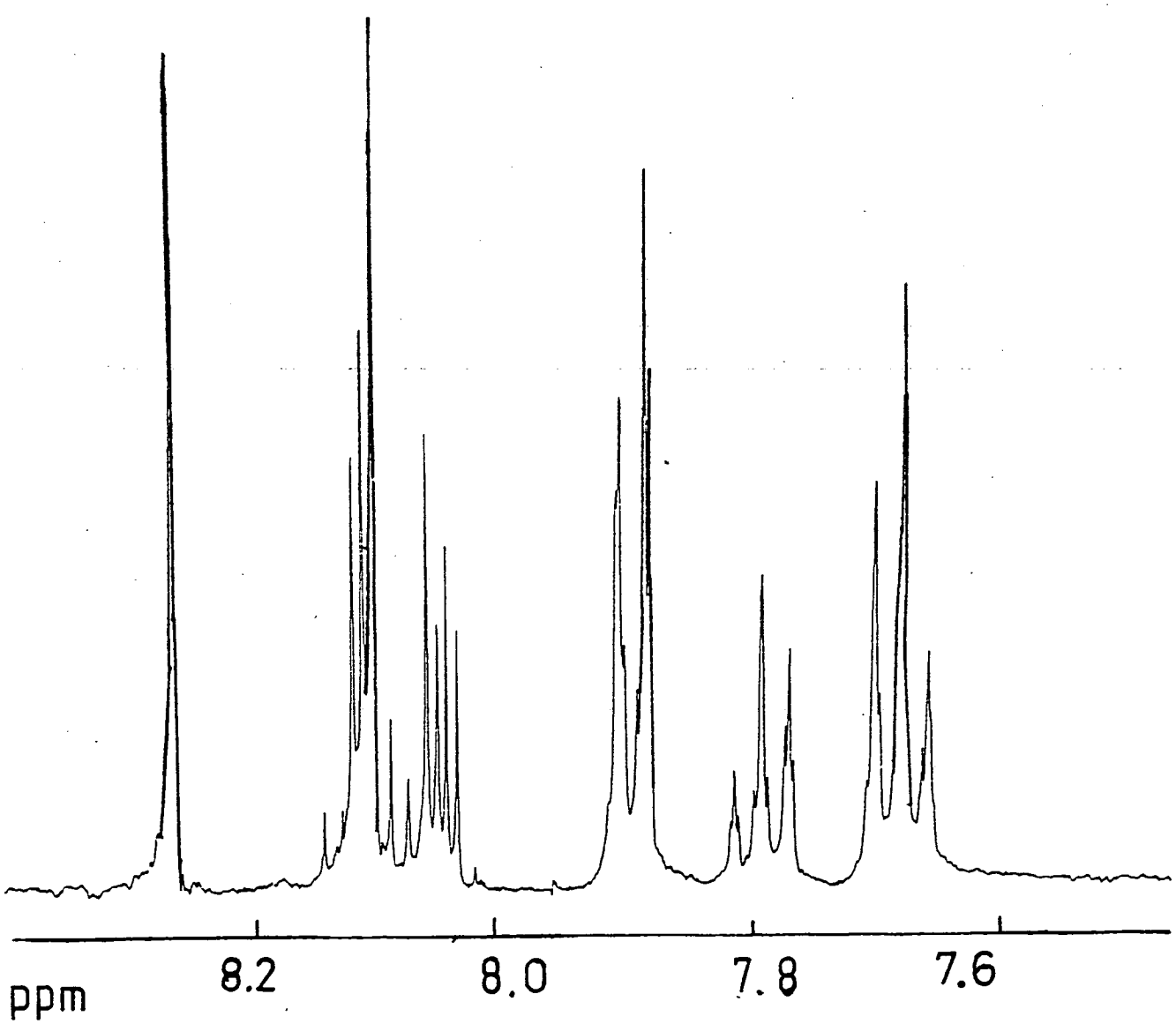
all seven aromatic protons were resolved. Several features were common to both spectra, notably the signal at lowest field being due to H-10, the signals due to H-8 and H-9 appearing as triplets of doublets, and the signal at highest field being due to H-9.



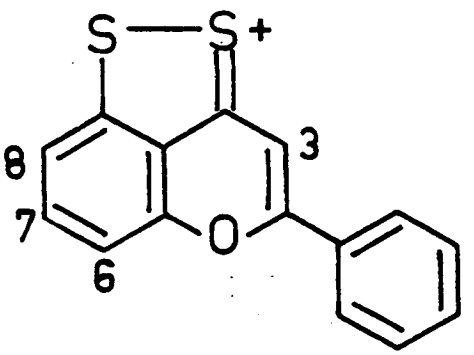
(129)

The ^{1}H n.m.r. spectrum of 4-phenyl [1,2] dithiolo [3,4,5-de] thiochromylium perchlorate (226) is shown in figure (XXV). The signal at lowest field was a singlet at δ 8.25 and was assigned to H-3. The phenyl ring protons were distinguishable, the ortho-protons appearing as a doublet of doublets at δ 7.88, the para-proton as a triplet of triplets at δ 7.79 and the meta-protons as a triplet at δ 7.68. Protons-6,7 and 8 were observed as a multiplet in the region δ 8.13-8.03. This spectrum contrasts sharply with that of the closely related chromylium system (229) which has been reported by Leaver and Thomson.[67] The most contrasting features were the signal at lowest field, which was due to H-7, and the observation of the ortho-phenyl protons at δ 8.21, downfield of H-3 at δ 8.15.





fin (XXV)



(229)

The observation that the ortho-phenyl protons in the chromylium system are shifted downfield relative to those in the thiochromylium system suggests that there is greater delocalisation of positive charge into the phenyl ring in the former system. Similar observations have been reported for xanthylium and thioxanthylium ring systems[76] where changing the heteroatom from oxygen to sulphur results in quite marked changes in the relative positions of spectral lines.

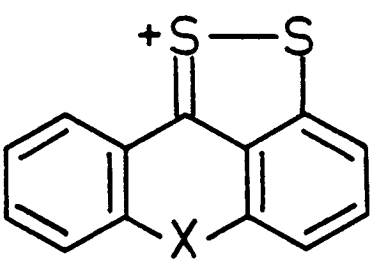
(4.3) MASS SPECTRA OF FUSED-RING 1,2-DITHIOLIUM SALTS

Although it is frequently difficult to obtain mass spectra of ionic substances, the chloride salts of the polycyclic dithiolium cations were all sufficiently volatile, the spectra exhibiting moderate to strong intensity molecular ions upon heating of the salts to 200-230°C. In those cases where the 1,2-dithiolium structures contained an N-methyl group, i.e. the quinolinium, isoquinolinium and acridinium systems, the molecular

ions were not observed, but the corresponding demethylated products, 1,2-dithioles gave strong ion peaks.

(4.4) ELECTRONIC SPECTRA OF FUSED-RING 1,2-DITHIOLIUM SALTS

U.V. - Visible spectra were recorded in the range 220-650 nm. The spectra of the dithiolium salts (129),[67](130), and (222) showed four absorptions of moderate to strong intensity in the regions 245-265, 275-295, 305-335 and 505-570 nm. A bathochromic shift (505→570 nm) was observed in the longest wavelength absorbance on going from the xanthylium ring system to the thioxanthylium system, but otherwise the two spectra were very similar in general form.



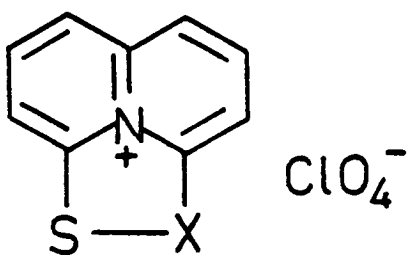
ClO_4^-

(129 , X = O)

(130 , X = S)

(222 , X = NMe)

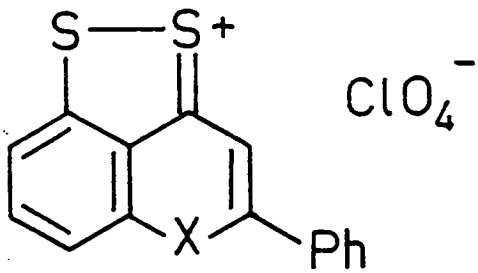
The spectra of the dithiazolium and the thiaselenazolium salts (223) and (225) showed great similarity. Four distinct regions of absorption were observed. In the case of the former salt these were at 227, 259, 370 and 510 nm, and for the latter, 233, 264, 380, 520 nm, the bathochromic shifts in the latter case being noteworthy.



(223, X = S)

(225, X = Se)

The spectra of the chromylium and thiochromylium salts (229)[67] and (226) also showed four distinct regions of absorption. In the chromylium system, absorptions were observed at 260, 310, 354 and 480 nm, while those of the thiochromylium system were observed at 250, 289, 348 and 532 nm. A marked bathochromic shift was observed for the longest wavelength absorption.



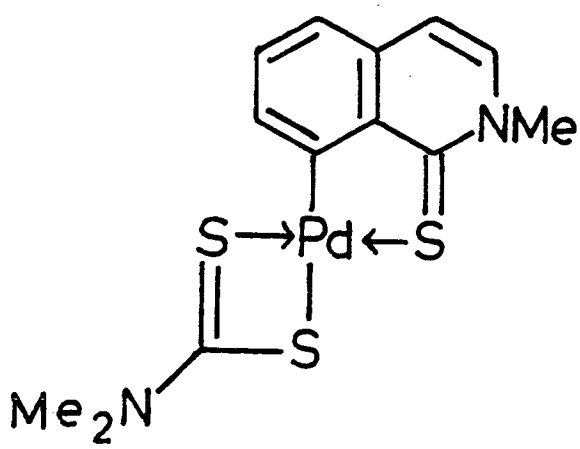
(229, X=O)

(226, X=S)

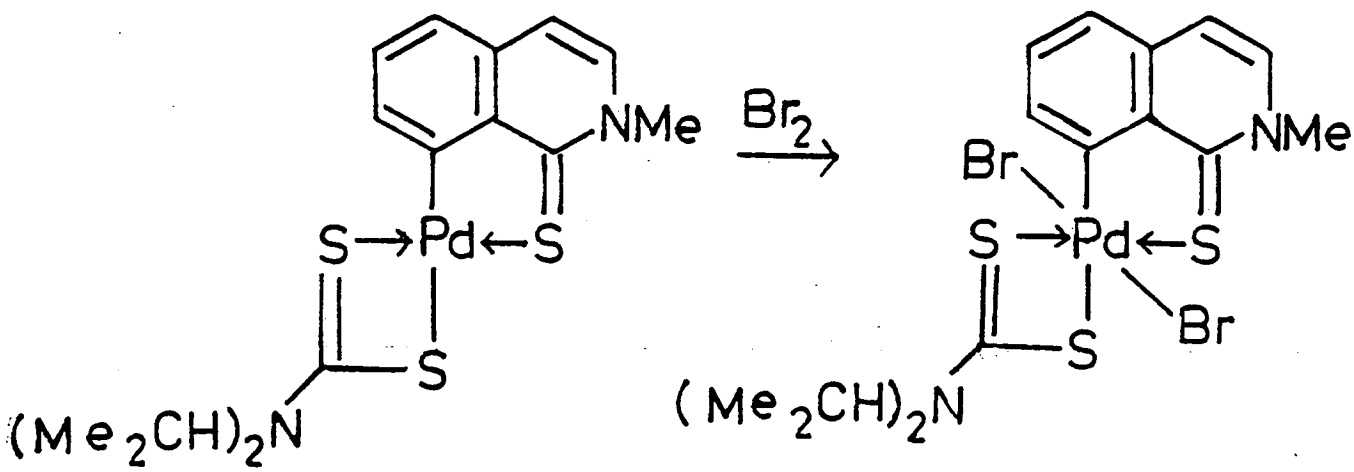
Three absorption bands were observed in the spectra of the isoquinolinium salt (213) (253, 335 and 419 nm) and the quinolinium salt (221) (268, 297 and 440 nm).

(5) ATTEMPTED SYNTHESIS OF 8-HALOGENO-2-METHYLISOQUINOLINE-1-THIONES FROM CYCLOPALLADATED COMPLEXES

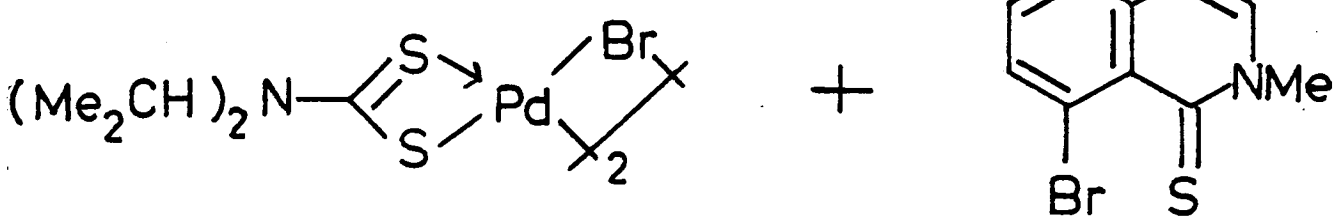
The replacement of palladium in cyclopalladated complexes by a halogen atom has been reported by several workers.[35,40,44] In these cases reaction was effected by direct action of the halogen on either dimeric halogen-bridged complexes or on monomeric phosphine or dithiocarbamate complexes. However, this type of reaction failed when the cyclopalladated ligand was a heterocyclic thioamide. It was reported, for example, that treatment of the dithiocarbamate complex (131) with bromine yielded quinolizine-4-thione and di-μ-bromo-bis (N,N-dimethyldithiocarbamato) palladium (II).[47]



(131)



(176) (232)



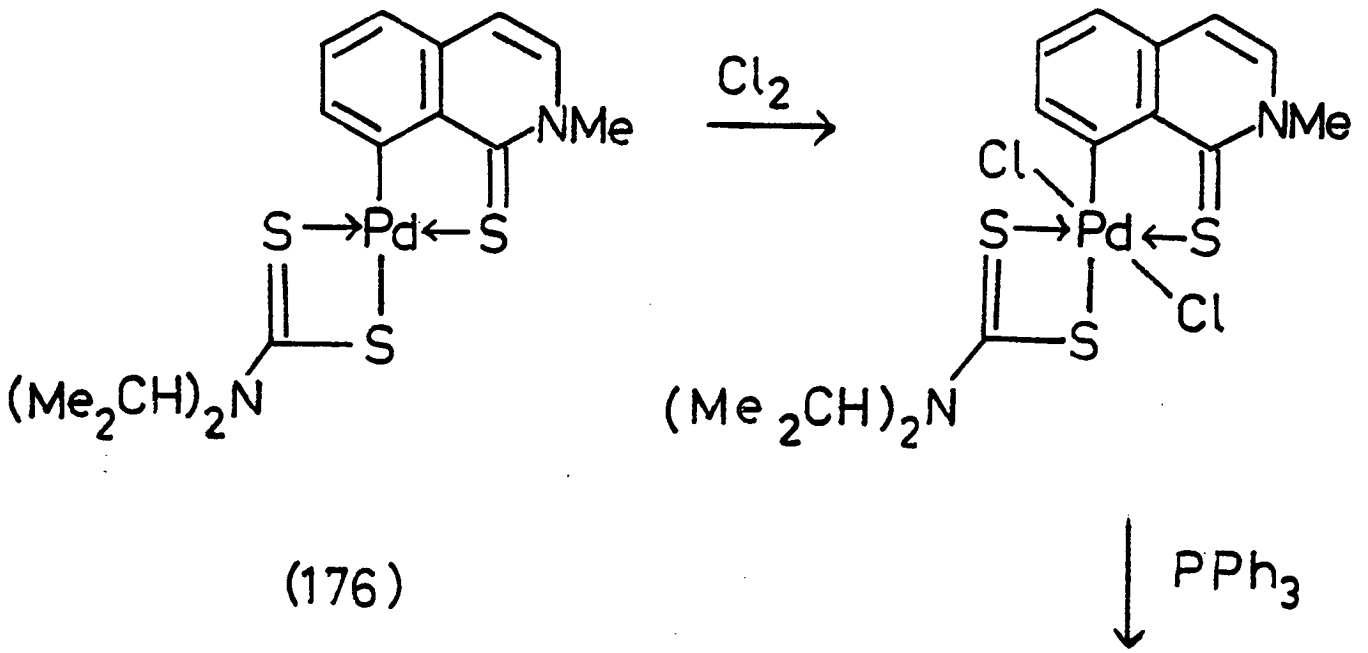
(231) (230)

Scheme (vii)

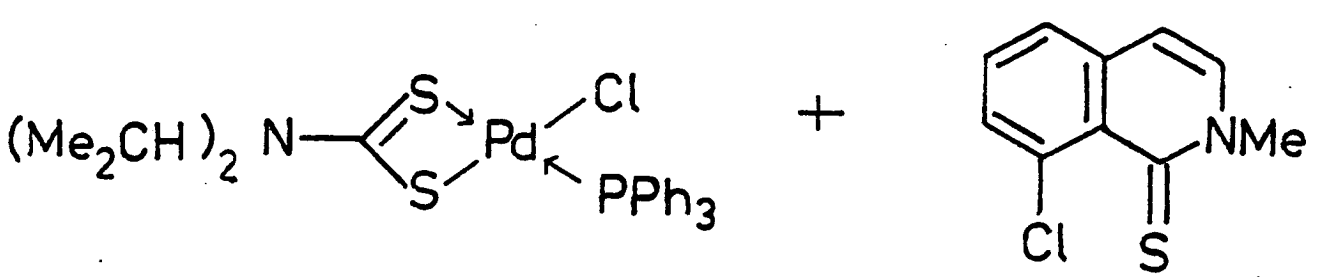
In view of the failure of such reactions, a study was made of other methods that might yield halogeno-substituted heterocycles of thioamide-type from their corresponding cyclopalladated complexes. Only complexes of 2-methylisoquinoline-1-thione were used in this investigation as their behaviour towards halogenating agents was likely to be typical of other thioamide complexes.

Despite the reported failure of related reactions, a direct bromination of the dithiocarbamate complex (176) with molecular bromine was attempted with a view to synthesising 8-bromo-2-methylisoquinoline-1-thione (230), according to Scheme (VII). Bromination in chloroform produced a deep red solution from which was isolated an orange-red solid, elemental analysis of which suggested that it was a bromine addition product of the original complex. The structure (232) is consistent with such a composition but is regarded as unlikely in view of the generally low stability of Pd (IV) complexes. Neither of the two envisaged products, (230) and (231) was isolated.

Chlorination of the dithiocarbamate complex (176) in chloroform produced a brown precipitate which was assumed to be an analogous addition product. One molar equivalent of triphenyl-phosphine was then added to the reaction mixture with a view to inducing reductive elimination of 8-chloro-2-methylisoquinoline-1-thione (233) and forming the phosphine complex (234) according to Scheme (VIII). Addition of the phosphine gave a deep red solution, from which was isolated a small quantity of di-μ-chloro-bis



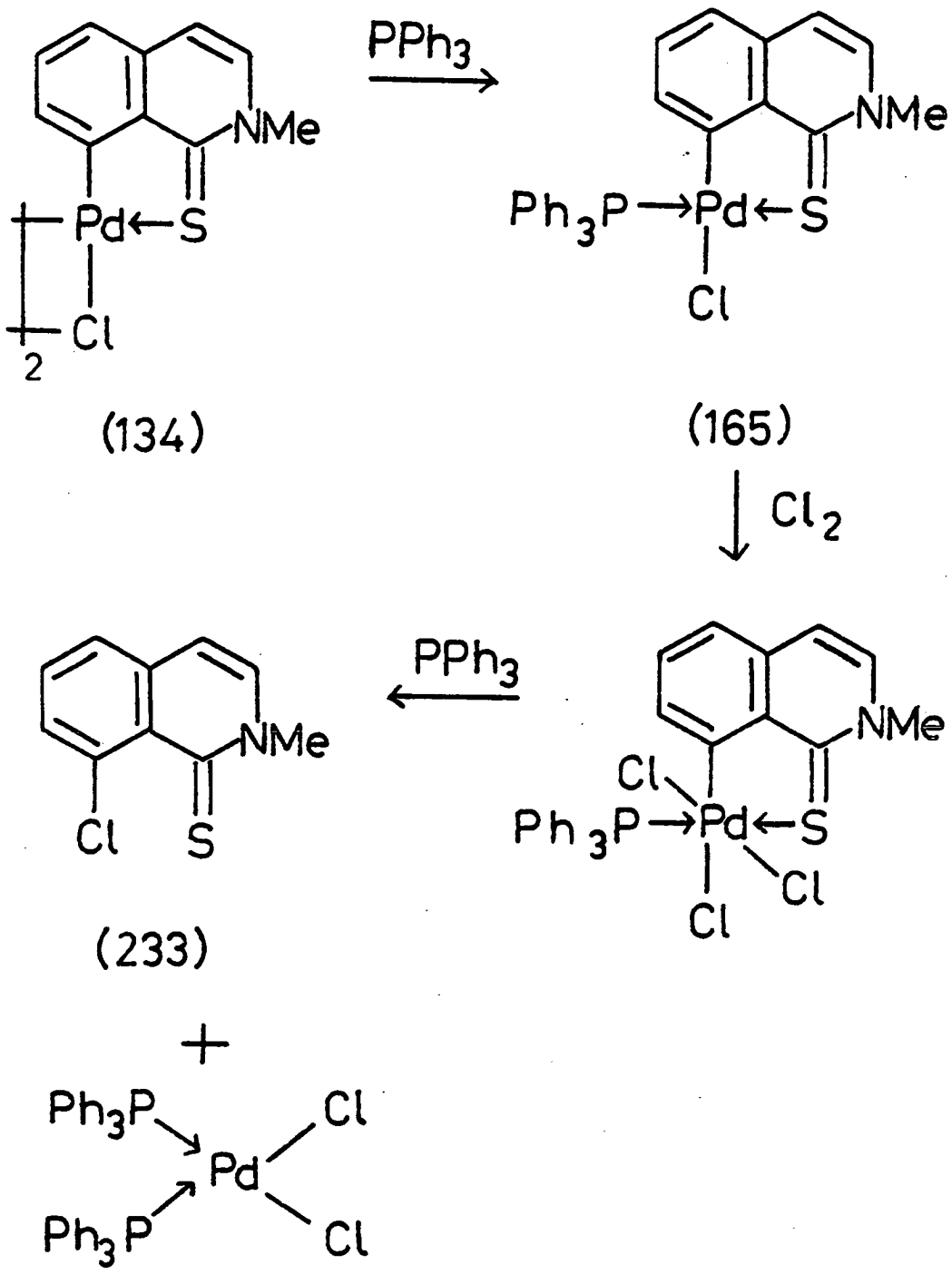
(176)



(234)

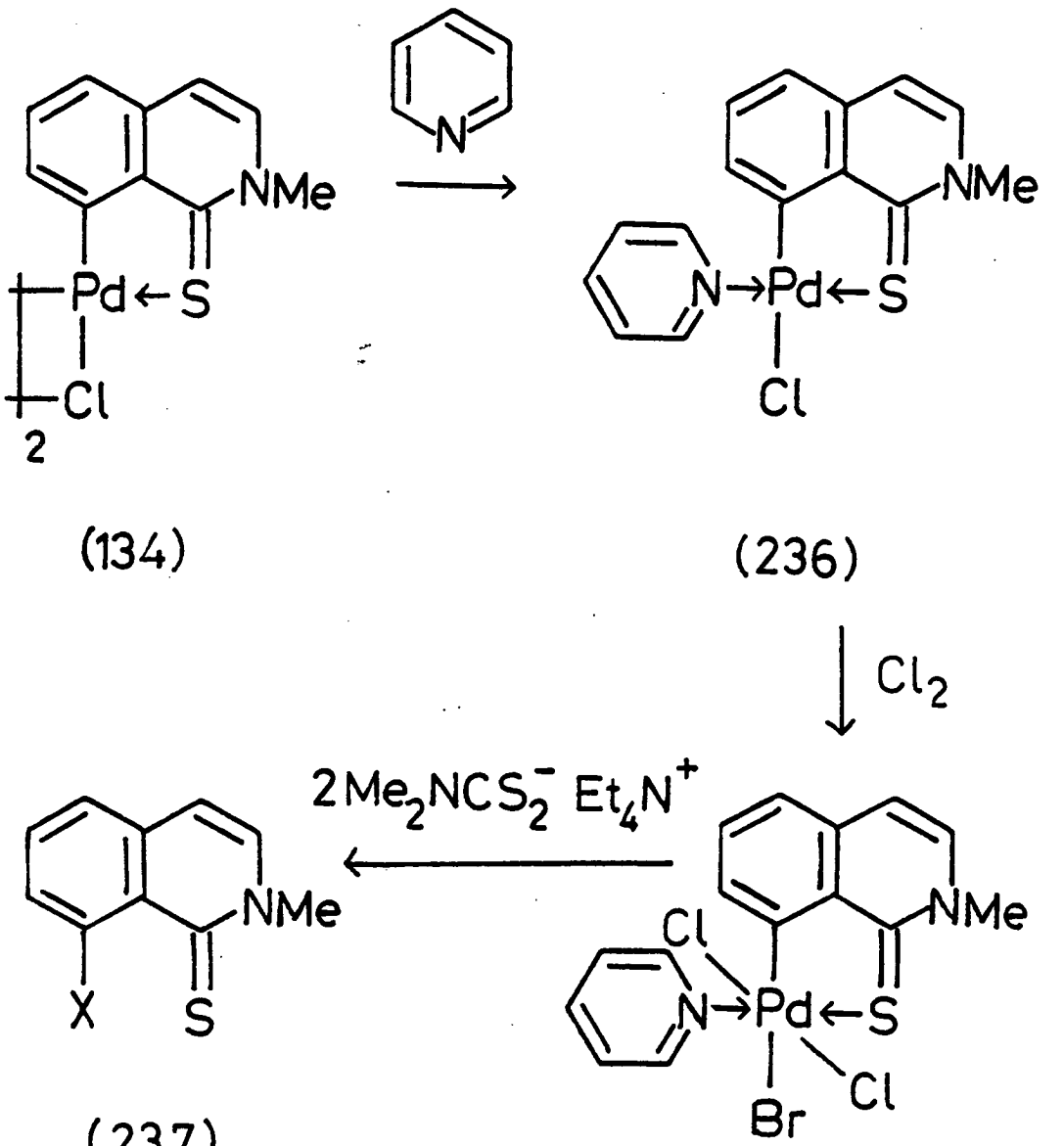
(233)

Scheme (viii)



(134) (165) (233) (235)

Scheme (ix)



(134)

(236)

(237)

+ $[Me_2NCS_2]_2Pd$

+ $2\,Et_4\overset{+}{N}\;X^-$

+ 

X = Cl or Br

Scheme (x)

(1-thioxo-2-methylisoquinolin-8-yl) dipalladium (II) (134). No other products could be isolated from the reaction mixture, although traces of the desired chlorinated thione (233) were detectable in the mixture by mass spectroscopy (m/e 211/209).

On the basis of these observations it seemed possible that the stabilising effect[47] of the electron donating dithiocarbamate and thioamide ligands on the electron deficient Pd (IV) intermediate might have prevented or hindered subsequent reductive elimination. In order to minimise this effect, complexes containing ligands other than dithiocarbamate were used in the subsequent investigation.

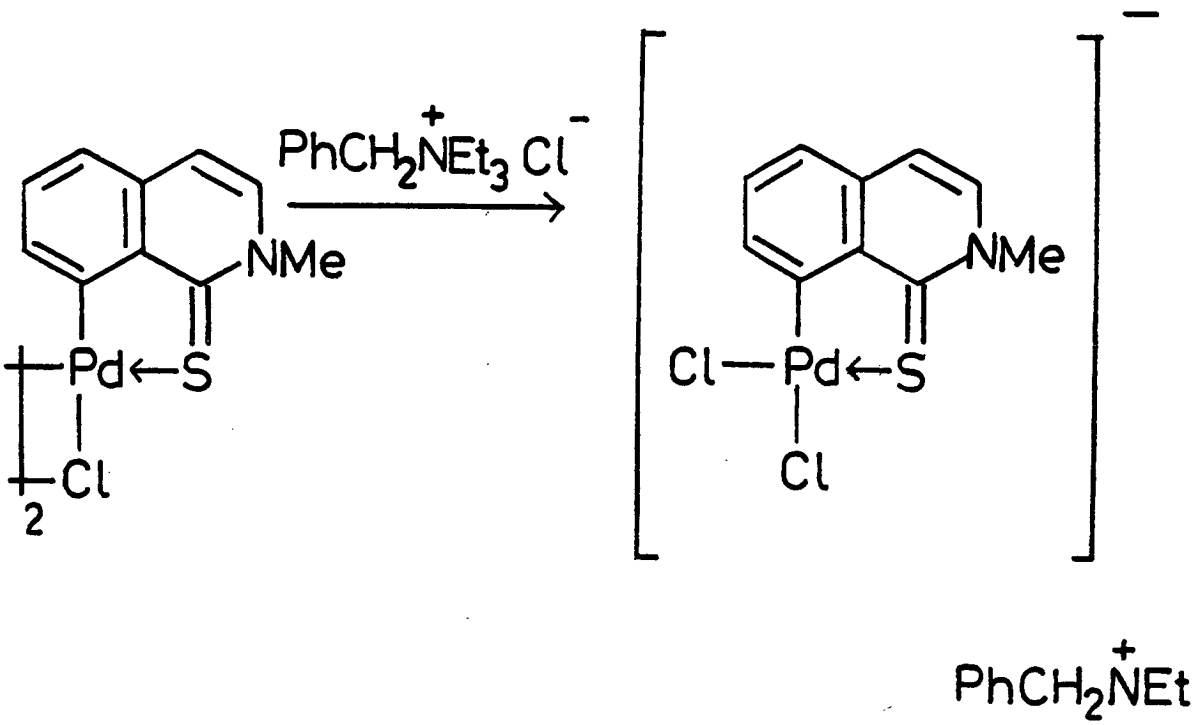
Addition of one molar equivalent of chlorine to a chloroform solution of the phosphine complex (165) produced a deep red solution, suggesting the formation of a Pd (IV) complex. A second equivalent of triphenylphosphine was therefore added in the hope that this would induce reductive elimination to form the chlorinated thione (233) and the bis phosphine complex (235) (Scheme (IX)). Addition of the phosphine did indeed cause lightening in colour of the reaction mixture and work-up yielded a small amount of bis (triphenylphosphine) palladium (II) dichloride (235). A solid, thought to contain mainly the phosphine complex (165), was also obtained but no other products could be isolated from the reaction mixture. The fact that the desired chlorinated thione was not isolated was surprising in view of the formation of the bis phosphine complex (235).

Bromination of the pyridine complex (236), prepared by treatment of the dimeric complex (134) with pyridine, was also attempted. The envisaged reaction sequence is shown in Scheme (X). Addition of one molar equivalent of bromine to a chloroform solution of the

pyridine complex formed a deep red solution. Two molar equivalents of tetraethylammonium N,N-dimethyldithiocarbamate were then added in the hope that, if oxidative addition of bromine had occurred, then reductive elimination would give the halogenothione (237) and the highly stable and very insoluble bis (N,N-dimethyldithiocarbamato) palladium (II). The bis (dithiocarbamate) complex did indeed precipitate but chromatography of the soluble portion of the reaction mixture yielded only a small amount of orange-red gum which was shown by mass spectroscopy to contain 2-methylisoquinoline-1-thione and 8-bromo-2-methyl-isoquinolin-1-one (238). The latter product would appear to have been formed by reaction of the desired thione (237, X=Br) with hydroxide ion derived from traces of water in the presence of pyridine. The formation of the unsubstituted thione might be attributed to hydrogen abstraction from the solvent by an initially formed 1-thioxo-2-methylisoquinolin-8-yl radical.

Traces of 8-chloro-2-methylisoquinolin-1-one (239, X=Cl) were formed, and detected mass spectrometrically, when the chloride-bridged dimer (134) was treated with N-chlorosuccinimide in N,N-dimethylformamide. Succinimide was formed and the dimer was recovered in 58% yield. A similar result was obtained when the reaction was carried out in pyridine, though in this solvent the main isolated product was a yellow-green unidentified solid.

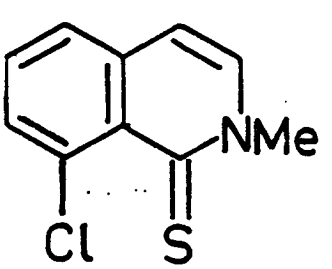
A final attempt was made to obtain the chlorothione (233) by excluding all ligands other than the cyclopalladated thione and chloride (Scheme (XI)). For this purpose the dimer (134), which was itself insufficiently soluble, was first treated with an excess of benzyltriethylammonium chloride in dichloromethane. The



(134)

(240)

Cl_2



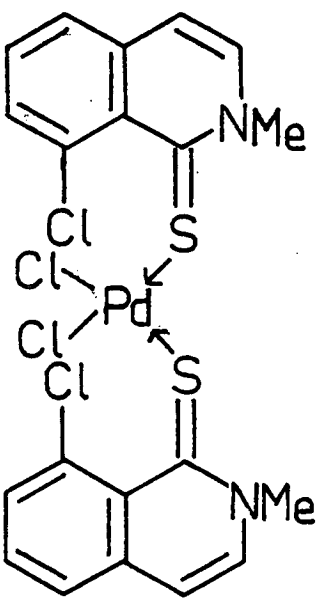
(233)

+ $PdCl_2$

+ $PhCH_2\overset{+}{N}Et_3\ Cl^-$

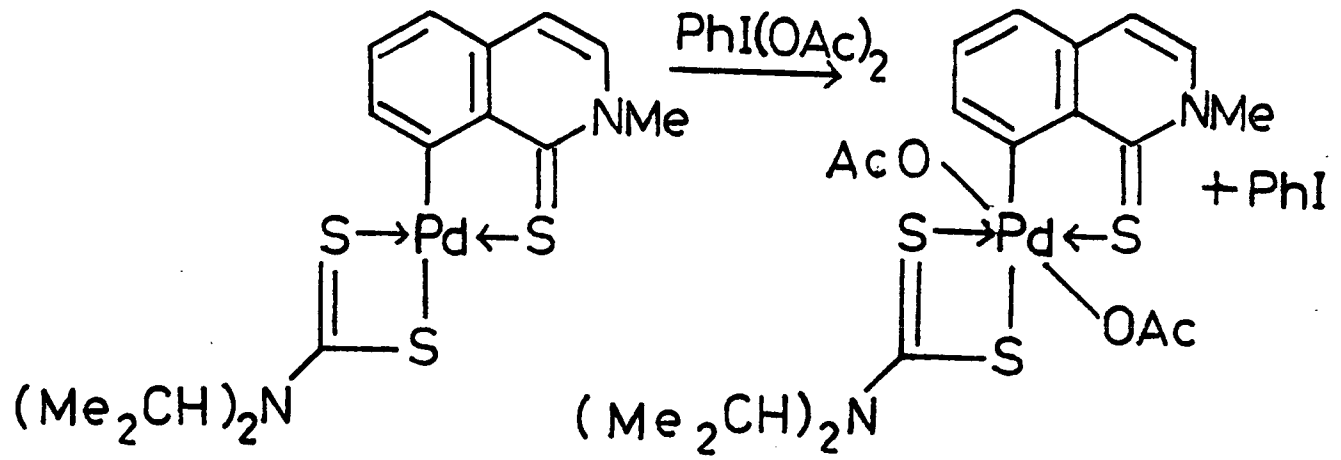
Scheme (xi)

resulting yellow solution, presumably contained the anionic complex (240), was then treated with one equivalent of chlorine. The solution became dark green and work-up by evaporation and aqueous wash yielded a highly insoluble yellow-brown solid, the elemental analysis of which was fairly close to that required for bis (8-chloro-2-methylisoquinoline-1-thione) palladium (II) dichloride (241). The formation of this complex could arise according to Scheme (XI) followed by recombination of the initially formed 8-chloro-2-methylisoquinoline-1-thione with palladium chloride or bis (benzyltriethylammonium) tetrachloropalladate .

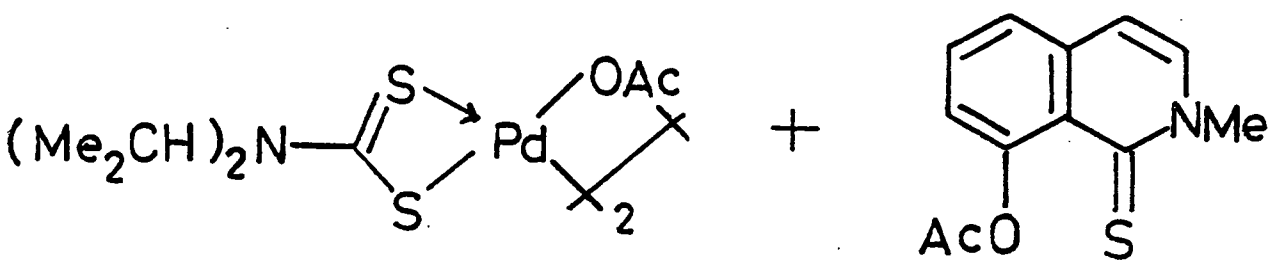


(241)

Unfortunately, lack of time has prevented the further investigation of this product but, if the structure (241) proves to be correct, it ought to be possible to liberate the desired chlorothione relatively easily by displacement with a stronger



(176) (242)



(244) (243)

Scheme (xii)

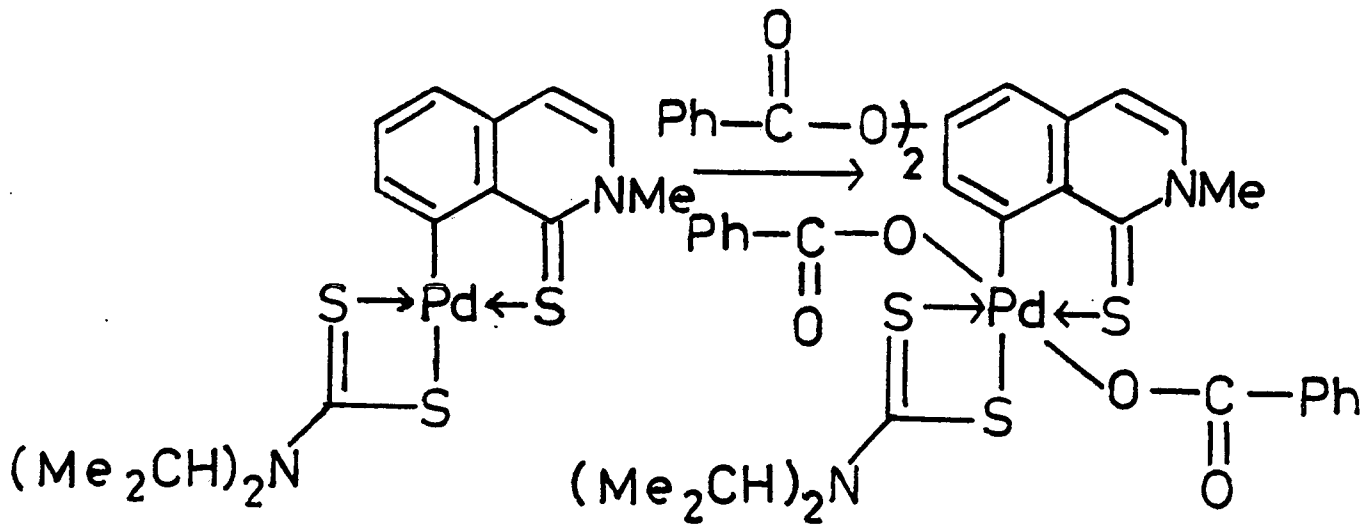
ligand.

(6) ATTEMPTED REPLACEMENT OF PALLADIUM IN CYCLOPALLADATED COMPLEXES BY OXYGEN-OR NITROGEN-CONTAINING GROUPS

(a) PALLADIUM-OXYGEN EXCHANGE

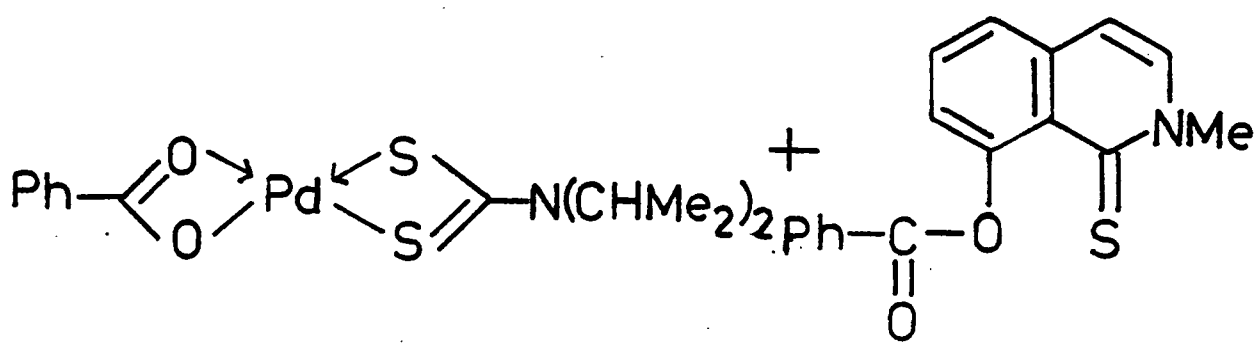
The successful use of thiocyanogen and morpholine-N-sulphenyl chloride in replacement of palladium by sulphur suggested that the corresponding replacement by oxygen would require a reagent containing electrophilic oxygen. Possible candidates are hypochlorites (ROCl), peroxides or peracids, and iodosocarboxylates [$ArI(OCOR)_2$]. The first of these were rejected, however, because of their low stability and possible behaviour as halogenating agents.

The introduction of an acyloxy function in place of palladium was first attempted by reaction of the dithiocarbamate complex (176) with phenyl iodosodiacetate. The envisaged reaction sequence is shown in Scheme (XII). Oxidative addition of the diacetate to yield the Pd (IV) complex (242) might be followed by reductive elimination of 8-acetoxy-2-methylisoquinoline-1-thione (243) and formation of the acetate-bridged complex (244). Treatment of complex (176) with one molar equivalent of the diacetate in chloroform produced a deep red non-oxidising solution. Heating gave a small quantity of purple solid which could not be characterised on account of its low solubility and involatility. Treatment of the chloroform solution with ether precipitated a quantity of bis (N,N-diisopropyldithiocarbamato) palladium (II). The ethereal filtrate gave a mass spectrum containing ion peaks consistent with the presence of 8-acetoxy-2-methylisoquinoline-1-thione (243), 8-acetoxy-2-methylisoquinolin-1-one (245), 8-hydroxy-2-methylisoquinoline-1-thione (246), 2-methylisoquinoline-1-thione



(176)

(248)

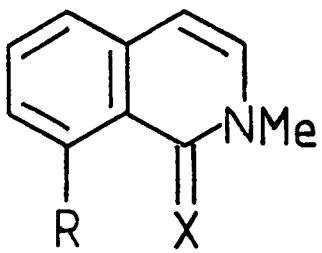


(249)

(247)

Scheme(xiii)

(140) and iodobenzene.

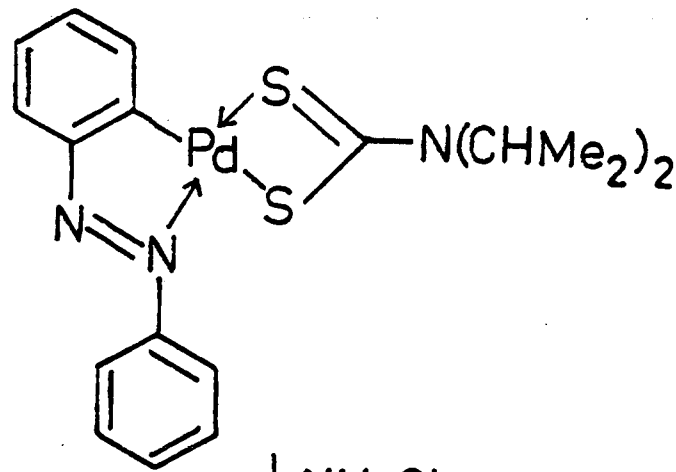


(243, R = OAc , X = S)
(245, R = OAc , X = O)
(246, R = OH , X = S)
(140, R = H , X = S)

Although steps were taken to exclude traces of water from this reaction, the formation of (246) could only be accounted for if water was present. Presumably (245) is formed by oxidation of (243). The formation of (140) could result from abstraction of hydrogen by an initially formed 1-thioxo-2-methylisoquinolin-8-yl radical.

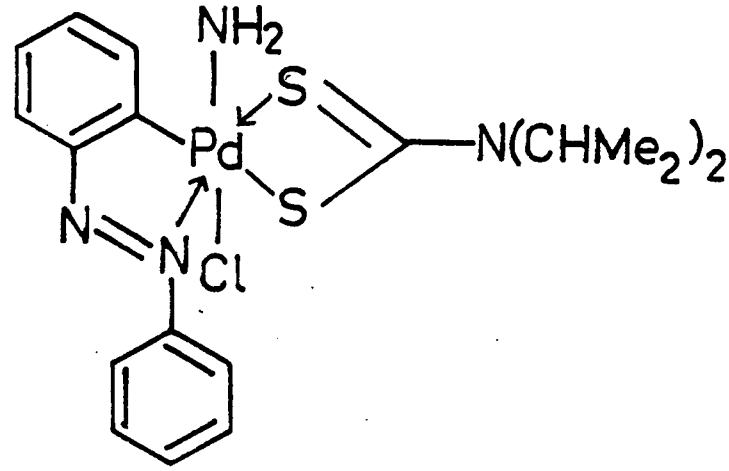
A similar type of reaction was attempted by treatment of the dithiocarbamate complex (176) with dibenzoyl peroxide. The envisaged reaction sequence is shown in Scheme (XIII). Oxidative addition of the peroxide to yield the Pd (IV) complex (248) might be followed by reductive elimination of the benzoyloxy compound (247) and the formation of the palladium complex (249).

Upon treatment of a chloroform solution of the dithiocarbamate complex with the peroxide, a red non-oxidising solution formed. A mass spectrum of the solution showed ion peaks corresponding to bis (N,N-diisopropyldithiocarbamato) palladium (II) and others which were thought to correspond to benzoic anhydride and benzoic acid. A possible mode of formation of benzoic anhydride

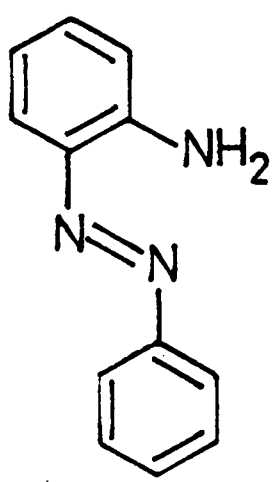


(183)

NH_2Cl

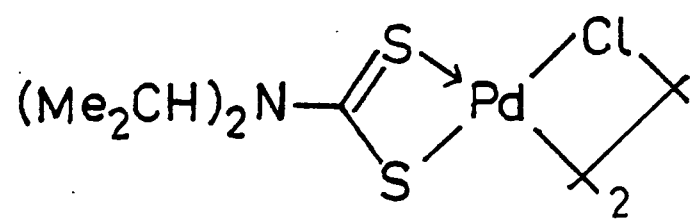


(252)



(251)

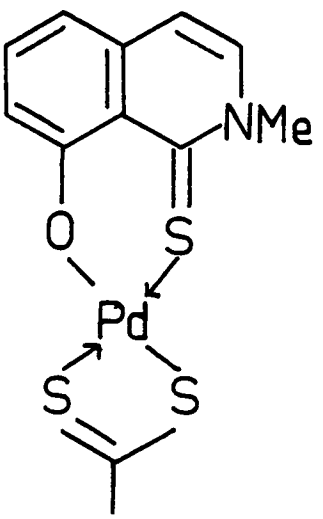
+



(218)

Scheme(xiv)

might be via elimination of oxygen from benzoyl peroxide, the oxygen being inserted into the palladium-carbon σ -bond of (176) to form the complex (250).

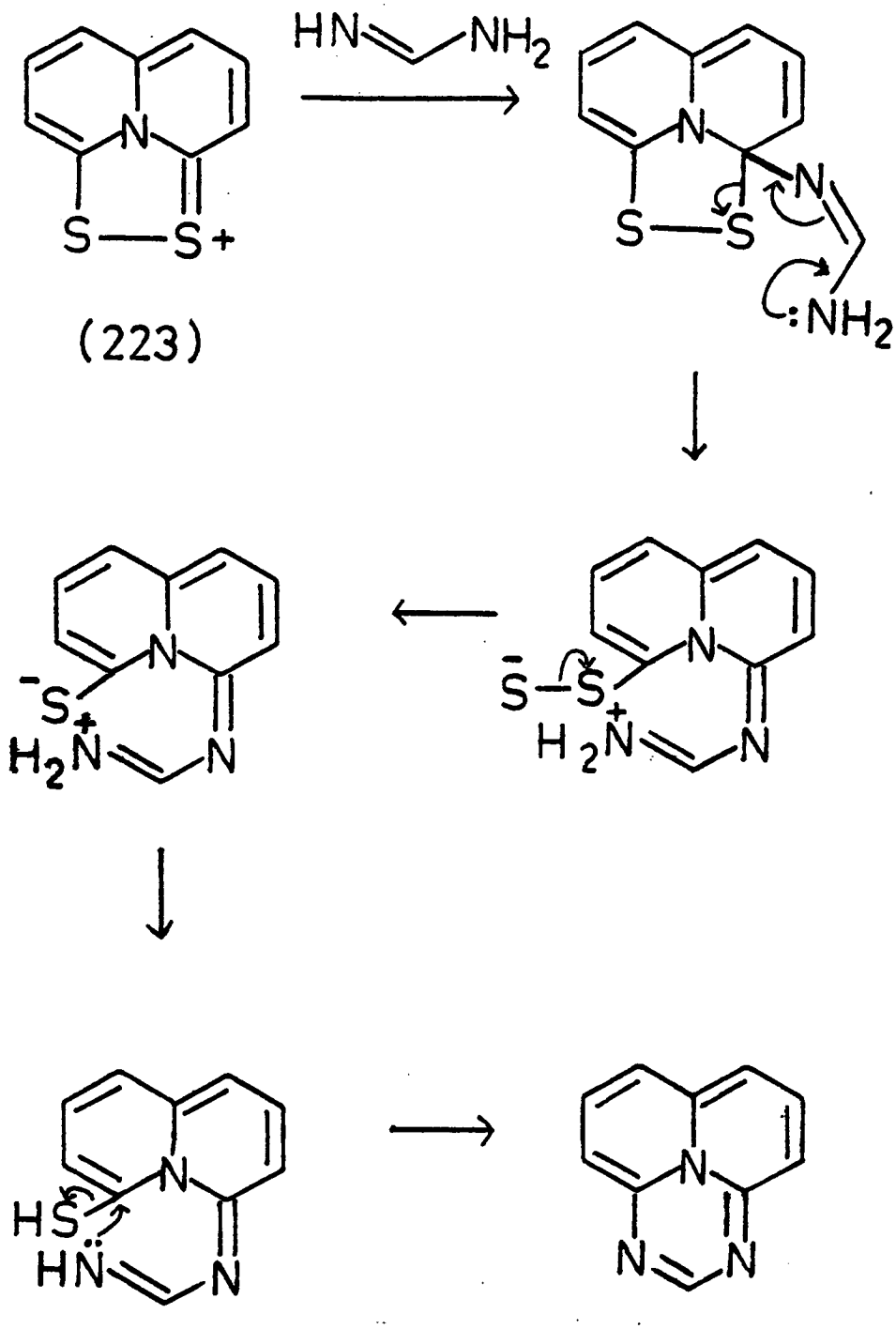


(250)

Accordingly, the evaporated reaction mixture was treated with sodium N,N-diisopropyldithiocarbamate in the hope that the sodium salt of 8-hydroxy-2-methylisoquinoline-4-thione and bis (N,N-diisopropyldithiocarbamato) palladium would be formed. In practice, approximately equal amounts of the dithiocarbamate complex (176) and the bis dithiocarbamate complex were formed. No evidence for the formation of the desired 8-benzoyloxy-or 8-hydroxyisoquinolinethione was obtained. The nature of this reaction therefore remains obscure.

(b) PALLADIUM-NITROGEN EXCHANGE

The synthesis of 2-aminoazobenzene (251) from the azobenzene complex (183) was attempted and the reaction sequence is shown in Scheme (XIV). The oxidative addition of chloramine to (183) might yield the $Pd^{(IV)}$ complex (252), which upon subsequent



(223)

(253)

Scheme (xv)

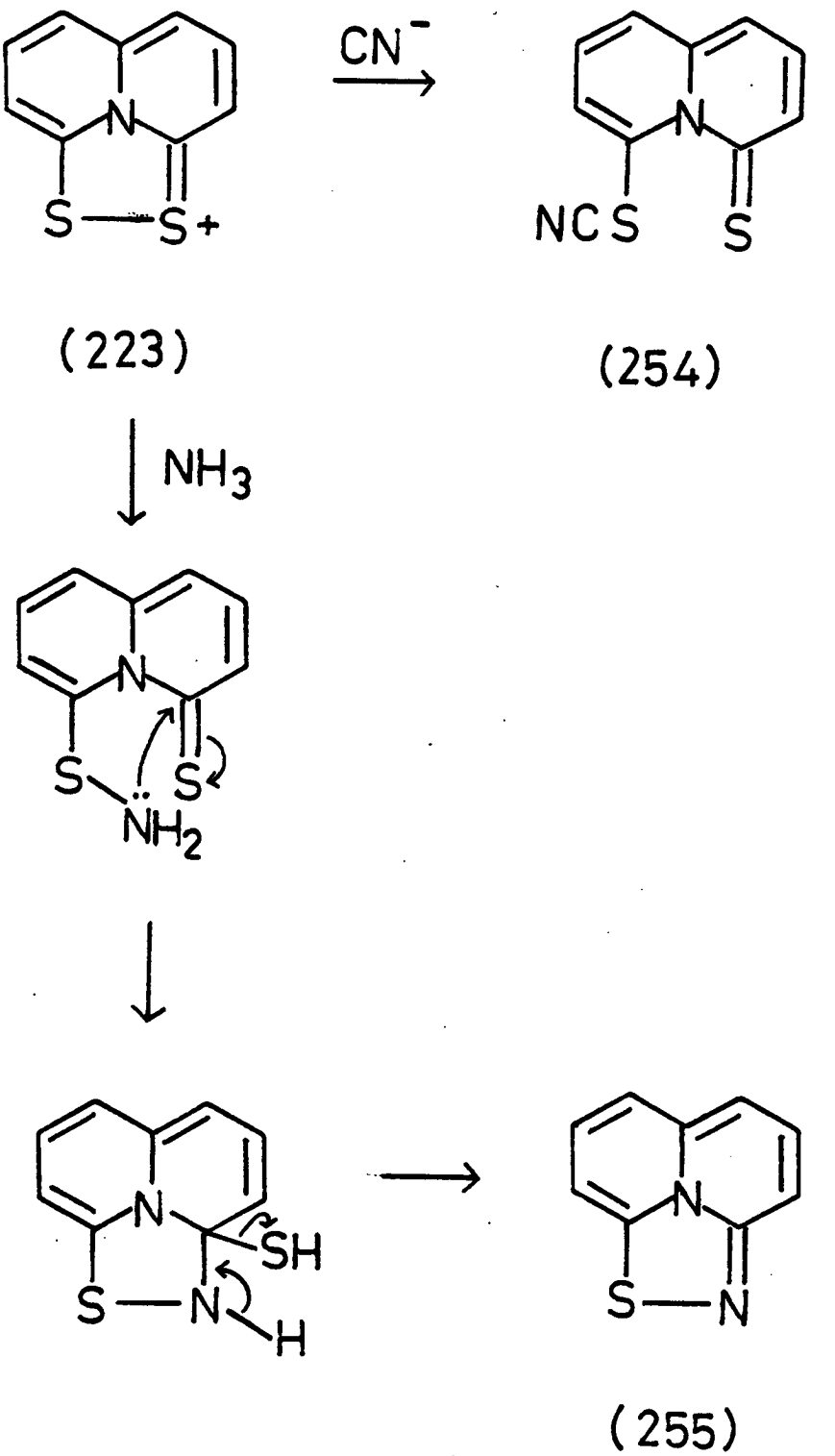
reductive elimination would yield 2-aminoazobenzene and the chloride-bridged complex (218). Unexpectedly, however, no reaction was observed between the reactants, either by stirring or by irradiation of an ethereal solution. The azobenzene complex (183) was recovered quantitatively upon removal of the solvent. In the light of the low nitrogen-chlorine bond energy, a factor which would promote oxidative addition, the lack of reaction of chloramine with the azobenzene complex is most surprising and cannot be rationalised.

(7) REACTIONS OF THE [1,2,4] DITHIAZOLO [3,4,5-de]-QUINOLIZINYLIUM CATION AND OTHER POTENTIAL PRECURSORS OF CYCLAZINE-LIKE MOLECULES

Having established a route to the novel [1,2,4] dithiazolo [3,4,5-de] quinolizinylium ring system (223) investigations were then carried out into its potential as an intermediate in the synthesis of other heterocyclic systems. Reactions involving attack by nucleophiles at the carbon-sulphur bonds, leading to the elimination of either or both sulphur atoms were envisaged.

The reaction of (223) with amidines was attempted with a view to synthesising [1,3,5] triazino [2,1,6-de] quinolizine (253), the as yet unknown 1,3-diaza-derivative of cycl [3,3,3] azine (224)[75] (Scheme (XV)). Although cycl [3,3,3] azine is a highly reactive, antiaromatic compound, the presence of electron withdrawing substituents or nitrogen atoms in positions β - to the bridgehead nitrogen is known to stabilise the system.[77] It is to be expected, therefore, that the triazine (253), like the 1,3-dicyanocyclazine and the 1,3-dicarboxylates, will be a stable substance.

When the dithiazolium chloride was heated with an equimolar amount of formamidine acetate in refluxing methanol a deep red solution



(223)

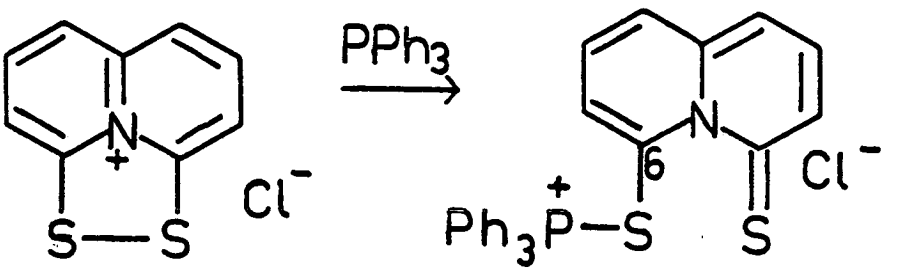
(254)

(255)

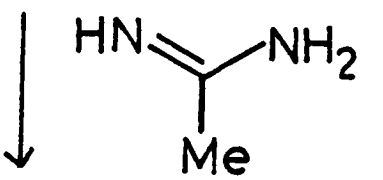
Scheme (xvi)

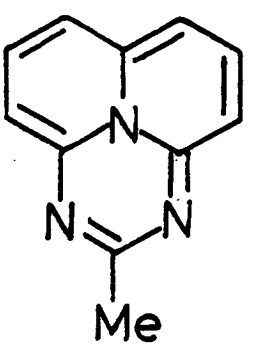
was formed. Examination of the reaction mixture at this stage by mass spectroscopy showed a peak at m/e 191 but no ion peak corresponding to the triazine. The solvent was then replaced with 2-methoxyethanol but still the desired reaction failed to occur at higher temperature under reflux in this solvent. The worked-up reaction mixture yielded a dark red gum which could not be crystallised and was not amenable to chromatography. The mass spectrum of this substance still showed an ion peak at m/e 191 which might possibly have been due to 6-methoxyquinolizine-4-thione, formed by attack of methoxide ion at a carbon atom of the dithiazolium ring and loss of one sulphur atom (cf. first three stages of Scheme (XV)). However, the exact mass of the ion peak at m/e 191 was not in accord with that required for 6-methoxyquinolizine-4-thione and so the identity of the reaction product remained unknown.

A different reaction was observed when an intimate mixture of the dithiazolium chloride and formamidine acetate were heated together in the absence of solvent. Examination of this reaction mixture by mass spectroscopy showed several products, two of which were thought to be 6-thiocyanatoquinolizine-4-thione (m/e 218) (254), and [1,2,4] thiadiazolo [3,4,5-de] quinolizine (m/e 174), (255). The formation of these products was thought to arise from thermal decomposition of formamidine to ammonia and hydrogen cyanide. These nucleophiles could then react with the dithiazolium salt to yield (254) and (255). The formation of (254) would require nucleophilic attack at sulphur and this type of reaction might also be involved in the formation of (255) as shown in Scheme (XVI). Alternatively, (255) could be formed by an addition-elimination mechanism involving nucleophilic attack at carbon as in the reaction of 1,2-dithiolium



(223) (256)





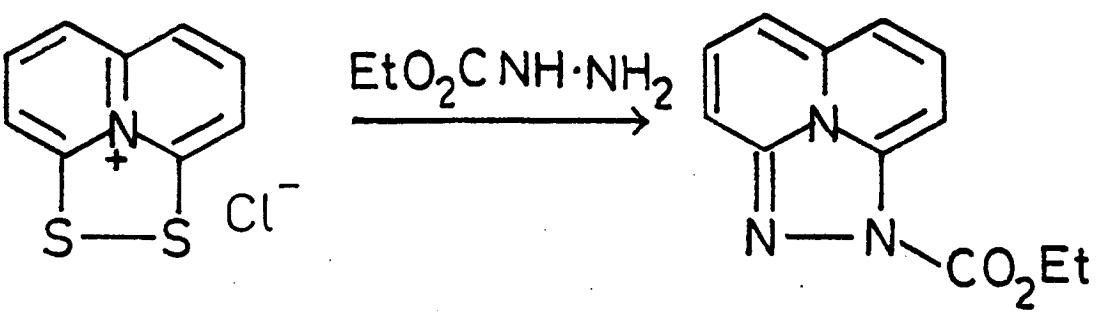
(257)

salts with ammonia to yield isothiazoles.[78] The presence of quinolizine-4-thione in this reaction was also detected by mass spectroscopy, although its formation could not be accounted for. An unidentified ion peak at m/e 223 was also observed.

In an attempt to eliminate the possibility of nucleophilic attack, by the amidine, directly on sulphur, the dithiazolium chloride was treated with one molar equivalent of triphenylphosphine prior to treatment with acetamidine. In this way the phosphonium salt (256) should be formed and subsequent nucleophilic attack by the amidine would be expected to occur at carbon (C-6 of 256) with displacement of triphenylphosphine sulphide.

In practice, no change was visible upon treatment of the dithiazolium salt with triphenylphosphine in boiling acetonitrile. Subsequent reaction with acetamidine hydrochloride in the presence of anhydrous potassium carbonate produced a deep red solution. Work-up of the reaction mixture yielded a dark red gum, the mass spectrum of which showed ion peaks corresponding to triphenylphosphine, triphenylphosphine sulphide and a peak of nominal m/e 183 which split into two peaks under high resolution. Exact mass measurements of these two peaks proved that they corresponded to the dibenzophospholylium ion, a normal fragment ion derived from triphenylphosphine, and the desired triazine (257). The intensity ratio of the former peak to the latter was approximately 30 : 1 and since the triazine was only present in trace amounts, it could not be isolated.

The reaction of 1,2-dithiolium salts with hydrazines has been shown to yield either pyrazoles[79] or pyrazolium salts[80] depending on the degree of substitution of the hydrazine used. In this light, reaction of the dithiazolium perchlorate with ethoxy-



(223) (258)

carbonylhydrazine was attempted with a view to synthesising the potentially antiaromatic, 12 π , 1,2,4-triazole (258). On account of electron withdrawal by the ethoxycarbonyl group, the lone pair of electrons on N-1 of the triazole would be less available for contribution into the π -system and therefore the triazole might be expected to be reasonably stable. However, the desired reaction was not observed. Upon heating of the reactants in dimethylformamide at 100° C for 3 hours, the only products that were isolated were the dithiazolium perchlorate and a mixture of ethoxycarbonylhydrazine and an unidentified substance which showed an ion peak at m/e 144 in the mass spectrometer. Treatment of the dithiazolium salt with one molar equivalent of triphenylphosphine prior to treatment with the hydrazine had no effect, the dithiazolium salt being recovered largely, after reaction in boiling acetonitrile for 5 hours.

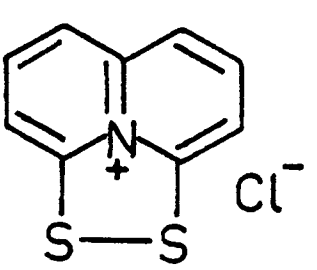
As discussed previously, the formation of the 1,2,4-thiadiazole (255) in the reaction of the dithiazolium salt (223) with formamidine acetate was thought to occur by reaction with ammonia. To test this hypothesis, an attempt was made to synthesise the thiadiazole by treatment of the dithiazolium salt with ammonia in dimethylformamide. Upon heating of the reaction mixture to 100° C, reaction was indicated by t.l.c. which showed several yellow spots. Work-up of the reaction mixture yielded a red gum. Any traces of ammonium chloride which might have been present were removed by aqueous extraction. Ether extraction of the residual gum yielded a small quantity of a yellow oil which was identified by mass spectroscopy as quinolizine-4-thione. The ether-insoluble substance was shown by mass spectroscopy to contain

the desired 1,2,4-thiadiazole (m/e 174) in addition to quinolizine-4-thione. Separation of the two products was attempted by sublimation *in vacuo*. However, owing to the small scale of this reaction, only a trace of yellow sublimate was obtained. A t.l.c. of the sublimate showed at least six spots, suggesting that it was either a mixture or was decomposing on the silica t.l.c. plate. The mass spectrum of the sublimate still showed an ion peak at m/e 174 and an exact mass measurement of this peak was in accord with that calculated for the 1,2,4-thiadiazole (255).

An attempt was also made to synthesise 6-thiocyanato-quinolizine-4-thione (254) by treatment of the dithiazolium salt (223) with cyanide ion and thus to confirm its formation in the reaction of (223) with formamidine acetate. Unexpectedly, however, no reaction was observed to occur between (223) and potassium cyanide in the presence of 18-crown-6 in boiling dichloromethane. The reason for this inertness of the dithiazolium ring towards nucleophilic attack remained obscure.

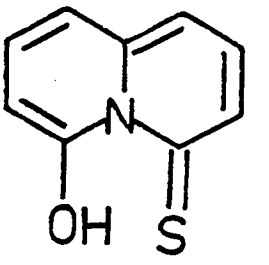
A characteristic property of 1,2-dithiolium salts is their sensitivity towards aqueous base.[81] In the presence of hydroxide ion, elimination of elemental sulphur occurs. This reaction was applied to the dithiazolium salt (223) with a view to synthesising 6-hydroxyquinolizine-4-thione (259). Subsequent reaction of this compound with phosphoryl chloride might yield the 4,6-dichloro-quinolizinylium salt (260) which would be a valuable intermediate for further heterocyclic synthesis.

Treatment of (223) with a two-fold excess of sodium hydroxide in aqueous methanol yielded a deep red solution, work up of which yielded an orange gum. Subsequent chromatography on silica yielded



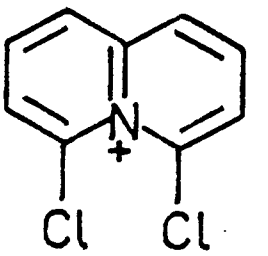
(223)

^{-}OH

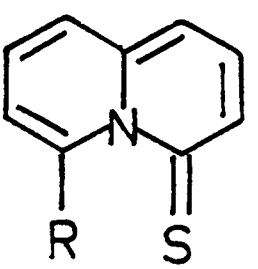


(259)

$POCl_3$



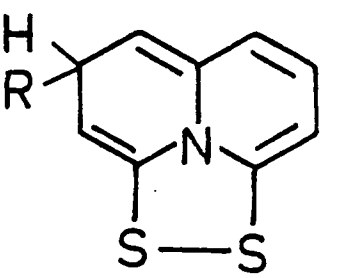
(260)



(140 , R = H)

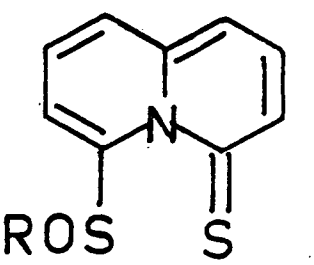
(259, R = OH)

(261 , R = OMe)



(262, R = OH)

(263, R = OMe)



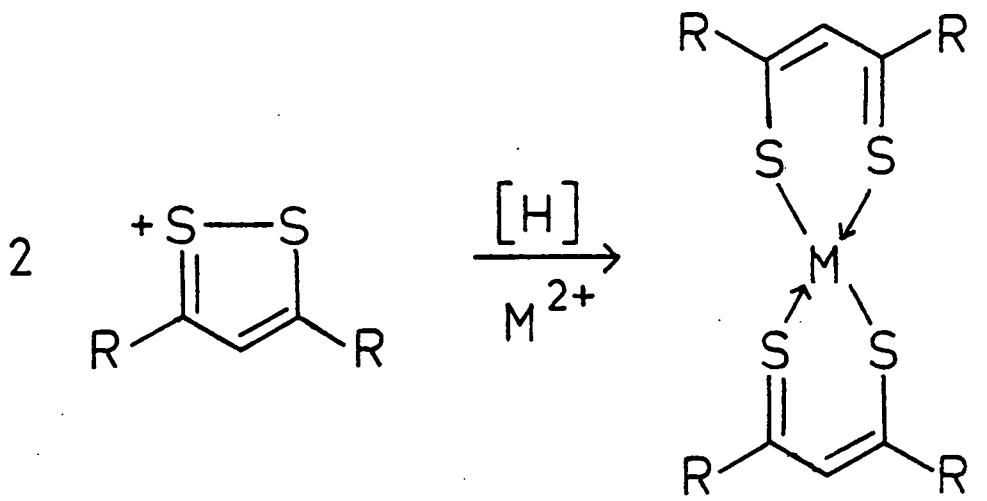
(264, R = H)

(265, R = Me)

a dark green gum which gave a complex mass spectrum consistent with the presence of five or more compounds. Two of these could have been 6-hydroxyquinolizine-4-thione (m/e 177/176) (259) and 6-methoxyquinolizine-4-thione (m/e 191) (261), formed according to the expected route but involving methoxide as well as hydroxide ion. Two other peaks (m/e 209 and 223) in the mass spectrum could have been due to addition products, presumably either (262) and (263) or (264) and (265). The probable formation of the methoxy-compounds (261) and (263) or (265) demonstrated the inappropriate choice of solvent system. A peak (m/e 161) attributable to quinolizine-4-thione (140) was also present in the mass spectrum, though the mode of formation of this compound remained obscure.

The foregoing observations suggest that there are at least two, and possibly, three centres in the dithiazolium ring system which are susceptible to nucleophilic attack. In addition to the desired attack by nucleophiles at C-2a, attack can also occur either at sulphur or at C-4. The formation of the addition products [possible structures (262-265)] by attack at the latter centres suggests that the synthesis of 6-hydroxyquinolizine-4-thione from the dithiazolium ring system in not practicable.

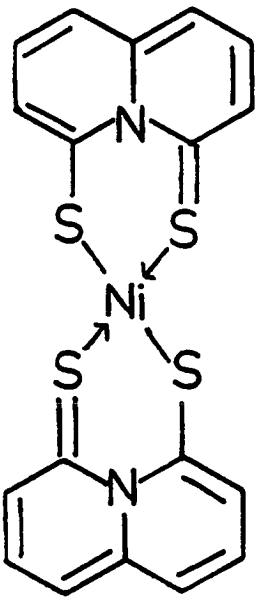
The reduction of 1,2-dithiolium salts (266) in the presence of di- and tri-valent metal ions to yield metal chelate complexes e.g. (267)[82,83] suggested the possibility of a similar reaction of the dithiazolium salt (223).



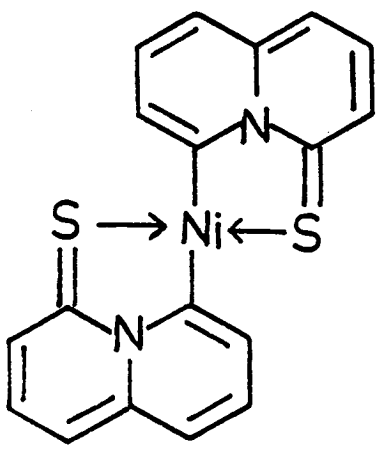
(266) (267)

Reduction of (223) with sodium borohydride in the presence of nickel chloride in aqueous solution yielded a highly insoluble deep purple solid, which was identified, on the basis of its elemental analysis, as bis (6-thioxoquinolizine-4-thiolato) nickel (II) (268). On account of its low solubility, this complex was unsuitable for n.m.r. studies.

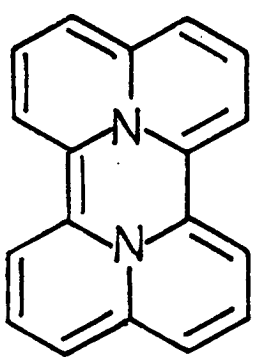
Interestingly, the mass spectrum of the complex (268) showed no molecular ion. Heating the sample to about 200° C on the mass spectrometer probe gave the spectrum of elemental sulphur [m/e 256 (S_8) and breakdown fragments, S_7 etc.] . Further heating above this temperature resulted in the disappearance of the sulphur ion peaks and the appearance of a nickel isotope pattern at m/e 378. This particular ion was thought to correspond to bis (4-thioxoquinolizin-6-yl) nickel (II) (269). The possibility that the proposed complex (268) was actually (269) containing two atom-equivalents of free sulphur can be discounted since free sulphur volatilises in the mass spectrometer at temperatures well below 200° C.



(268)



(269)



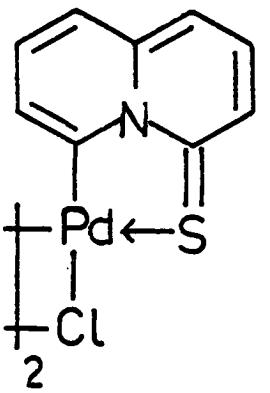
(270)

It is probable, therefore, that this doubly cyclometallated complex is formed by in vacuo thermolysis of (268). Such a complex might be potentially important as an intermediate in further heterocyclic synthesis; e.g. further thermolysis or heating with triphenylphosphine might yield the pyrazinodiquinolizine (270) via reductive elimination and further loss of sulphur and nickel or nickel sulphide. This cyclazine-like molecule possesses a perimeter π -system containing 18 π electrons and is potentially aromatic. Other routes to it were briefly explored and the results of these experiments are conveniently included in this section.

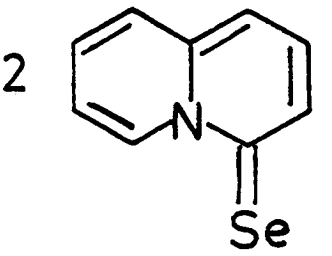
The reaction of the dimeric complex (141) with copper or zinc powder was envisaged as yielding this ring system by reductive dehalogenation, loss of palladium sulphide, and coupling of two quinolizine residues. The thermolysis of an intimate mixture of (141) and copper (or zinc) powder at 300° C in vacuo yielded a small quantity of dark yellow sublimate which was identified as quinolizine-4-thione by ^{1}H n.m.r. and mass spectroscopy. An involatile, intractable black residue was also formed in this reaction but there was no mass spectrometric evidence for the presence of compound (270).

As a first step towards the synthesis of the pyrazinodiquinolizine, Mathur[84] had previously attempted, unsuccessfully, to couple two quinolizine units to form (271) by desulphurisation of quinolizine-4-thione with copper powder and with triethyl phosphite. It has since been reported[85] that related coupling reactions (e.g. to form tetrathiafulvalenes) proceed much more efficiently from selenoxo-compounds (2-selenoxo-1,3-dithioles) than from thioxo compounds. Accordingly, the reaction of quinolizine-4-selone with triphenylphosphine was investigated.

Thermolysis of an intimate mixture of the reactants at 120°C



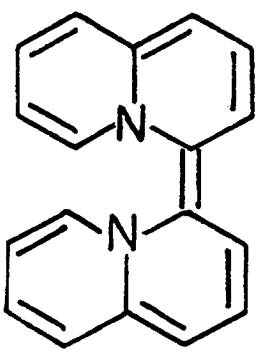
(141)



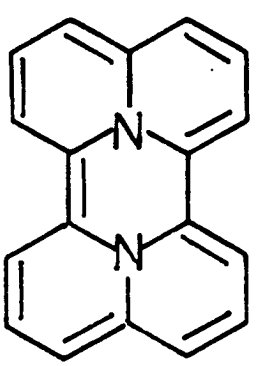
(142)

↓ 2 PPh_3

↓ Zn or Cu



↙ -2H (271)



(270)

under nitrogen yielded a black molten mass. Subsequent chromatography of this substance yielded a small quantity of triphenylphosphine selenide and quinolizine-4-selone (48% recovery). There was, however, no mass spectrometric evidence for the formation of (270) or (271).

(8) CONCLUSIONS

During the course of this work several conclusions were drawn, the most important of which, are listed below.

(1) The cyclopalladation of the nitrogen and sulphur ligands used in this work was in general facilitated by heating the reaction mixtures under reflux for several hours. When shorter reaction times were employed, mixtures of cyclopalladated and non-cyclopalladated ligands were obtained.

(2) In general, the synthesis of N,N-diisopropyldithiocarbamate complexes resulted in more crystalline and soluble solids in comparison with their N,N-dimethyl analogues.

(3) The treatment of cyclopalladated complexes of heterocyclic thioamides with thiocyanogen did not result in the replacement of palladium by a thiocyanato group. In these reactions the nature of the products was not entirely clear, although some evidence was obtained which suggested that dimeric thiocyanate-bridged palladium complexes were formed.

(4) The general applicability of morpholine-N-sulphenyl chloride as a reagent for the replacement of palladium in cyclopalladated complexes by sulphur has been established and illustrated by the synthesis of several novel condensed ring systems incorporating isothiazolium or 1,2-dithiolium nuclei.

E X P E R I M E N T A L

General Notes

(1) NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Routine 60MHz proton magnetic resonance spectra were recorded on a Varian EM 360 spectrometer. Where possible the proton n.m.r. spectra of all new compounds were recorded at 100MHz either on a Varian HA 100 spectrometer or on a Varian XL 100 spectrometer. ^{13}C n.m.r. spectra were recorded at 20MHz on a Varian CFT 20 spectrometer using a deuterium lock signal ($CDCl_3$).
Chemical shifts were recorded as delta (δ) values in parts per million from tetramethylsilane ($\delta = 0.0$), which was used as internal reference.
^{31}P n.m.r. spectra were recorded at 24.2MHz on a Jeol JNM-FX60Q spectrometer in $CDCl_3$ solution. Chemical shifts were measured relative to external 85% H_3PO_4, positive to high frequency.
In certain cases ^{1}H, ^{31}P and ^{77}Se n.m.r. spectra were recorded on a Bruker WH 360 spectrometer. ^{77}Se chemical shifts were measured relative to external Me_2Se.

(2) INFRARED SPECTROSCOPY

Infrared spectra were recorded as nujol mulls on a Perkin-Elmer 157G grating spectrometer.

(3) MASS SPECTROSCOPY

Mass spectra and exact mass measurements were recorded on an AEI MS 902 double-focussing spectrometer.

(4) ELECTRONIC SPECTROSCOPY

Electronic spectra were recorded on a Perkin-Elmer 402 spectrometer.

(5) ELEMENTAL ANALYSIS

The elemental analyses were recorded for most new compounds on a Perkin-Elmer 240 Analyser.

(6) MELTING POINTS

Melting points of all new compounds were determined on a Reichert hot-stage instrument and are uncorrected.

(7) CHROMATOGRAPHY

Alumina for chromatography was supplied by Laporte Industries Ltd. and was deactivated with water (10% W/W) before use. Silica gel for chromatography was supplied by Fisons Ltd. and was used as supplied.

(8) THIN LAYER CHROMATOGRAPHY

Thin layer chromatograms were obtained on alumina (Merck, aluminium oxide G) or silica gel (Merck, silica gel G). Detection of components in the developed chromatograms was by either observing the plate under U.V. light or by staining with iodine.

(9) SOLVENTS

Light petroleum refers to petroleum - ether. The fraction boiling between 40-60°C was used for chromatography and that boiling between 60-80°C for recrystallisations.

When employed as reaction solvent, chloroform was rendered free of ethanol prior to use by passing it through a column of activated alumina.

Organic extracts were dried over anhydrous magnesium sulphate.

Abbreviations

b.p.	boiling point
m.p.	melting point
d	decomposes
decomp.	decomposition temperature
t.l.c.	thin layer chromatography
n.m.r.	nuclear magnetic resonance
I.R.	infrared
U.V.	ultra-violet
M^+	mass of molecular ion
m/e	mass to charge ratio
a.m.u.	atomic mass units

n.m.r. abbreviations

br.	broad
s	singlet
d	doublet
dd	doublet of doublets
ddd	doublet of doublets of doublets
dt	doublet of triplets
t	triplet
td	triplet of doublets
tt	triplet of triplets
q	quartet
m	multiplet
J	coupling constant

(1) SYNTHESIS OF CYCLOPALLADATED COMPLEXES

Unless stated otherwise, three general methods, A, B and C were employed for the synthesis of dimeric cyclopalladated complexes from their corresponding substrate ligands.

Method A is described below for the cyclopalladation of 2-methylisoquinoline-1-thione.

METHOD A

REACTION OF 2-METHYLISOQUINOLINE-1-THIONE WITH SODIUM TETRACHLOROPALLADATE

A solution of sodium tetrachloropalladate (2.94g; 0.01 mole) in methanol (100 ml) was added dropwise to a stirred solution of 2-methylisoquinoline-1-thione (1.75g; 0.01 mole) in methanol (100 ml). A brown precipitate formed immediately and the reaction mixture was stirred for 1 hour and heated under reflux for a further hour, during which time the suspension became yellow in colour. The reaction mixture was cooled and the yellow solid was filtered off, washed with water, methanol, and then with ether, and finally dried *in vacuo* yielding di-μ-chloro-bis (1-thioxo-2-methylisoquinolin-8-yl) dipalladium (II), (2.95g; 94%), m.p. $>300^{\circ}C$.

I.R. SPECTRUM: ν max 1620, 1585, 1485, 1340, 1200, 925, 880, 805, 765, 750, 730 cm^{-1}

ANALYSIS: Found: C,37.9%; H,2.5%; N,4.3%

$C_{20}H_{16}Cl_2N_2Pd_2S_2$ requires: C,38.0%; H,2.5%; N,4.4%

Di-μ-chloro-bis (9-thioxothioxanthen-1-yl) dipalladium (II) was prepared by similar reaction of methanolic sodium tetrachloropalladate with thioxanthene-9-thione to yield a purple solid, (91%), m.p.> $300^{\circ}C$.

I.R. SPECTRUM: ν max 1600, 1550, 1520, 1420, 1405, 1375, 1250, 1230, 1100, 1030, 990, 760, 735, 705 cm^{-1}

ANALYSIS: Found: C,42.1%; H,1.8%

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

Di-μ-chloro-bis (2-phenyl-4-thioxothiochromen-5-yl) dipalladium (II) was prepared by similar reaction of methanolic sodium tetrachloropalladate with 2-phenylthiochromen-4-thione (4 hours reflux) to yield a red solid, (96%), m.p. > 300°C.

I.R. SPECTRUM: ν max 1545, 1500, 1485, 1425, 1245, 1200, 1170, 760, 745, 720, 695 cm^{-1}

ANALYSIS: Found: C,45.8%; H,2.2%

$C_{30}H_{18}Cl_2Pd_2S_4$ requires: C,45.6%; H,2.3%

Di-μ-chloro-bis (N-methyl-N-thiobenzoylaminomethyl)dipalladium (II) was prepared by similar reaction of methanolic sodium tetrachloropalladate with N,N-dimethylthiobenzamide. A brown suspension was formed initially, and became pale yellow upon heating the mixture under reflux for 5 hours, to yield the title complex, (82%), m.p. 273-4°C (d).

I.R. SPECTRUM: ν max 1590, 1440, 1300, 1260, 975, 755, 690 cm^{-1}

ANALYSIS: found: C,35.1%; H,3.3%; N,4.5%

$C_{18}H_{20}Cl_2N_2Pd_2S_2$ requires: C,35.3%; H,3.3%; N,4.6%

Di-μ-chloro-bis [N-methyl-N(4-methylthiobenzoyl)] aminomethyl dipalladium (II) was prepared by similar reaction of methanolic sodium tetrachloropalladate with 4-methyl-N,N-dimethylthiobenzamide. A brown suspension was formed initially and became grey upon heating the mixture under reflux for 5 hours, to yield the title complex, (88%), decomp. 275-80°C.

I.R. SPECTRUM: ν max 1600, 1310, 1295, 1265, 805 cm^{-1}

ANALYSIS: Found: C.37.5%; H,3.9%; N,4.2%

$C_{20}H_{24}Cl_2N_2Pd_2S_2$ requires: C.37.5%; H,3.8%; N,4.4%

Di-μ-chloro-bis [2-(phenylazo)phenyl] dipalladium (II) was prepared by similar reaction of methanolic sodium tetrachloropalladate with azobenzene (1 hour reflux) to yield a red solid, (86%), m.p. 287-9°C (d), (lit. m.p.[4] 279-81°C (d)).

METHOD B is essentially the same as Method A, with the exception that the reaction is carried out in solutions more dilute. This general method is described below for the cyclopalladation of quinolizine-4-thione.

REACTION OF QUINOLIZINE-4-THIONE WITH SODIUM TETRACHLOROPALLADATE

A solution of sodium tetrachloropalladate (0.588g; 0.002 mole) in methanol (50 ml) was added dropwise to a stirred solution of quinolizine-4-thione (0.37g; 0.0023 mole) in methanol (100 ml) over a period of 10-15 minutes. A deep red solution was formed initially, which then became lighter in colour with the simultaneous precipitation of an orange-brown solid. The reaction mixture was stirred for 1 hour and was then heated under reflux for 5 hours, during which time the suspension became yellow-orange in colour. The reaction mixture was cooled and the yellow-orange solid was filtered off, washed with water, methanol, and then with ether, and finally dried *in vacuo* yielding di-μ-chloro-bis (4-thioxoquinolizin-6-yl) dipalladium (II), (0.56g; 93%), m.p. >300°C.

I.R. SPECTRUM: ν max 1615, 1585, 1555, 1355, 1290, 1220, 1205, 1165, 1120, 795, 745 cm^{-1}

ANALYSIS: Found: C,35.5%; H,2.0%; N,4.5%

$C_{18}H_{12}Cl_2N_2Pd_2S_2$ requires: C,35.8%; H,2.0%; N,4.6%

Di-μ-chloro-bis (4-selenoxoquinolizin-6-yl) dipalladium (II) was prepared by similar reaction of methanolic sodium tetrachloropalladate with quinolizine-4-selone under nitrogen, to yield an orange-brown solid (91%), decomp. 285-90°C.

I.R. SPECTRUM: ν max 1620, 1595, 1560, 1355, 1295, 1220, 1205, 1170, 1120, 860, 800, 750 cm^{-1}

ANALYSIS: Found: C,31.0%; H,1.7%; N,3.9%

$C_{18}H_{12}Cl_2N_2Pd_2Se_2$ requires: C,31.0%; H,1.7%; N,4.0%

METHOD C was employed in cases where the substrate ligand was only sparingly soluble in methanol. The general method is described below for the cyclopalladation of 10-methylacridine-9-thione.

REACTION OF 10-METHYLACRIDINE-9-THIONE WITH LITHIUM TETRACHLOROPALLADATE

A solution of lithium tetrachloropalladate (0.785g; 0.003 mole) in methanol (400 ml) was added dropwise to a stirred solution of 10-methylacridine-9-thione (0.68g; 0.003 mole) in dichloromethane (400 ml). A purple precipitate formed immediately and the reaction mixture was stirred overnight. The dichloromethane was then fractionated off and the remaining methanolic suspension was heated under reflux for 3 hours, during which time the suspension became red in colour. The reaction mixture was cooled and the red solid was filtered off, washed with water, methanol and then with dichloromethane, and finally dried in vacuo yielding di-μ-chloro-bis (10-methyl-9-thioxoacridin-1-yl) dipalladium (II), (1.05g; 96%), m.p. > 300°C.

I.R. SPECTRUM: ν max 1620, 1575, 1545, 1515, 1325, 1255, 1185, 1055, 980, 780, 740, 725 cm^{-1}

ANALYSIS: Found: C,46.2%; H,2.7%; N,3.7%

$C_{28}H_{20}Cl_2N_2Pd_2S_2$ requires: C,45.9%; H,2.7%; N,3.8%

Di-μ-chloro-bis (7-chloro-1-methyl-4-thioxoquinolin-5-yl) dipalladium (II) was prepared by similar reaction of methanolic lithium tetrachloropalladate with a dichloromethane solution of 7-chloro-1-methylquinoline-4-thione. A brown suspension formed initially, and then became yellow-orange upon heating the mixture under reflux for 8 hours, to yield the title complex, (90%), m.p.>300°C.

I.R. SPECTRUM: ν max 1595, 1575, 1530, 1500, 1350, 1310, 1220, 1185 1100, 960, 865, 830, 820 cm^{-1}

ANALYSIS: Found: C,34.5%; H,2.0%; N,3.9%

$C_{20}H_{14}Cl_4N_2Pd_2S_2$ requires: C,34.3%; H,2.0%; N,4.0%

REACTION OF 10-METHYLACRIDINE-9-THIONE WITH LITHIUM TETRACHLORO-PALLADATE IN METHANOL-2-METHOXYETHANOL

A solution of 10-methylacridine-9-thione (0.225g; 0.001 mole) in hot 2-methoxyethanol (50 ml) was added dropwise to a stirred solution of lithium tetrachloropalladate (0.261g; 0.001 mole) in methanol (20 ml). The reaction mixture was stirred for one hour, during which time a purple precipitate formed. The reaction mixture was filtered and the precipitate (0.105g) was collected. On account of its insolubility and involatility this substance was thought to be a palladium salt. The filtrate was reduced in volume and treated with water until precipitation of pale yellow solid was complete. The solid, (0.165g), m.p. 191-4°C was identified as 10-methylacridin-9-one (lit. m.p.[86] 199°C), by infrared spectroscopy.

REACTION OF 3-PHENYL-1,2-BENZISOTHIAZOLE WITH SODIUM TETRACHLORO-PALLADATE

A solution of sodium tetrachloropalladate (0.294g; 0.001 mole) in methanol (10 ml) was added to a stirred solution of 3-

phenyl-1,2-benzisothiazole (0.21g; 0.001 mole) in methanol (10 ml). A yellow precipitate formed immediately and the reaction mixture was stirred for 1 hour and was then heated under reflux for 6 hours, during which time no further chemical reaction was observed. The reaction mixture was cooled and the yellow solid was filtered off, washed with water, methanol, and then with ether, and finally dried in vacuo yielding bis (3-phenyl-1,2-benziso-thiazole) palladium (II) dichloride, (0.20g; 65%), m.p. >300°C.

I.R. SPECTRUM: ν max 1360, 790, 775, 730, 700 cm^{-1}

ANALYSIS: Found: C,51.0%; H,2.9%; N,4.4%

$C_{26}H_{18}Cl_2N_2Pd\ S_2$ requires: C,52.1%; H,3.0%; N,4.7%

REACTION OF 3-PHENYL-1,2-BENZISOTHIAZOLE WITH PALLADIUM ACETATE

3-phenyl-1,2-benzisothiazole (0.21g; 0.001 mole) and palladium acetate (0.22g; 0.001 mole) were mixed together in glacial acetic acid (10 ml). The mixture was heated under reflux with stirring for 30 minutes. The mixture was then cooled and poured into water (50 ml) and the resulting yellow precipitate was filtered off. The aqueous filtrate was neutralised with sodium bicarbonate solution and extracted with dichloromethane (50 ml) and the extract was dried over magnesium sulphate. The dried extract was filtered and the filtrate was evaporated. The residue from evaporation was combined with the reaction product from above and the whole was chromatographed on alumina. Eluting with dichloromethane-ethanol (9:1) yielded di-μ-acetato-bis [2-(1,2-benzisothiazol-3-yl) phenyl] dipalladium (II), as a yellow solid, (0.09g; 24%), decomp.250-5°C. Recrystallisation from toluene gave the analytically pure product, m.p. unchanged.

I.R. SPECTRUM: ν max 1580, 1560, 1410, 775, 725 cm^{-1}

^{1}H n.m.r. SPECTRUM: ($CDCl_3$) δ 7.96 [d, (J = 7Hz), 2H, proton ortho to palladium]; δ 7.7-6.3 [m, 14 aromatic protons]; δ 2.28 [s, 6H, 6 acetate methyl protons].

ANALYSIS: Found: C,47.9%; H,3.0%; N,3.6%

$C_{28}H_{22}N_2O_4Pd_2S_2$ requires: C,48.0%; H,2.9%; N,3.7%

Di μ-acetato-bis [2-(N-phenylformimidoyl)phenyl] dipalladium (II) was prepared by reaction of benzylideneaniline with palladium acetate in 42% yield, decomp. 215-20°C, (lit.[7] decomp. 210-20°C) by the method of Onoue and Moritani[7].

Di-μ-chloro-bis [2-(2-pyridyl)phenyl] dipalladium (II) was prepared by reaction of 2-phenylpyridine with sodium tetrachloropalladate in 77% yield, decomp. 270°C, (lit.[36] decomp. 270°C) by the method of Kasahara.[36]

REACTION OF TRIPHENYLPHOSPHINE-N-p-TOLYLIMIDE WITH SODIUM TETRACHLOROPALLADATE

This reaction was carried out under conditions identical with those reported by Alper[30]. However, despite many attempts, the reaction failed to yield the desired cyclopalladated phosphinimine complex. Under Alper's reaction conditions a brown solid, m.p. 186-9°(d) was formed. On the basis of its elemental analysis this compound was thought to be a co-ordination complex of the type $[LPdCl_2]_2$, where L = triphenylphosphine-N-p-tolylimide. The yield of this complex was 75-85%.

I.R. SPECTRUM: ν max 1610, 1500, 1435, 1375, 1245, 1110, 1015, 990, 840, 800, 750, 740, 720, 690 cm^{-1}

ANALYSIS: Found: C,55.2%; H,4.5%; N,2.7%

$C_{50}H_{44}Cl_4N_2P_2Pd_2(LPdCl_2)_2$ requires: C,55.1%; H,4.0%; N,2.6%

$C_{50}H_{42}Cl_2N_2P_2Pd_2$ requires: C,59.1%; H,4.1%; N,2.8%
(cyclopalladated complex)

REACTION OF TRIPHENYLPHOSPHINE SULPHIDE WITH SODIUM TETRACHLORO-PALLADATE

A solution of sodium tetrachloropalladate (0.588g; 0.002 mole) in methanol (50 ml) was added dropwise to a stirred solution of triphenylphosphine sulphide (0.60g; 0.002 mole) in methanol (300 ml). A creamy-yellow precipitate formed immediately and the reaction mixture was stirred for 3 hours and was then heated under reflux for 3 hours, during which time no further chemical reaction was observed. The reaction mixture was cooled and the creamy-yellow solid was filtered off, washed with water, methanol, and then with chloroform, and finally dried *in vacuo* yielding bis (triphenylphosphine sulphide) palladium (II) dichloride (0.72g; 94%), m.p. 238-40°C (d).

I.R. SPECTRUM: ν max 1435, 1105, 750, 710, 690 cm^{-1}

ANALYSIS:

	Found:	C,55.2%; H,3.9%
$C_{36}H_{30}Cl_2P_2Pd\ S_2$	requires:	C,56.5%; H,3.9%
$[C_{18}H_{14}ClPdSP]_2$ (cyclopalladated complex)	requires:	C,49.7%; H,3.2%

(2) SYNTHESIS OF MONOMERIC PHOSPHINE COMPLEXES

REACTION OF DI-μ-CHLORO-BIS (1-THIOXO-2-METHYLISOQUINOLIN-8-YL) DIPALLADIUM (II) WITH TRIETHYLPHOSPHINE

To a stirred suspension of di-μ-chlorobis (1-thioxo-2-methylisoquinolin-8-yl) dipalladium (II) (0.315g; 0.5 mmole)

in dichloromethane (25 ml) was added a solution of triethylphosphine (0.12g; 1 mmole) in dichloromethane (10 ml). The resulting yellow solution was stirred for 1 hour. The solvent was removed and the residue was chromatographed on alumina (50g), eluting with dichloromethane. The product was initially obtained as a yellow oil and was triturated with ether - light petroleum yielding chloro-(1-thioxo-2-methylisoquinolin-8-yl) triethylphosphinepalladium (II) as a pale yellow solid, (0.35g; 81%), m.p. 172-5°C (d). Recrystallisation from benzene gave the analytically pure product, m.p. 175-7°C (d).

I.R. SPECTRUM: ν max 1620, 1580, 1530, 1335, 1195, 1035, 820, 810, 770 cm^{-1}

^1H n.m.r. SPECTRUM: ($CDCl_3$) δ 8.60 [t, (J = 8Hz), ca.0.5H, H-7]; δ 7.6-7.2 (m, ca.3.5H, aromatic protons); δ 6.95 [d, (J = 7Hz), 1H, H-4]; δ 4.07 (s, ca.1.5H, NCH_3); δ 3.99 (s, ca.1.5H, NCH_3); δ 1.97 (m, 6H) and 1.18 (m, 9H), PEt_3

Irradiation at ^{31}P frequency 40,482,690 Hz collapses low field triplet into a doublet, $^3J_{HH}$ = 7Hz and affects intensities of PEt_3 multiplets. Irradiation at ^{31}P frequency 40,483,180Hz affects intensities of PEt_3 multiplets only.

^{31}P n.m.r. SPECTRUM: ($CDCl_3$) 11.5 p.p.m. (s); 23.3 p.p.m. (s)

ANALYSIS: Found: C,44.4%; H,5.3%; N,3.2%

$C_{16}H_{23}Cl\ N\ P\ Pd\ S$ Requires: C,44.3%; H,5.3%; N,3.2%

REACTION OF DI-μ-CHLORO-BIS (1 THIOXO-2-METHYLISOQUINOLIN-8-YL) DIPALLADIUM (II) WITH TRIPHENYLPHOSPHINE

To a stirred suspension of di-μ-chloro-bis (1-thioxo-2-methylisoquinolin-8-yl) dipalladium (II) (0.63g; 1 mmole) in chloroform (100 ml) was added triphenylphosphine (0.52g; 2 mmole).

The resulting yellow-orange solution was stirred overnight. The solvent was removed and the residue was chromatographed on alumina (50g). Eluting with dichloromethane yielded chloro (1-thioxo-2-methylisoquinolin-8-yl) triphenylphosphinepalladium (II), (0.58g; 50%), m.p. 225-7°C (d), as a pale yellow solid. Continued elution with dichloromethane-ethanol (9:1) yielded another pale yellow solid (0.35g), m.p. 223-4°C (d), initially thought to be an isomer of the former reaction product. However, spectroscopic studies (I.R. and ^{1}H n.m.r.) showed both reaction products to be the same, i.e. both products were a mixture of cis-and trans-isomers. Recrystallisation of the former and latter products from dichloromethane - light petroleum yielded the analytically pure products, m.p. 229-30°C (d) and 223-4° (d), (unchanged), respectively.

I.R. SPECTRUM: ν max 1620, 1580, 1530, 1340, 1200, 1095, 805, 740, 690 cm^{-1}

^{1}H n.m.r. SPECTRUM: ($CDCl_3$) δ 7.9-6-8 (m, 20 aromatic protons); δ 4.05 (s,ca.2H,NCH_3); δ 3.80 (s,ca.1H,NCH_3)

^{31}P n.m.r. SPECTRUM: ($CDCl_3$) 16.8 p.p.m. (s); 37.4 p.p.m. (s)

ANALYSIS: Found: (former product) C,57.5%; H,4.0%; N,2.3%

Found: (latter product) C,57.4%; H,4.0%; N,2.4%

$C_{28}H_{23}Cl\ N\ P\ Pd\ S$ requires: C,57.3%; H,4.1%; N,2.5%

Chloro (4-selenoxoquinolizin-6-yl) triethylphosphinepalladium was prepared from the corresponding chloride-bridged dimer complex and triethylphosphine, under conditions identical with those of the preceding experiment, to yield a yellow solid, (64%), m.p. 164-5°C (d) (from benzene).

I.R. SPECTRUM: ν max 1615, 1555, 1410, 1305, 1190, 1045, 1035, 810, 775, 760, 725 cm^{-1}

^{1}H n.m.r. SPECTRUM: ($CDCl_3$) δ 9.25 (m, 1H, H-7); δ 7.85 (m,1H,H-3); δ 7.7-7.5 (m,4H,H-1,2,8 and 9); δ 1.94 (m,6H) and δ 1.18 (m,9H),(PEt_3).

^{13}C n.m.r. SPECTRUM : ($CDCl_3$) p.p.m. 145.6 (C=Se), 133.1, 133.0, 131.1, 130.8, 130.2, 123.9, 121.6, 120.2, 15.3 [d, ($^1J_{CP}$=25.2Hz)] and 8.1 (PEt_3)

^{31}P n.m.r. SPECTRUM: ($CDCl_3$) 14.7 p.p.m. [s with ^{77}Se satellites, ($^2J_{PSe}$= 10 Hz)]

^{77}Se n.m.r. SPECTRUM: ($CDCl_3$) 359.3 p.p.m. [d, ($^2J_{SeP}$= 10.0Hz)]

ANALYSIS: Found: C,38.7%; H,4.4%; N,2.9%

$C_{15}H_{21}Cl$ N P Pd Se requires: C,38.6%; H,4.5%; N,3.0%

REACTION OF DI-μ-CHLORO-BIS (N-METHYL-N-THIOBENZOYLAMINOMETHYL) DIPALLADIUM (II) WITH TRIETHYLPHOSPHINE

To a stirred suspension of di-μ-chloro-bis (N-methyl-N-thiobenzoylaminomethyl) dipalladium (II) (0.31g; 0.5 mmole) in dichloromethane (20 ml) was added a solution of triethylphosphine (0.12g; 1 mmole) in dichloromethane (10 ml). The resulting yellow solution was stirred for 1 hour. The solvent was removed and the residue was chromatographed on alumina (40g), eluting with dichloromethane and then with dichloromethane - ethanol (4:1) The product, initially obtained as a pale yellow oil, was triturated with ether - light petroleum to yield chloro (N-methyl-N-thiobenzoylaminomethyl) triethylphosphinepalladium (II) as a white solid, (0.27g; 62%), m.p. 173-5°C. Recrystallisation from benzene gave the analytically pure product, m.p. 178-9°C.

I.R. SPECTRUM: ν max 1605, 1585, 1280, 1035, 985, 770, 760, 730, 700 cm^{-1}

^{1}H N.M.R. SPECTRUM: ($CDCl_3$) δ 7.2-7.5 (m,5H, aromatic ring protons);

δ 4.15 [d, ($^3J_{PH}$= 4Hz), 2H,NCH_2] ;δ 3,12 (s,3H,NCH_3); δ 1.82 (m,6H) and δ 1.15 (m,9H), PEt_3

^{13}C n.m.r. SPECTRUM: ($CDCl_3$) p.p.m. 194.5 (C=S); 137.0, 130.2, 128.5, 126.7 (aromatic ring carbons); 55.4 [d, ($^2J_{CP}$= 4.4Hz), NCH_2]; 45.4 (NCH_3); 14.3 [d, ($^1J_{CP}$= 25.9Hz)] and 8.0 (PEt_3).

^{31}P n.m.r. SPECTRUM: ($CDCl_3$) 20.2 p.p.m. (s)

MASS SPECTRUM: m/e 423 (M^+,Pd), 412(Pd), 387(Pd), 201/199 (Cl), 164, 155/153(Cl), 121, 118

ANALYSIS: Found: C,42.3%; H,5.8%; N,3.7%

$C_{15}H_{25}Cl\ N\ P\ Pd\ S$ requires: C,42.5%; H,5.9%; N,3.3%

Chloro [N-methyl-N-(4-methylthiobenzoyl)aminomethyl] triethylphosphinepalladium (II) was prepared from the corresponding chloride-bridged dimeric complex and triethylphosphine under conditions identical with those of the preceding experiment to yield a white solid (82%), m.p. 200-1°C (from benzene).

I.R. SPECTRUM: ν max 1610, 1585, 1290, 1265, 1035, 815, 765, 730 cm^{-1}

^{1}H n.m.r. SPECTRUM: ($CDCl_3$) δ 7.2 (br.s,4H, aromatic ring protons); δ 4.15 [d, ($^3J_{PH}$= 4Hz), 2H, NCH_2] ; δ 3.16 (s,3H,NCH_3); δ 2.35 (s,3H,$ArCH_3$); δ 1.85 (m,6H) and δ 1.18 (m,9H), PEt_3.

^{13}C n.m.r. SPECTRUM: ($CDCl_3$) p.p.m. 194.6 (C=S), 140.7, 134.2, 129.1, 126.8 (aromatic ring carbons); 55.1 [d, ($^2J_{CP}$= 3.9Hz), NCH_2]; 45.4 (NCH_3); 14.2 [d,($^1J_{PC}$=25.6Hz)] and 7.9 (PEt_3)

^{31}P n.m.r. SPECTRUM: ($CDCl_3$) 20.2 p.p.m.

MASS SPECTRUM: m/e 437 (M^+, Pd), 265, 215/213(Cl), 206, 178, 155/153(Cl), 135, 118

ANALYSIS: Found: C,43.9%; H,6.1%; N,3.2%

$C_{16}H_{27}Cl\ N\ P\ Pd\ S$ requires: C,43.9%; H,6.1%; N,3.2%

REACTION OF DI-μ-CHLORO BIS (9-THIOXO-10-METHYLACRIDIN-1-YL) DIPALLADIUM (II) WITH TRIETHYLPHOSPHINE

To a stirred suspension of di-μ-chloro-bis (9-thioxo-10-methylacridin-1-yl) dipalladium (II) (0.25g; 0.34 mmole) in chloroform (100 ml) was added triethylphosphine (0.08g; 0.68 mmole). The reaction mixture was stirred for 3 hours and filtered to yield unchanged dimeric complex (0.09g). The filtrate was evaporated and the residue was chromatographed on alumina (50g), eluting with dichloromethane. The product, chloro(9-thioxo-10-methylacridin-1-yl)triethylphosphinepalladium (II), was obtained as a red solid, (0.09g; 28%), m.p. $>300^{\circ}C$. Recrystallisation from benzene gave the analytically pure product.

I.R. SPECTRUM: ν max 1570, 1320, 1250, 1035, 970, 745, 725 cm^{-1}

^1H n.m.r. SPECTRUM: ($CDCl_3$) δ 8.7 (m,1H,H-8); δ 8.36 [t,(J=8Hz), 1H, H-2]; δ 7.9-7-2 (m,5H, remaining aromatic protons); δ 4.10 (s,3H,NCH_2); δ 1.96 (m,6H) and δ 1.22 (m,9H), PEt_3.

^{31}P n.m.r. SPECTRUM: ($CDCl_3$) 21.4 p.p.m. (s); 11.6 p.p.m. (s)

ANALYSIS:	Found:	C,49.4%;	H,5.3%;	N,2.7%
$C_{20}H_{25}Cl\ N\ P\ Pd\ S$	requires:	C,49.6%;	H,5.2%;	N,2.9%

REACTION OF DI-μ-CHLORO-BIS (9-THIOXO-10-METHYLACRIDIN-1-YL DIPALLADIUM (II) WITH TRIMETHYLPHOSPHITE

To a stirred suspension of di-μ-chloro-bis (9-thioxo-10-methylacridin-1-yl) dipalladium (II) (0.08g; 0.11 mmole) in chloroform (25 ml) was added trimethylphosphite (0.027g; 0.22mmole). The resulting orange-red solution was stirred for 2 hours. The reaction mixture was reduced to one quarter of the original volume and light petroleum was added to precipitate the product, chloro (9-thioxo-10-methylacridin-1-yl)trimethylphosphitepalladium (II),

(0.075g; 70%), m.p. 200-3°C (d). Recrystallisation from chloroform - light petroleum gave the analytically pure product, m.p. 204-5°C (d).

I.R. SPECTRUM: ν max 1615, 1585, 1570, 1540, 1325, 1250, 1185, 1005, 805, 795, 765, 745 cm^{-1}

ANALYSIS:	Found:	C,41.6%;	H,3.8%;	N,2.8%
$C_{17}H_{16}Cl\ NO_3P\ Pd\ S$	requires:	C,41.7%;	H,3.9%;	N,2.9%

(3) SYNTHESIS OF DITHIOCARBAMATE AND RELATED COMPLEXES

Unless stated otherwise, dimeric chloride-bridged complexes were converted to the corresponding monomeric dithiocarbamate complexes by the general method which is described below for the conversion of di-μ-chloro-bis (1-thioxo-2-methylisoquinolin-8-yl) dipalladium (II) to 1-thioxo-2-methylisoquinolin-8-yl (N,N-diisopropyldithiocarbamato) palladium (II).

REACTION OF DI-μ-CHLORO-BIS (1-THIOXO-2-METHYLISOQUINOLIN-8-YL) DIPALLADIUM (II) WITH SODIUM N,N-DIISOPROPYLDITHIOCARBAMATE

To a stirred suspension of di-μ-chloro-bis (1-thioxo-2-methylisoquinolin-8-yl) dipalladium (II) (1.10g; 1.75 mmole) in dimethylformamide (150 ml) was added a solution of sodium diisopropyldithiocarbamate (0.70g; 3.5. mmole) in dimethylformamide (20 ml). The resulting yellow solution was stirred for 5 hours. The solvent was removed under high vacuum and the residue was chromatographed on alumina (50g). Eluting with dichloromethane

yielded 1-thioxo-2-methylisoquinolin-8-yl (N,N-diisopropyldithiocarbamato) palladium (II) as a yellow solid, (1.60g; 100%), m.p. 257-9°C (d). Recrystallisation from benzene gave the analytically pure product, m.p. 264-6°C (d).

I.R. SPECTRUM: ν max 1620, 1580, 1530, 1490 (C=N), 1335, 1195, 1145, 1050, 1035, 810, 795, 775 cm^{-1}

^1H n.m.r. SPECTRUM: ($CDCl_3$) δ 7.5-7.1 (m, 4 aromatic protons; δ 6.88 [d,($^3J_{HH}$= 7Hz), 1H, H-4]; δ 5.2-4.3 (m,2H,2 methine protons); δ 4.02 (s,3H,NCH_3); δ 1.51 and 1.46 [2 br.d (overlapping), ($^3J_{HH}$= 7Hz), 12H, isopropyl CH_3]

MASS SPECTRUM: m/e 456 (Pd,M^+), 280 (Pd)

ANALYSIS: Found: C,44.6%; H,4.7%; N,5.9%

$C_{17}H_{22}N_2Pd\ S_3$ requires: C,44.7%; H,4.8%; N,6.1%

The following complexes were prepared from the appropriate chloride-bridged dimeric complexes by the same general method:

7-Chloro-1-methyl-4-thioxoquinolin-5-yl (N,N-diisopropyldithiocarbamato) palladium (II)

Yellow solid, yield 79%, m.p. 291-4°C (d) (from benzene).

I.R. SPECTRUM: ν max 1595, 1570, 1485 (C=N), 1330, 1220, 1180, 1145, 1105, 1045, 960, 865, 815, 800 cm^{-1}

^1H n.m.r. SPECTRUM: ($CDCl_3$) δ 7.40 [d,($^3J_{HH}$= 7Hz),1H]; δ 7.03 [d, ($^4J_{HH}$= 1.5Hz),1H]; δ 6.90 [d,($^3J_{HH}$= 7Hz),1H]; δ 6.88 [d,($^4J_{HH}$ = 1.5Hz),1H]; δ 5.2-4.2 (m,2H,2 methine protons); δ 4.00 (s,3H,NCH_3); δ 1.51 [2 br.d (overlapping), ($^3J_{HH}$= 7Hz),12H, isopropyl CH_3]

MASS SPECTRUM: m/e 490 (Pd, M^+), 458 (Pd) 282 (Pd), 251 (Pd)

ANALYSIS: Found: C,41.4%; H,4.2%; N,5.4%

$C_{17}H_{21}Cl\ N_2Pd\ S_3$ requires: C,41.6%; H,4.3%; N,5.7%

4-Thioxoquinolizin-6-yl (N,N-diisopropyldithiocarbamato) palladium (II)

Yellow solid, yield 78%, m.p. 165-8°C, 117-8°C (from benzene, 0.5 benzene solvate) .

I.R. SPECTRUM: ν max 1610, 1555, 1490 (C=N), 1400, 1335, 1285, 1215, 1190, 1155, 1110, 1050, 1030, 790, 740, 695 cm^{-1}

^1H n.m.r. SPECTRUM AT 360 MHz in $CDCl_3$

δ 7.70 [dd, ($^3J_{HH}$= 7.96Hz; $^4J_{HH}$= 1.33Hz), 1H,H-7]; δ 7.57 [t, ($^3J_{HH}$= 7.96Hz),1H,H-8]; δ 7.53-7-46(m,H-1/2/3); δ 7.35 [dd, ($^3J_{HH}$= 8.07Hz; $^4J_{HH}$= 1.33Hz),1H,H-9]; δ 7.33 (s,3H,benzene); δ 5.2-4.3 (m,2H,2 methine protons); δ 1.55 (br.s,12H, isopropyl CH_3).

^{13}C n.m.r. SPECTRUM: ($CDCl_3$) p.p.m. 208.1, 171.9, 165.0, 144.9, 131.2, 130.1, 129.4, 128.2 (benzene), 122.0, 120.9, 117.6, 51.1 and 50.9 (Me_2CH), 19.8 (Me_2CH).

MASS SPECTRUM: m/e 458 (Pd), 442 (Pd, M^+), 266 (Pd), 160

ANALYSIS: Found: C,47.1%; H,4.8%; N,5.6%

$C_{16}H_{20}N_2Pd\ S_3.0.5\ C_6H_6$ requires: C,47.4%; H,4.8%; N,5.8%

4-Selenoxoquinolizin-6-yl(N,N-diisopropyldithiocarbamato)palladium (II)

Yellow solid, yield 77%, m.p. 156-8°C, 127-30°C (from benzene, 0.5 benzene solvate) .

I.R. SPECTRUM: ν max 1615, 1560, 1490 (C=N), 1330, 1195, 1150, 1115, 1040, 795, 755 cm^{-1}.

^1H n.m.r. SPECTRUM AT 360 MHz in $CDCl_3$ δ 7.96 [dd,($^3J_{HH}$= 7.09Hz; $^4J_{HH}$= 1.93Hz),1H,H-7]; δ 7.74 [dd,($^3J_{HH}$= 6.12Hz; $^4J_{HH}$= 2.80Hz), 1H,H-3]; δ 7.58-7.48(m,4 aromatic protons); δ 7.34(s,3H,benzene); δ 5.2-4.4(m,2H,2 methine protons); δ 1.5 (br.s,12H,isopropyl CH_3).

MASS SPECTRUM: m/e 490 (Pd, M^+), 458 (Pd), 442 (Pd), 426 (Pd), 314 (Pd), 272 (Pd), 266 (Pd), 251 (Pd), 208, 160, 117, 101, 43

ANALYSIS: Found C,43.4%; H,4.5%; N,5.2%

$C_{16}H_{20}N_2Pd\ S_2Se.0.5\ C_6H_6$ requires: C,43.2%; H,4.4%; N,5.3%

9-Thioxothioxanthen-1-yl (N,N-diisopropyldithiocarbamato) palladium (II)

Deep purple solid, yield, 72%, m.p. 216-8°C (d) (from toluene).

I.R. SPECTRUM: ν max 1595, 1550, 1480 (C=N), 1420, 1330, 1250, 1220, 1190, 1145, 1100, 1035, 985, 765, 740, 710 cm^{-1}

^1H n.m.r. SPECTRUM: ($CDCl_3$) δ 9.07 [d,($^3J_{HH}$= 8Hz),1H,H-8] ; δ 7.7-7.2 (m,6 aromatic protons); δ 5.2-4.3 (m,2H,2 methine protons); δ 1.56 and 1.52 [2 br.d (overlapping), ($^3J_{HH}$= 7H),12H,isopropyl CH_3].

MASS SPECTRUM: m/e 509 (Pd, M^+), 458 (Pd), 349 (Pd), 282 (Pd), 228

ANALYSIS: Found: C,47.0%; H,4.1%; N,2.6%

$C_{20}H_{21}N\ Pd\ S_4$ requires: C,47.1%; H,4.1%; N,2.7%

2-Phenyl-4-thioxothiochromen-5-yl (N,N-diisopropyldithiocarbamato) palladium (II)

Purple solid, yield, 71%, m.p. 262-4°C (d) (from toluene).

I.R. SPECTRUM: ν max 1545, 1485 (C=N), 1380,1335, 1245, 1195, 1170, 1145, 1035, 760, 750, 715 cm^{-1}

^1H n.m.r. SPECTRUM: ($CDCl_3$) δ 8.08 (s,1H,H-3); δ 7.8-7.3 (m, 8 aromatic protons); δ 5.2-4.2 (m,2H,2 methine protons); δ 1.52 and 1.47 [2 br.d (overlapping), ($^3J_{HH}$= 7Hz), 12H, isopropyl CH_3]

MASS SPECTRUM: m/e 535 (Pd,M^+), 506, 472, 458 (Pd), 442, 359, 282 (Pd), 254, 253, 221, 105

ANALYSIS: Found: C,49.4%; H,4.4%; N,2.6%

$C_{22}H_{23}N\ Pd\ S_4$ requires: C,49.3%; H,4.3%; N,2.6%

[2-(phenylazo)phenyl] (N,N-diisopropyldithiocarbamato) palladium (II)

Dark red needles, yield, 76%, m.p. 188-9°C (d) from ethanol).

I.R. SPECTRUM: ν max 1575, 1490 (C=N), 1335, 1195, 1145, 1040, 765, 710, 685 cm^{-1}.

^1H n.m.r. SPECTRUM: ($CDCl_3$) δ 8.1-7.1 (m, 9 aromatic protons); δ 5.2-4.2 (m,2H,2 methine protons); δ 1.52 and 1.40 [2 br.d (overlapping), ($^3J_{HH}$= 7Hz), 12H,isopropyl CH_3] .

MASS SPECTRUM: m/e 463 (Pd,M^+), 458 (Pd), 426 (Pd), 420 (Pd), 319 (Pd), 287 (Pd), 257, 213, 185, 184, 153, 152

ANALYSIS: Found: C,48.9%; H,5.0%; N,9.0%

$C_{19}H_{23}N_3PdS_2$ requires: C,49.2%; H,5.0%; N,9.1%

[2-(2-pyridyl)phenyl] (N,N-diisopropyldithiocarbamato) palladium (II)

Pale yellow solid, yield 73%, m.p. 233-5°C (d) (from benzene).

I.R. SPECTRUM: ν max 1605, 1580, 1495 (C=N), 1340, 1195, 1150, 1040, 845, 800, 750 cm^{-1}.

^1H n.m.r. SPECTRUM: ($CDCl_3$) δ 8.36 [d,($^3J_{HH}$= 6Hz),1H,6-pyridyl proton]; δ 5.2-4.2 (m,2H,2 methine protons), δ 1.52 [2 br.d (overlapping), ($^3J_{HH}$= 7Hz),12H, isopropyl CH_3]. δ 7.8-7.0 (m, 7H)

MASS SPECTRUM: m/e 458 (Pd), 436 (Pd,M^+), 403 (Pd), 393 (Pd), 340, 312, 260 (Pd), 186, 155, 154

ANALYSIS: Found: C,49.6%; H,5.2%; N,6.3%

$C_{18}H_{22}N_2S_2Pd$ requires: C,49.5%; H,5.0%; N,6.4%

REACTION OF DI-μ-CHLORO BIS (9-THIOXO-10-METHYLACRIDIN-1-YL DIPALLADIUM (II) WITH SODIUM N,N-DIMETHYLDITHIOCARBAMATE

To a stirred suspension of di-μ-chloro-bis (9-thioxo-10-

methylacridin-1-yl) dipalladium (II) (0.20g; 0.275 mmole) in dimethylformamide was added a solution of sodium N,N-dimethyldithiocarbamate (0.10g; 0.55 mmole) in dimethylformamide (10 ml). The red suspension was stirred overnight. The reaction mixture was filtered and the solid residue was washed with water and then dried in vacuo yielding 9-thioxo-10-methylacridin-1-yl (N,N-dimethyldithiocarbamato) palladium (II) as a red solid, (0.21g; 85%), m.p.> 300°C.

I.R. SPECTRUM: ν max 1615, 1580, 1500 (C=N), 1395, 1375, 1315, 1240, 1185, 1145, 970, 780, 740 cm^{-1}

MASS SPECTRUM: m/e 450 (Pd,M^+), 384, 369, 346 (Pd), 330 (Pd), 246, 225

ANALYSIS: Found: C,45.1%; H,3.6%; N,6.2%

$C_{17}H_{16}N_2PdS_3$ requires: C,45.3%; H,3.6%; N,6.2%

REACTION OF DI-μ-CHLORO-BIS (9-THIOXO-10-METHYLACRIDIN-1-YL) DIPALLADIUM (II) WITH SODIUM N,N-DIISOPROPYLDITHIOCARBAMATE

To a stirred suspension of di-μ-chloro-bis (9-thioxo-10-methylacridin-1-yl)dipalladium (II) (0.73g; 1 mmole) in dimethylformamide (200 ml) was added a solution of sodium N,N-diisopropyldithiocarbamate (0.40g; 2 mmole) in dimethylformamide (20 ml). The red suspension was stirred overnight. The solvent was removed under high vacuum and the residue was extracted with dichloromethane (1000 ml). Evaporation of the extract yielded 9-thioxo-10-methylacridin-1-yl (N,N-diisopropyldithiocarbamato)palladium (II) as a red solid, (0.72g; 71%), m.p.> 300°C. Recrystallisation from benzene gave the analytically pure product.

I.R. SPECTRUM: ν max 1615, 1585, 1485 (C=N), 1330, 1250, 1195, 1145, 1035, 975, 740, 720 cm^{-1}

^1H n.m.r. (F.T., d_6-Me_2SO): δ 8.78 [d,($^3J_{HH}$= 7Hz),1H,H-8];

δ 8.3-8.0(m,2 aromatic protons); δ 7.8-7.5 (m,3 aromatic protons); δ 7.3 (m,1 aromatic proton); δ 5.2-4.3 (m,2H,2 methine protons); δ 4.25 (s,3H,NCH_3); δ 1.45 [2 br.d (overlapping), ($^3J_{HH}$= 7Hz), 12H,isopropyl CH_3].

MASS SPECTRUM: m/e 506 (Pd,M^+), 458 (Pd), 349 (Pd), 324 (Pd), 282 (Pd), 250 (Pd)

ANALYSIS: Found: C,49.6%; H,4.7%; N,5.3%

$C_{21}H_{24}N_2Pd\ S_3$ requires: C,49.8%; H,4.7%; N,5.5%

REACTION OF DI-μ-ACETATO-BIS[2-(1,2-BENZISOTHIAZOL-3-YL)PHENYL] DIPALLADIUM (II) WITH TETRAETHYLAMMONIUM N,N-DIMETHYLDITHIOCARBAMATE

To a stirred solution of di-μ-acetato-bis[2-(1,2-benzisothiazol-3-yl)phenyl]dipalladium (II) (0.41g; 0.55 mmole) in chloroform (50 ml) was added a solution of tetraethylammonium N,N-dimethyldithiocarbamate (0.27g; 1.1 mmole) in chloroform (10 ml). The resulting dark yellow solution was stirred overnight. The solvent was removed and the residue was chromatographed on alumina (50g). Eluting with dichloromethane yielded [2-(1,2-benzisothiazol-3-yl)phenyl](N,N-dimethyldithiocarbamato)palladium (II) as a yellow-orange solid, (0.41g; 81%), m.p. 216-8°C (d). Recrystallisation from benzene gave the analytically pure product, m.p. unchanged.

I.R. SPECTRUM: ν max 1595, 1570, 1530, 1250, 1160, 1140, 970, 775, 725, 705 cm^{-1}

^1H n.m.r. SPECTRUM ($CDCl_3$): δ 8.7 (m,1H,proton ortho to palladium); δ 8.2-7.2 (m,7 aromatic protons); δ 3.42 and 3.39 (2s,6H,$N(CH_3)_2$)

MASS SPECTRUM: m/e 452, 436 (Pd,M^+), 420, 346 (Pd), 286, 242, 211, 210

ANALYSIS: Found: C,43.7%; H,3.2%; N,6.3%

$C_{16}H_{14}N_2Pd\ S_3$ requires: C,44.0%; H,3.2%; N,6.4%

[2-(1,2-benzisothiazol-3-yl) phenyl] (N,N-diisopropyldithiocarbamato) palladium (II) was prepared from the corresponding acetate-bridged dimeric complex and tetraethylammonium N,N-diisopropyldithiocarbamate under conditions identical with those of the preceding experiment to yield a yellow-orange solid, (76%), m.p. 210-11°C (d) (from benzene).

I.R. SPECTRUM: ν max 1595, 1335, 1145, 1035, 780, 730 cm^{-1}

^1H n.m.r. SPECTRUM: ($CDCl_3$) δ 8.65 (m,1H,proton ortho to palladium); δ 8.2-7.1 (m,7 aromatic protons); δ 5.2-4.2 (m,2H,2 methine protons); δ 1.56 and 1.43 [2 br.d (overlapping), ($^3J_{HH}$ = 7Hz),12H,isopropyl CH_3].

MASS SPECTRUM: m/e 492 (Pd,M^+), 458 (Pd), 452, 426 (Pd), 420, 286, 282 (Pd), 242, 211, 210

ANALYSIS:	Found:	C,49.0%;	H,4.6%;	N,5.4%
$C_{20}H_{22}N_2PdS_3$	requires:	C,48.7%;	H,4.5%;	N,5.7%

[2-(N-phenylformimidoyl)phenyl] (N,N-dimethyldithiocarbamato) palladium (II) was prepared from the corresponding acetate-bridged dimeric complex and tetraethylammonium N,N-dimethyldithiocarbamate in 80% yield, m.p. 215-7°C (d), (lit. m.p.[44] 222-3°C (d), by the method of Davis.[44]

REACTION OF DI-μ-CHLORO-BIS (1-THIOXO-2-METHYLISOQUINOLIN-8-YL) DIPALLADIUM (II) WITH TETRAETHYLAMMONIUM O,O-DIETHYLDITHIOPHOSPHATE

To a stirred suspension of di-μ-chloro-bis (1-thioxo-2-methylisoquinolin-8-yl)dipalladium (II) (0.61g; 0.97 mmole) in dimethylformamide (50 ml) was added a solution of tetraethylammonium O,O-diethyldithiophosphate (0.61g; 1.94 mmole) in dimethylformamide (10 ml). The resulting yellow solution was stirred for 3 hours. The solvent was removed under high vacuum and the residue was chromatographed on alumina (50g). Eluting with dichloromethane yielded 1-thioxo-2-methylisoquinolin-8-yl (O,O-diethyldithiophosphato)

palladium (II) as a yellow solid, (0.75g; 83%) m.p. 205-8°C (d). Recrystallisation from benzene gave the analytically pure product, m.p. unchanged.

I.R. SPECTRUM: ν max 1625, 1585, 1530, 1340, 1200, 1020, 975, 950, 810, 775, 730 cm^{-1}

^1H n.m.r. SPECTRUM AT 360MHz in $CDCl_3$: δ 7.64 [ddd, ($^3J_{HH}$=7.41Hz; $^5J_{PH}$= 1.88Hz; $^4J_{HH}$= 1.10Hz), 1H, H-7] ; δ 7.43 [t, ($^3J_{HH}$= 7.63Hz), 1H, H-6] ; δ 7.35 [d, ($^3J_{HH}$= 6.85Hz), 1H, H-3] ; δ 7.25 [dd, ($^3J_{HH}$= 7.85Hz; $^4J_{HH}$= 1.10Hz), 1H, H-5] ; δ 6.97 [d, ($^3J_{HH}$= 6.85Hz), 1,H, H-4] ; δ 4.23 (m, 4H, ethoxy CH_2); δ 4.04 (s, 3H, NCH_3), δ 1.38 [t, ($^3J_{HH}$= 7.08Hz), 6H, ethoxy CH_3]

^{31}P n.m.r.: ($CDCl_3$) 104.6 p.p.m. (s)

MASS SPECTRUM: m/e 476 (Pd), 465 (Pd, M^+), 280 (Pd), 206, 175

ANALYSIS: Found: C,36.0%; H,3.8%; N,3.0%

$C_{14}H_{18}NO_2P\,Pd\,S_3$ requires: C,36.1%; H,3.9%; N,3.0%

REACTION OF DI-μ-CHLORO-BIS (1-THIOXO-2-METHYLISOQUINOLIN-8-YL) DIPALLADIUM (II) WITH BIS (p-PERTHIOTOLUATO) ZINC (II)

To a stirred suspension of di-μ-chloro-bis (1-thioxo-2-methylisoquinolin-8-yl) dipalladium (II) (0.315g; 0.5 mmole) in dimethylformamide (50 ml) was added bis (p-perthiotoluato) zinc (II) (0.23g; 0.5 mmole). The resulting deep red solution was stirred for 3 hours. The solvent was removed under high vacuum and the residue was chromatographed on alumina (50g). Eluting with dichloromethane yielded 1-thioxo-2-methylisoquinolin-8-yl (p-perthiotoluato) palladium (II) as a purple solid, (0.38g; 79%), m.p. 211-2°C (d). Recrystallisation from dichloromethane - petrol gave the analytically pure product, m.p. unchanged.

I.R. SPECTRUM: ν max 1620, 1600, 1575, 1530, 1335, 1310, 1260, 1190, 1025, 815, 800, 765 cm^{-1}

MASS SPECTRUM: m/e 479 (M^+,Pd), 472 (Pd), 447 (Pd), 440 (Pd), 280 (Pd), 206, 191, 175, 135, 91

ANALYSIS: Found: C,45.3%; H,3.1%; N,2.9%

$C_{18}H_{15}N\ Pd\ S_4$ requires: C,45.1%; H,3.1%; N,2.9%

(4) REACTIONS OF CYCLOPALLADATED COMPLEXES WITH THIOCYANOGEN

REACTION OF [2-(N-PHENYLFORMIMIDOYL)PHENYL] (DIMETHYLDITHIOCARBAMATO) PALLADIUM (II) WITH THIOCYANOGEN

This reaction was carried out under conditions similar to those reported by Davis.[44] Reaction of the title complex with an equimolar amount of thiocyanogen in chloroform* yielded N-(2-thiocyanatobenzylidene) aniline as a yellow oil, (86%) and di-μ-thiocyanato-bis (dimethyldithiocarbamato) palladium (II) as a yellow solid, (85%), m.p. 262-4°C (d). The identity of these two products was checked by infrared and ^1H n.m.r. spectroscopy.

* In this reaction and in subsequent reactions the chloroform was passed through an alumina column before use to render it free of ethanol.

REACTION OF [2-(1,2-BENZISOTHIAZOL-3-YL) PHENYL] (N,N-DIMETHYL-DITHIOCARBAMATO) PALLADIUM (II) WITH THIOCYANOGEN

A solution of thiocyanogen (68mg; 0.58 mmole) in

chloroform was added to a stirred solution of [2-(1,2-benzisothiazol-3-yl] (N,N-dimethyldithiocarbamato) palladium (II) (0.25g; 0.58 mmole) in chloroform (30 ml). A deep red solution formed immediately and then became lighter in colour with the simultaneous precipitation of a yellow solid. The reaction mixture was stirred for 1 hour. Filtration of the mixture yielded di-μ-thiocyanato-bis (dimethyldithiocarbamato) palladium (II) as a yellow solid (0.18g; 83%), m.p. 260-3°C (d), [lit.[44] 262-4°C (d)]. The filtrate was evaporated and the residue was chromatographed on alumina (10g). Eluting with ether yielded 3-(2-thiocyanatophenyl)-1,2-benzisothiazole as a white solid, (0.14g; 87%), m.p. 100-1°C.

I.R. SPECTRUM: ν max 2150, 1590, 1350, 960, 770, 755, 730, 690, 650 cm^{-1}

^1H n.m.r. ($CDCl_3$): δ 8.1-7.4 (m)

MASS SPECTRUM: m/e 268 (M^+), 242 (M^+ - CN)

EXACT MASS MEASUREMENT:

	Found:	268.012639
$C_{14}H_8N_2S_2$	requires:	268.012890
		error < 1 p.p.m.
	Found:	242.008716
$C_{13}H_8NS_2$	requires:	242.009816
		error < 5 p.p.m.

REACTION OF 1-THIOXO-2-METHYLISOQUINOLIN-8-YL (N,N-DIISOPROPYL-DITHIOCARBAMATO) PALLADIUM (II) WITH THIOCYANOGEN

A solution of thiocyanogen (0.13g; 1.1 mmole) in chloroform (10 ml) was added to a stirred solution of 1-thioxo-2-methylisoquinolin-8-yl (N,N-diisopropyldithiocarbamato) palladium (II) (0.50g; 1.1 mmole) in chloroform (100 ml). A deep red

solution resulted immediately and then became lighter in colour with the simultaneous precipitation of a yellow solid. The reaction mixture was stirred for 2 hours and the yellow solid was filtered off (0.07g), decomp. 165°C. The elemental analysis of this compound was reasonably close to that required for di-μ-thiocyanato-bis (1-thioxo-2-methylisoquinolin-8-yl) dipalladium (II) and the I.R. spectrum was in agreement with this structure (SCN absorptions at 2140 and 2100 cm^{-1}).

ANALYSIS: Found: C,41.3%; H,2.8%; N,8.6%

$C_{22}H_{16}N_4Pd_2S_4$ requires: C,39.0%; H,2.4%; N,8.3%

I.R. SPECTRUM: ν max 2140, 2100, 1620, 1590, 1530, 1340, 1325, 1200, 1145, 815 cm^{-1}

The filtered reaction mixture was evaporated and the residue was chromatographed on silica (50g). Eluting with dichloromethane yielded bis (N,N-diisopropyldithiocarbamato) palladium (II), (0.085g), m.p.> 300°C. Continued chromatography, eluting with methanol containing a trace of hydrochloric acid yielded an unidentifiable yellow solid, (0.16g), decomp.250°C. Its I.R. spectrum contained no C≡N absorption and its mass spectrum showed peaks at m/e 458 and 282 (bis dithiocarbamate complex) and m/e 191 (isoquinoline-1,8-disulphide).

REACTION OF 1-THIOXO-2-METHYLISOQUINOLIN-8-YL (O,O-DIETHYLDITHIOPHOSPHATO) PALLADIUM (II) WITH THIOCYANOGEN

A solution of thiocyanogen (0.10g; 0.86 mmole) in chloroform (10 ml) was added to a stirred solution of 1-thioxo-2-methylisoquinolin-8-yl (O,O-diethyldithiophosphato) palladium (II) (0.40g; 0.86 mmole) in chloroform (10 ml). A deep red solution resulted immediately and then became lighter in colour with the simultaneous

precipitation of a yellow solid. The reaction mixture was stirred for 2 hours and the yellow solid was filtered off (0.30g), decomp. 150°C. The elemental analysis of this compound was reasonably close to that required for di-μ-thiocyanato-bis (1-thioxo-2-methyl-isoquinolin-8-yl) dipalladium (II) and the I.R. spectrum was identical with that of the analogous compound from the preceding experiment.

ANALYSIS: Found: C,38.4%; H,2.5%; N,8.1%

$C_{22}H_{16}N_4Pd_2S_4$ requires: C,39.0%; H,2.4%; N,8.3%

The filtrate was evaporated and the residue was chromatographed on alumina (20g). Eluting with light petroleum and then with ether - light petroleum (1:1) yielded bis (O,O-diethyldithiophosphato) palladium (II) (0.032g), m.p. 116-9°C, 121-2°C (from light petroleum).

I.R. SPECTRUM: ν max 1155, 1100, 1050, 1005, 970, 810 cm^{-1}

^1H n.m.r. SPECTRUM: $CDCl_3$): δ 4.23 (m,8H,ethoxy CH_2); δ 1.39 [t, ($^3J_{HH}$=7Hz), 12H,ethoxy CH_3]

MASS SPECTRUM: m/e 476 (Pd,M^+), 291 (Pd), 263 (Pd), 235 (Pd)

ANALYSIS: Found: C,20.1%; H.4.2%

$C_8H_{20}O_4P_2Pd\,S_4$ requires: C,20.1%; H,4.2%

No other products were isolated by column chromatography.

REACTION OF 9-THIOXO-10-METHYLACRIDIN-1-YL (N,N-DIISOPROPYLDITHIO-CARBAMATO) PALLADIUM (II) WITH THIOCYANOGEN

A solution of thiocyanogen (10mg; 0.085 mmole) in chloroform (10 ml) was added to a stirred solution of 9-thioxo-10-methyl-acridin-1-yl (N,N-diisopropyldithiocarbamato) palladium (II) (40 mg; 0.080 mmole) in chloroform (40 ml). A deep red solution resulted immediately and then became lighter in colour with the simultaneous precipitation of a red solid. The reaction mixture was stirred for 2 hours and the red solid was filtered off, (25 mg),

m.p. > 300°C. The elemental analysis of this compound was near that required for di-μ-thiocyanato-bis (9-thioxo-10-methylacridin-1-yl) dipalladium (II) and the I.R. spectrum was in agreement with this structure (SCN absorptions at 2140 and 2100 cm^{-1}).

ANALYSIS: Found: C,48.8%; H,2.8%; N,7.4%

$C_{30}H_{20}N_4Pd_2S_4$ requires: C,46.4%; H,2.6%; N,7.2%

I.R. SPECTRUM: ν max 2140, 2100, 1615, 1570, 1320, 1245, 1180, 1050, 750 cm^{-1}

The filtrate was evaporated yielding a red sticky solid (20 mg). The mass spectrum of this substance exhibited peaks at m/e 234 and 202 which were thought to correspond to N,N-diisopropylthiocarbamoylsulphenyl thiocyanate and N,N-diisopropylthiocarbamoyl thiocyanate respectively. Bis (N,N-diisopropyldithiocarbamato) palladium (II) (m/e 458, 282) was also observed in the mass spectrometer.

(5) REACTIONS OF THIOCYANATO COMPOUNDS WITH PERCHLORIC ACID

REACTION OF N-(2-THIOCYANATOBENZYLIDENE)ANILINE WITH PERCHLORIC ACID

To a stirred solution of N-(2-thiocyanatobenzylidene) aniline (0.12g) in glacial acetic acid (5 ml) were added a few drops of 70% perchloric acid. A pale yellow precipitate formed

immediately and the reaction mixture was stirred for 1 hour. Ether (5 ml) was added and the mixture was stirred for a further 30 minutes. Filtration of the mixture yielded 2-phenyl-1,2- benzisothiazolium perchlorate as a pale yellow solid (0.062g; 40%), m.p. 205-8°C (d). Recrystallisation from glacial acetic acid containing a trace of perchloric acid gave the analytically pure product as cream coloured flakes, m.p. 212°C (d).

I.R. SPECTRUM: ν max 1605, 1510, 1360, 1200, 1170, 1100, 915, 770, 755, 720, 700, 685 cm^{-1}

^1H n.m.r. SPECTRUM: (CF_3CO_2D)

δ 9.74 (s,1H,H-3); δ 8.55 [d,($^3J_{HH}$= 7Hz),1H,H-4]; δ 8.31[d, ($^3J_{HH}$= 7Hz),1H,H-7]; δ 8.12[td,($^3J_{HH}$= 7Hz, $^4J_{HH}$= 1Hz),1H,H-6]; δ 7.99 (m,1H,H-5); δ 7.9-7.7 (m,5H, phenyl ring protons).

ANALYSIS: Found: C,49.9%; H,3.1%; N,4.4%

$C_{13}H_{10}Cl\,N\,O_4S$ requires: C,50.1%; H,3.2%; N,4.5%

REACTION OF 3-(2-THIOCYANATOPHENYL)-1,2-BENZISOTHIAZOLE WITH PERCHLORIC ACID

To a stirred solution of 3-(2-thiocyanatophenyl)-1,2-benzisothiazole (40 mg) in glacial acetic acid (3 ml) were added a few drops of 70% perchloric acid. After stirring for 24 hours, no obvious reaction was observed. Addition of ether to the mixture did not induce any precipitation. The ether was removed and the remaining acetic acid solution was warmed gently to 60°C. After cooling, ether was again added but did not induce precipitation. Evaporation of the reaction mixture under high vacuum to dryness yielded an intractable tar.

(6) REACTIONS OF 1-THIOXO-2-METHYLISOQUINOLIN-8-YL (N,N-DIISOPROPYLDITHIOCARBAMATO)PALLADIUM (II) WITH VARIOUS POTENTIAL SULPHUR-TRANSFER REAGENTS

(a) With dibenzoyl disulphide

To a stirred solution of the title complex (0.42g; 0.92 mmole) in chloroform (25 ml) was added a solution of dibenzoyl disulphide (0.26g; 0.95 mmole) in chloroform (50 ml). The reaction mixture was heated under reflux for 1 hour. Examination of the reaction mixture by t.l.c. showed that only the starting materials were present. The solvent was removed and the residue was taken up in 1,1,2-trichloroethane (20 ml). The reaction mixture was then heated under reflux for 5 hours, during which time a colour change from yellow to orange and then to red was observed. The solvent was removed and the residue was chromatographed on alumina (50g). Eluting with light petroleum yielded dibenzoyl disulphide as a white solid, (15 mg), m.p. 126-8°C. Eluting with ether yielded a sticky orange-red solid (0.10g), the mass spectrum of which showed dibenzoyl disulphide and elemental sulphur. Eluting with dichloromethane yielded the title complex as an orange-red solid, (0.35g; 83% recovery), m.p. 218-222°C (identified by I.R. and ^{1}H n.m.r.).

(b) With N,N'dithiobismorpholine

The title complex (0.46g; 1 mmole) and N,N'-dithiobismorpholine (0.24g 1 mmole) were heated together under reflux in 50 ml toluene with stirring for 6 hours. The reaction mixture was cooled, whereupon the title complex precipitated from the mixture and was isolated by filtration (0.30g), m.p. 256-60°C (d), (identified by ^{1}H n.m.r.). The filtrate was evaporated and the

residue was chromatographed on alumina (30g). Eluting with ether yielded (N,N'-dithiobismorpholine as a pale yellow solid (0.22g), m.p. 120-3°C. Eluting with dichloromethane yielded a further 0.13g of the title complex as a yellow solid, m.p. 248-54°C (d), (identified by ^{1}H n.m.r.). Recovered yield of title complex 96%.

(c) With N,N'-dithiobisphthalimide

The title complex (0.33g; 0.73 mmole) and N,N'-dithiobisphthalimide (0.26g; 0.73 mmole) were heated together under reflux in toluene (100 ml), with stirring for 6 hours. Examination of the reaction mixture by t.l.c. after this time showed that the disulphide had been consumed. The reaction mixture was evaporated and the residue was chromatographed on alumina (50g). Eluting with dichloromethane yielded the title complex as a yellow solid, (0.28g; 85% recovery), m.p. 232-7°C (d), (identified by I.R.). Continued elution with more polar solvents yielded only polymeric material which could not be characterised.

(d) With bis (p-perthiotoluato) zinc (II)

The title complex (0.46g; 1 mmole) and bis (p-perthiotoluato) zinc (II) (0.46g; 1 mmole) were heated together under reflux in dimethylformamide (50 ml), with stirring for 3 hours. The reaction mixture was cooled, and a brown precipitate which had formed during the reaction was filtered off, (0.11g), m.p.> 300°C. This substance liberated hydrogen sulphide when treated with hydrochloric acid and was assumed to be zinc sulphide. The filtered reaction mixture was evaporated to dryness yielding a dark red gum (0.80g). Examination of this substance by t.l.c. showed that it was a multi-component mixture which was not likely to be separable by column

chromatography. The substance could not be purified by trituration with organic solvents.

(e) The thermolysis of 1-thioxo-2-methylisoquinolin-8-yl (p-perthiotoluato)palladium (II) in 1,1,2-trichloroethane

The title complex (0.15g) was heated under reflux in 1,1,2-trichloroethane with stirring for 6 hours. After this time, only the title complex was present as shown by t.l.c. Removal of the solvent yielded the starting material, m.p. 204-6°C (d).

(f) The thermolysis of 1-thioxo-2-methylisoquinolin-8-yl (p-perthiotoluato)palladium (II) in 1,2,4-trichlorobenzene

The title complex (0.10g) was heated at 190° in 1,2,4-trichlorobenzene (10 ml) with stirring for 3 hours, during which time a thin dark film appeared on the walls of the reaction vessel. Evaporation of the decanted reaction mixture yielded a gum which, when triturated with light petroleum yielded the title complex, (0.08g; 80% recovery), m.p. 198-201°C (d).

(g) With n-butoxycarbonylsulphenyl chloride

To a stirred solution of the title complex (0.23g; 0.5 mmole) in ethanol-free chloroform (20 ml) was added a solution of n-butoxycarbonylsulphenyl chloride (85 mg; 0.5 mmole) in 2 ml of the same solvent. A yellow precipitate resulted immediately and the reaction mixture was stirred for 3 hours. After this time the reaction mixture was heated under reflux for 30 minutes. The mixture was then cooled and filtered yielding di-μ-chloro-bis (1-thioxo-2-methylisoquinolin-8-yl)dipalladium (II) as a yellow solid, (0.13g; 82%), m.p. > 300°C. The I.R. spectrum of this compound was identical with that of an authentic sample. A fairly satisfactory elemental analysis was also obtained.

Analysis: Found: C,38.8%; H,2.6%; N,4.3%

$C_{20}H_{16}Cl_2N_2Pd_2S_2$ requires: C,38.0%; H,2.5%; N,4.4%

The filtered reaction mixture was evaporated and the residue was chromatographed on alumina (25g). Eluting with ether yielded a sticky yellow solid (0.09g) which could not be fully characterised. Its I.R. spectrum showed absorptions characteristic of bis (N,N-diisopropyldithiocarbamato)palladium (II), (1490, 1335, 1190, 1140 and 1035 cm^{-1}) and its mass spectrum showed peaks at m/e 458 and 282 corresponding to the bis dithiocarbamate complex. The other components of this substance, which was assumed to be a mixture were not identified. No other products were obtained by column chromatography.

(7) REACTIONS OF DITHIOCARBAMATE COMPLEXES WITH MORPHOLINE-N-SULPHENYL CHLORIDE

Unless stated otherwise, dithiocarbamate complexes were converted to the corresponding cationic ring systems by the general method which is described below for the conversion of 7-chloro-1-methyl-4-thioxoquinolin-5-yl (N,N-diisopropyldithiocarbamato) palladium (II) to 7-chloro-5-methyl[1,2] dithiolo[3,4,5-de]-quinolinium chloride.

REACTION OF 7-CHLORO-1-METHYL-4-THIOXOQUINOLIN-5-YL (N,N-DIISOPROPYLDITHIOCARBAMATO)PALLADIUM (II) WITH MORPHOLINE-N-SULPHENYL CHLORIDE

A solution of 7-chloro-1-methyl-4-thioxoquinolin-5-yl (N,N-diisopropyldithiocarbamato)palladium (II) (0.49g; 1 mmole) in chloroform* (25 ml) was added dropwise over a period of 15 minutes to a stirred solution of morpholine-N-sulphenyl chloride (0.31g; 2 mmole) in chloroform (10 ml). A yellow precipitate formed immediately and the reaction mixture was stirred for 1 hour. The reaction mixture was then filtered and the solid product was suspended in dichloromethane (20 ml), pyridine (1 ml) was added, and the mixture was stirred vigorously for 15 minutes. The mixture was filtered and the filter cake was washed with dichloromethane and then dried <u>in vacuo</u> yielding 7-chloro-5-methyl [1,2]dithiolo[3,4,5-<u>de</u>] quinolinium chloride as a yellow solid, (0.21g; 76%), m.p. 289-92°C (d). The chloride salt was converted to a perchlorate by dissolving it in 20 ml hot methanol and treating with a few drops of 70% perchloric acid. The perchlorate salt precipitated as a yellow solid, (0.24g; 71% overall yield), m.p. 295-8°C (d).

<u>I.R. SPECTRUM</u>: ν max 1605, 1580, 1510, 1460, 1075, 875, 840, 820 cm^{-1}

<u>^{1}H n.m.r. SPECTRUM</u>: (d_6-Me_2SO): δ 8.71 [d, ($^3J_{HH}$=7Hz), 1H, H-4]; δ 8.10 [d, ($^4J_{HH}$=1.5Hz), 1H, H-3]; δ 7.86 [d, ($^4J_{HH}$=1.5Hz), 1H]; δ 7.82 [d, ($^3J_{HH}$=7Hz), 1H]; δ 4.09 (s, 3H, NCH_3)

<u>U.V. SPECTRUM</u>: (EtOH-trace $Me_2SO/HClO_4$): λ max (nm): 268, 297, 440

ε=21,953, 8,031, 14,457

<u>MASS SPECTRUM (CHLORIDE SALT)</u> m/e 227/225 (M^+-MeCl)

<u>ANALYSIS</u>:	Found:	C,35.1%;	H,2.1%;	N,4.2%
$C_{10}H_7Cl_2NO_4S_2$	requires:	C,35.3%;	H,2.1%;	N,4.1%

* In this reaction and in subsequent reactions the chloroform was passed through an alumina column before use to render it free of

ethanol.

The following cationic ring systems were prepared from the appropriate dithiocarbamate complexes by reaction with morpholine-N-sulphenyl chloride under conditions similar to those of the preceding experiment.

[1,2,4]dithiazolo[3,4,5-de]quinolizinylium chloride

Red solid, yield, 62%, decomp. 250-70°C. Converted to perchlorate (bright red crystals), decomp.300-5°C, overall yield from dithiocarbamate complex 44%.

I.R. SPECTRUM: ν max 1630, 1600, 1570, 1315, 1235, 1225, 1140, 1100, 825, 785, 760 cm^{-1}

^1H n.m.r. SPECTRUM AT 360 MHz in d_6-Me_2SO : δ 7.88 [t, $^3J_{HH}$ = 8.18Hz), 2H, H-4/7]; δ 7.76 [dd,($^3J_{HH}$ = 8.67Hz), ($^4J_{HH}$ = 1.10Hz), 2H, H-5/6]; δ 7.70 [dd($^3J_{HH}$ = 7.86Hz), ($^4J_{HH}$ = 1.10Hz), 2H, H-3/8]

U.V. SPECTRUM: (EtOH-trace $HClO_4$) λ max (nm) : 227, 259, 370, 510

ϵ : 17,876, 8,730, 10,185, 1,663

MASS SPECTRUM (CHLORIDE SALT): m/e 192 (M^+), 161, 160, 117

ANALYSIS: Found: C,37.2%; H,2.1%; N,4.7%

$C_9H_6Cl\,N\,O_4S_2$ requires: C,37.1%; H,2.1%; N,4.8%

[1,2,4]thiaselenazolo[3,4,5-de]quinolizinylium chloride

Red solid, yield, 47%, decomp. 275-80°C. Converted to perchlorate (dark red crystals), m.p. 233-5°C (d), overall yield from dithiocarbamate complex 38%.

I.R. SPECTRUM: ν max 1630, 1595, 1565, 1310, 1220, 1080, 825, 780, 755 cm^{-1}

^1H n.m.r. SPECTRUM AT 360 MHz IN d_6-Me_2SO : δ 7.8 - 7.7 (m, 4 aromatic protons); 7.66 [dd,($^3J_{HH}$ = 8.38Hz, $^4J_{HH}$ = 1.29Hz), 1H]; δ 7.54 [dd,($^3J_{HH}$ = 7.74Hz, $^4J_{HH}$ = 1.50Hz), 1H]

U.V. SPECTRUM: (EtOH-trace $HClO_4$) λ max (nm) : 233, 264, 380, 520

ε : 15,831, 7.916, 10,153, 1,549

MASS SPECTRUM (CHLORIDE SALT) : m/e 240 (M^+), 160

ANALYSIS: Found: C,32.0%; H,1.8%; N,4.1%

$C_9H_6Cl\ N\ O_4S\ Se$ requires: C,31.9%; H,1.8%; N,4.1%

[1,2]dithiolo[3,4,5-kl]thioxanthylium chloride

Purple solid, yield, 61%, decomp.180°C. Converted to perchlorate (purple needles), m.p. 220-2°C (d) (from methanol), overall yield from dithiocarbamate complex 53%.

I.R. SPECTRUM: ν max 1590, 1565, 1335, 1320, 1255, 1195, 1080, 775, 715 cm^{-1}

^1H n.m.r. SPECTRUM AT 360 MHz in d_6-Me_2CO δ 8.78 [d,($^3J_{HH}$= 8.46Hz), 1H, H-10]; δ 8.56 [d,($^3J_{HH}$= 8.82 Hz), 1H]; δ 8.4-8.25 (m, 3 aromatic protons); δ 8.15 [br.t,($^3J_{HH}$= 7.8Hz), 1H, H-8]; δ 7.92 [td,($^3J_{HH}$= 7.72Hz, $^4J_{HH}$= 1.28Hz), 1H, H-9]

U.V. SPECTRUM: (EtOH-trace $HClO_4$) λ max (nm): 238, 254, 288, 314, 330, 375, 570

ε : 9,523, 12,874, 7,407, 10,052, 7,407, 2,469, 8,112

MASS SPECTRUM (CHLORIDE SALT): m/e 259 (M^+), 129.5 (M^{2+})

ANALYSIS: Found: C,43.7%; H,2.0%

$C_{13}H_7Cl\ O_4S_3$ requires: C,43.5%; H,2.0%

4-phenyl[1,2]dithiolo[3,4,5-de]thiochromylium chloride

Purple-red solid, yield, 66%, m.p. 263-4°C (d). Converted to perchlorate (purple-red crystals), m.p. 182-4°C (d) (from methanol), overall yield from dithiocarbamate complex 50%.

I.R. SPECTRUM: ν max 1570, 1550, 1510, 1335, 1245, 1200, 1095, 770, 745 cm^{-1}

^{1}H n.m.r. SPECTRUM at 360MHz in CF_3CO_2H - $CDCl_3$ δ 8.25 (s, 1H, H-3); δ 8.13-8.03 (m, H-6/7/8); δ 7.88 [dd, $^3J_{HH}$ = 8.39Hz, $^4J_{HH}$ = 1.22Hz), 2H, ortho phenyl protons] ; δ 7.79 [tt, ($^3J_{HH}$ = 7.63Hz, $^4J_{HH}$ = 1.22Hz), 1H, para phenyl proton] ; δ 7.68 [t, ($^3J_{HH}$ = 8.24Hz), 2H, meta phenyl protons]

U.V. SPECTRUM: (EtOH-trace $HClO_4$) λ max (nm) : 250, 289, 348, 532

ε : 13,227, 11,520, 17,280, 17,280

MASS SPECTRUM (CHLORIDE SALT): m/e 285 (M^+), 253, 142.5 (M^{2+})

ANALYSIS: Found: C,47.0%; H,2.4%

$C_{15}H_9Cl\ O_4S_3$ requires: C,46.8%; H,2.3%

[1,2]benzothiazolo[2,3-a]pyridinium chloride

Cream coloured solid, yield, 84%, m.p. 220-3°C. Converted to perchlorate (cream coloured solid), m.p. 168-9°C (lit. m.p.[44] 168-9°C). The identity of this compound was checked by comparison of its infrared and ^{1}H n.m.r. spectra with those of the specimen synthesised by Davis.[44]

REACTION OF 9-THIOXO-10-METHYLACRIDIN-1-YL (N,N-DIISOPROPYLDITHIOCARBAMATO) PALLADIUM (II) WITH MORPHOLINE-N-SULPHENYL CHLORIDE

A solution of 9-thioxo-10-methylacridin-1-yl (N,N-diisopropyldithiocarbamato)palladium (II) (0.30g; 0.59 mmole) in chloroform (350 ml) was added dropwise over a period of 15 minutes to a stirred solution of morpholine-N-sulphenyl chloride (0.18g; 1.18 mmole) in chloroform (10 ml). The reaction mixture was stirred for 2 hours, the solvent was removed, and the residue was washed with ether (50 ml). The ether-insoluble solid was then suspended in dichloromethane (20 ml), pyridine (1 ml) was added, and the mixture was stirred vigorously for 15 minutes.

The mixture was filtered and the filter cake was washed with

dichloromethane and then dried <u>in vacuo</u> yielding 6-methyl [1,2]-dithiolo [3,4,5-<u>kl</u>] acridinium chloride as a purple-red solid (0.14g; 81%), m.p. 250-3°C (d). The chloride salt was converted into a perchlorate by dissolving it in methanol (10 ml) and treating with a few drops of 70% perchloric acid. The perchlorate salt precipitated as a purple-red solid, (0.15g; 71% overall yield), m.p. 259-263°(d). Recrystallisation from glacial acetic acid gave the analytically pure product, m.p. 266-8°C (d).

<u>I.R. SPECTRUM</u>: ν max 1610, 1590, 1320, 1260, 1090, 770, 760 cm^{-1}

<u>^{1}H n.m.r. SPECTRUM AT 360MHz in d_6-Me_2SO</u> δ 8.47 [d,($^3J_{HH}$= 8.25Hz), 1H, H-10]; δ 8.44 [d,($^3J_{HH}$= 9.07Hz), 1H, H-7]; δ 8.34 [t,($^3J_{HH}$= 8.25Hz), 1H, H-4]; δ 8.31 [td,($^3J_{HH}$= 9.07Hz, $^4J_{HH}$= 1.48Hz), 1H, H-8]; δ 8.17 [d,($^3J_{HH}$= 7.92Hz), 1H, H-5]; δ 8.07 [d,($^3J_{HH}$= 8.58Hz), 1H, H-3]; δ 7.82 [t,($^3J_{HH}$= 7.50Hz); 1H,H-9]; δ 4.36 (s,3H,NCH_3).

<u>U.V. SPECTRUM</u> : (EtOH-trace $Me_2SO/HClO_4$) λ max (nm) : 245, 257, 279, 305, 240, 520, 548

ε : 23,404, 14,463, 17,881, 24,981, 2,892, 9,729, 12,622

<u>MASS SPECTRUM (CHLORIDE SALT)</u> : m/e 241 (M^+-MeCl), 120.5 (M^{2+}-MeCl), 52/50 ($MeCl^+$).

<u>ANALYSIS</u>: Found: C,47.1%; H,2.8%; N,3.8%

$C_{14}H_{10}Cl\ N\ O_4S_2$ requires: C,47.3%; H,2.8%; N,3.9%

<u>REACTION OF [2-(PHENYLAZO)PHENYL] (N,N-DIISOPROPYLDITHIOCARBAMATO) PALLADIUM (II) WITH MORPHOLINE-N-SULPHENYL CHLORIDE</u>

A solution of [2-(phenylazo)phenyl] (N,N-diisopropyldithiocarbamato)palladium (II) (0.46g; 1 mmole) in chloroform (15 ml) was added dropwise over a period of 15 minutes to a stirred solution of morpholine-N-sulphenyl chloride (0.31g; 2 mmole) in chloroform (10 ml). A deep orange solution resulted immediately. The reaction

mixture was stirred for 2 hours, the solvent was removed, and the residue was extracted with ether (50 ml). The ether extract was discarded. The ether-insoluble residue was then suspended in dichloromethane (20 ml), pyridine (1 ml) was added, and the mixture was stirred vigorously for 15 minutes. Ether (20 ml)was added to the mixture and the solid product was filtered off, washed with ether, and dried in vacuo yielding 2-phenylbenzo-1,2,3-thiadiazolium chloride as a yellow solid, (0.22g; 89%), m.p. 172-82°C (d), [lit. m.p.[87] 227-8°C]. The chloride was converted to a perchlorate by dissolving it in methanol (5 ml) and treating with a few drops of 70% perchloric acid. The perchlorate precipitated as a yellow solid, (0.17g; 54% overall yield), m.p. 211-3°C (d). Recrystallisation from methanol gave the analytically pure product as bright yellow needles, m.p. 213-5°C (d), lit. m.p.[87] 214-6°C (d).

I.R. SPECTRUM: ν max 1600, 1545, 1315, 1110, 770, 730, 710, 680 cm^{-1}

^1H n.m.r. SPECTRUM: (CF_3CO_2H): δ 8.87 [d,($^3J_{HH}$= 8Hz), 1H]; δ 8.61 [d,($^3J_{HH}$= 8Hz), 1H]; δ 8.3-8.0 (m, 4 aromatic protons); δ 7.9-77 (m, 3 aromatic protons)

ANALYSIS: Found: C,46.2%; H,2.9%; N,8.9%

$C_{12}H_9ClN_2O_4S$ requires: C,46.1%; H,2.9%; N,9.0%

REACTION OF 1-THIOXO-2-METHYLISOQUINOLIN-8-YL (N,N-DIISOPROPYLDITHIOCARBAMATO)PALLADIUM (II) WITH 1 MOLAR EQUIVALENT OF MORPHOLINE-N-SULPHENYL CHLORIDE

A solution of morpholine-N-sulphenyl chloride (0.15g; 1 mmole) in chloroform (2 ml) was added to a stirred solution of 1-thioxo-2-methylisoquinolin-8-yl (N,N-diisopropyldithiocarbamato)palladium (II) (0.46g; 1 mmole) in chloroform (25 ml). A yellow precipitate formed immediately and after stirring for 3 hours, the precipitate was

filtered off (0.33g), m.p. > 300°C. On the basis of its I.R. and mass spectrum, this substance was thought to be a mixture of di-μ-chloro-bis (1-thioxo-2-methylisoquinolin-8-yl) dipalladium (II), and 3-methyl[1,2]dithiolo[3,4,5-ij]isoquinolinium chloride. [m/e 191, (M^+-MeCl) observed in the mass spectrometer for the latter product].

The filtered reaction mixture was evaporated and the residue was chromatographed on alumina (25g). Eluting with light petroleum and then with ether yielded N,N'-dimorpholinyl sulphide as a cream coloured solid, (40 mg), m.p. 126-7°C, [lit. m.p.[88] 125-6°C]. Eluting with dichloromethane yielded bis (N,N-diisopropyldithiocarbamato)palladium (II) as an orange-yellow solid, (85 mg), m.p. > 300°C. No other products were isolated by column chromatography.

REACTION OF 1-THIOXO-2-METHYLISOQUINOLIN-8-YL (N,N-DIISOPROPYLDITHIOCARBAMATO)PALLADIUM (II) WITH 2 MOLAR EQUIVALENTS OF MORPHOLINE-N-SULPHENYL CHLORIDE

A solution of 1-thioxo-2-methylisoquinolin-8-yl (N,N-diisopropyldithiocarbamato)palladium (II) (0.46g; 1 mmole) in chloroform (30 ml) was added dropwise over a period of 15 minutes to a stirred solution of morpholine-N-sulphenyl chloride (0.31g; 2 mmole) in chloroform (10 ml). A yellow precipitate formed immediately and the reaction mixture was stirred for 3 hours. The reaction mixture was evaporated to dryness and the residue was extracted with ether (25 ml). The ether extract was evaporated, yielding N,N'-dimorpholinyl sulphide as a cream coloured solid, (0.18g; 88%), m.p. 125-6°C, [lit. m.p.[88] 125-6°C]. The identity of this compound was verified by its mass spectrum (M^+ 204) and by

its elemental analysis.

ANALYSIS: Found: C,46.8%; H,7.9%; N,13.3%

$C_8H_{16}N_2O_2S$ requires: C,47.1%; H,7.8%; N,13.7

The ether-insoluble residue was suspended in dichloromethane (40 ml), pyridine (1 ml) was added, and the mixture was stirred vigorously for 15 minutes. The mixture was filtered and the filter cake was washed with dichloromethane and then dried *in vacuo*, yielding 3-methyl [1,2] dithiolo[3,4,5-*ij*] isoquinolinium chloride as a yellow solid, (0.22g; 91%), m.p. 269-70°C (d), with prior decomposition at 230-5°C.

I.R. SPECTRUM: ν max 1625, 1550, 1490, 1350, 1330, 1210, 1110, 935, 815, 765 cm^{-1}

^1H n.m.r. at 360 MHz in d_6-Me_2SO : δ 8.35 [d, ($^3J_{HH}$ = 7.09 Hz), 1H, H-4]; δ 8.30 [d, ($^3J_{HH}$ = 8.25 Hz), 1H, H-6]; δ 8.18 [t, ($^3J_{HH}$ = 7.92 Hz), 1H, H-7]; δ 7.92 [d, ($^3J_{HH}$ = 7.92 Hz), 1H, H-8]; δ 7.86 [d, ($^3J_{HH}$ = 7.09 Hz), 1H, H-5]; δ 4.16 (s, 3H, NCH_3).

U.V. SPECTRUM : (EtOH-trace HCl) λ max (nm) : 253, 335, 419

ε : 14,023, 3,636, 9,349

MASS SPECTRUM : m/e 191 (M^+-MeCl), 52/50 ($MeCl^+$).

ANALYSIS: Found: C,49.5%; H,3.2%; N,5.6%

$C_{10}H_8Cl\,N\,S_2$ requires: C,49.7%; H,3.3%; N,5.8%

The dichloromethane-pyridine filtrate was evaporated and the residual orange gum was triturated with ether-dichloromethane to yield chloro (N,N-diisopropyldithiocarbamato) pyridinepalladium (II)as an orange solid (0.31g; 78%), decomp. 155-60°C. Recrystallisation from dichloromethane - light petroleum gave the analytically pure product, decomp. 165-70°C.

I.R. SPECTRUM : ν max 1600, 1510, 1340, 1195, 1150, 1070, 1040, 760, 700 cm^{-1}.

^{1}H n.m.r. SPECTRUM : ($CDCl_3$) δ 8.75 [d,($^3J_{HH}$= 6 Hz), 2H, 2 (2-pyridyl) protons]; δ 7.78 [t,($^3J_{HH}$= 7 Hz), 1H, 4-pyridyl proton]; δ 7.4-7.26 [m, 2H, 2 (3-pyridyl) protons]; δ 4.8-4.2 (m, 2H, 2 methine protons); δ 1.45 and 1.40 [2 br.d. (overlapping), ($^3J_{HH}$= 7Hz), 12H, isopropyl CH_3)].

ANALYSIS: Found : C,36.6%; H,4.7%; N,6.8%

$C_{12}H_{19}Cl\ N_2Pd\ S_2$ requires : C,36.3%; H,4.8%; N,7.1%

THE THERMOLYSIS OF 3-METHYL [1,2] DITHIOLO [3,4,5-ij] ISOQUINOLINIUM CHLORIDE

The title compound (0.10g) was heated to 250°C under vacuum in a sublimation tube and the resulting yellow-orange sublimate (70 mg), m.p. 83-87°C (d), was chromatographed on alumina (5g). Eluting with chloroform yielded [1,2] dithiolo [3,4,5-ij]-isoquinoline as a yellow solid (30 mg), m.p. 87-89°C (d). The product was found to be unstable in air and decomposed after standing several days.

^{1}H n.m.r. ($CDCl_3$) : δ 8.02 [d,($^3J_{HH}$= 6 Hz), 1H, H-4]; δ 7.5-7.2 (m, 3 aromatic protons); δ 7.05 [d,($^3J_{HH}$= 6 Hz), 1H, H-5]

MASS SPECTRUM : m/e 191 (M^+)

EXACT MASS MEASUREMENT : (m/e 191) Found : 190.986722 a.m.u.

$C_9H_5N\ S_2$ requires : 190,986342 a.m.u.

error : < 2 p.p.m

REACTION OF [2-(1,2-BENZISOTHIAZOL-3-YL)PHENYL](N,N-DIISOPROPYL-DITHIOCARBAMATO)PALLADIUM (II) WITH MORPHOLINE-N-SULPHENYL CHLORIDE

A solution of the title complex (0.42g; 0.85 mmole) in chloroform (30 ml) was added dropwise over a period of 15 minutes to a stirred solution of morpholine-N-sulphenyl chloride (0.27g; 0.87 mmole) in chloroform (10 ml). An orange solution resulted

immediately and was stirred for 2 hours. The reaction mixture was evaporated to dryness and the residue was extracted with ether (50 ml). Evaporation of the ether extract yielded a pale yellow gum (0.11g) which was shown by mass spectroscopy to contain N,N'-dimorpholinyl sulphide (m/e 204) and N,N'-dimorpholinyl trisulphide (m/e 268).

The ether - insoluble residue was dissolved in dichloromethane (20 ml), pyridine (1 ml) was added and the mixture was stirred for 15 minutes, during which time a white precipitate formed. Precipitation was completed by the addition of ether. The mixture was filtered and the precipitate (0.10g) was collected. This solid was identified as morpholine hydrochloride by infrared and mass spectroscopy. The ethereal filtrate was evaporated to yield an orange gum (0.63g). The gum was then dissolved in the minimum amount of methanol, a few drops of perchloric acid were added and the resulting orange precipitate (0.30g) was filtered off. This substance could not be identified by spectroscopic methods.

I.R. SPECTRUM: 1510 cm^{-1}, 1100 cm^{-1} (broad)

^1H n.m.r. : Shows both aromatic and isopropyl protons (poorly resolved).

MASS SPECTRUM: m/e 458 (Pd), 242, 211, 210

The methanolic filtrate was evaporated to yield an orange gum which was shown by mass spectroscopy to contain elemental sulphur, 3-phenyl-1,2-benzisothiazole (m/e 211) and bis (N,N-diisopropyldithiocarbamato)palladium (II) (m/e 458).

REACTION OF 1-THIOXO-2-METHYLISOQUINOLIN-8-YL (N,N-DIISOPROPYLDITHIOCARBAMATO)PALLADIUM (II) WITH SULPHUR DICHLORIDE

A solution of the title complex (0.46g; 1 mmole) in

chloroform (25 ml) was added dropwise over a period of 15 minutes to a stirred solution of sulphur dichloride (0.11g; 1 mmole) in chloroform (10 ml). A deep red solution resulted immediately and then became lighter in colour with the simultaneous precipitation of a brown solid. The reaction mixture was stirred for 3 hours and then filtered. The solid product was then suspended in dichloromethane (20 ml), pyridine (1 ml) was added, and the mixture was stirred vigorously for 15 minutes. The mixture was filtered and the filter cake was washed with dichloromethane and then dried *in vacuo* yielding 3-methyl [1,2] dithiolo [3,4,5 - ij] isoquinolinium chloride as a yellow solid, (0.18g; 75%), m.p. 252-5°C (d).

(8) ATTEMPTED SYNTHESIS OF 8-HALOGENO-2-METHYLISOQUINOLINE-1-THIONES FROM CYCLOPALLADATED COMPLEXES

(a) By reaction of 1-thioxo-2-methylisoquinolin-8-yl (N,N-diisopropyldithiocarbamato)palladium (II) with bromine

A stirred solution of the title complex (0.50g; 1.1 mmole) in chloroform (25 ml) was treated with a solution of bromine (0.175g; 1.1 mmole) in chloroform (5 ml). A deep red solution resulted immediately and the reaction mixture was stirred overnight. The solution was decanted leaving an intractable black tar on the walls of the reaction vessel. The decanted solution was reduced to small volume and treated with light petroleum until precipitation

of orange-red solid was complete. The precipitate was filtered off (0.19g) and purified by dissolving it in the minimum volume of chloroform and re-precipitating with light petroleum. The purified compound, (0.14g), decomp. 125-30°C, was thought to be a bromine addition product MBr_2 [M = 1-thioxo-2-methylisoquinolin-8-yl (N,N-diisopropyldithiocarbamato)palladium (II)] on the basis of its elemental analysis.

ANALYSIS: Found C,34.2%; H,4.0%; N,4.5%

$C_{17}H_{22}Br_2N_2Pd\ S_3$ requires: C,33.1%; H,3.6%; N,4.5%

(b) By reaction of 1-thioxo-2-methylisoquinolin-8-yl (N,N-diisopropyldithiocarbamato)palladium (II) with chlorine followed by treatment with triphenylphosphine.

A stirred solution of 1-thioxo-2-methylisoquinolin-8-yl (N,N-diisopropyldithiocarbamato)palladium (II) (0.23g; 0.5 mmole) in chloroform (15 ml) was treated with a solution of chlorine (36 mg; 0.5 mmole) in carbon tetrachloride (0.5 ml). A brown precipitate formed immediately and the mixture was stirred for 10 minutes. Triphenylphosphine (0.13g; 0.5 mmole) was added, forming a deep red solution, and the reaction mixture was stirred overnight, during which time a yellow precipitate formed. Filtration of the reaction mixture yielded di-μ-chloro-bis (1-thioxo-2-methylisoquinolin-8-yl)dipalladium (II) as a yellow solid, (30 mg), m.p. 263-6°C (d). The identity of this compound was established by comparison of its infrared spectrum with that of an authentic specimen.

The filtrate was evaporated, yielding a red gum which was not amenable to column chromatography. The gum was triturated with ether yielding an orange-red solid, (70 mg), m.p. 172-181°C (d).

Mass spectroscopic analysis of this substance showed very weak intensity peaks at m/e 211 and 209 corresponding to 8-chloro-2-methylisoquinoline-1-thione, and a strong intensity peak at m/e 262 corresponding to triphenylphosphine.

(c) By reaction of di-μ-chloro-bis (1-thioxo-2-methylisoquinolin-8-yl)dipalladium (II) with triphenylphosphine followed by treatment with chlorine and then with triphenylphosphine

A stirred suspension of di-μ-chloro-bis (1-thioxo-2-methylisoquinolin-8-yl)dipalladium (II) (0.31g; 0.5 mmole) in chloroform (25 ml) was treated with triphenylphosphine (0.26g; 1 mmole). The resulting yellow solution was treated with a solution of chlorine (71 mg; 1 mmole) in carbon tetrachloride (1 ml), forming a deep red solution. The reaction mixture was then treated with triphenylphosphine (0.26g; 1 mmole) and stirred for 6 hours, during which time the solution became orange in colour. The reaction mixture was evaporated, yielding an orange-red gum which was not amenable to column chromatography. The gum was triturated with a small amount of chloroform yielding bis (triphenylphosphine) palladium (II) dichloride as a yellow solid, (0.23g), decomp. 270-5°C, [lit.[89] decomp.250-70°C]. The identity of this compound was confirmed by comparison of its infrared spectrum with that of an authentic sample. The chloroform extract from trituration was treated with light petroleum until precipitation of orange-red solid was complete. The solid was filtered off, (0.11g), m.p. 138-42°C, and was thought to consist mainly of chloro (1-thioxo-2-methylisoquinolin-8-yl)triphenylphosphinepalladium (II) on the basis of its ^{1}H n.m.r. spectrum. No other products were isolated from the reaction mixture.

(d) By reaction of di-μ-chloro-bis (1-thioxo-2-methylisoquiolin-8-yl)dipalladium (II) with pyridine, followed by treatment with bromine and then tetraethylammonium N,N-dimethyldithiocarbamate

A stirred suspension of di-μ-chloro-bis (1-thioxo-2-methylisoquinolin-8-yl)dipalladium (II) (0.26g; 0.41 mmole) in chloroform (100 ml) was treated with pyridine (68 mg; 0.82 mmole). The resulting yellow solution was treated with a solution of bromine (0.13g; 0.82 mmole) in chloroform (5 ml). A deep red solution formed immediately and the reaction mixture was stirred for 2 hours. Tetraethylammonium N,N-dimethyldithiocarbamate (0.41g; 1.64 mmole) was then added and the reaction mixture was stirred overnight, during which time a yellow precipitate formed. Filtration of the reaction mixture yielded bis (N,N-dimethyldithiocarbamato)palladium (II) as a yellow solid, (70 mg) m.p. > 300°C. The identity of this compound was confirmed by comparison of its infrared spectrum with that of an authentic sample. The filtrate was evaporated, yielding an orange-red gum, trituration of which with dichloromethane yielded a further quantity (0.19g) of bis (N,N-dimethyldithiocarbamato)palladium (II). The dichloromethane extract was evaporated and the residue was chromatographed on alumina (50g). Eluting with ether yielded an orange gum (50 mg) which was shown by mass spectroscopy to contain 2-methylisoquinoline-1-thione (m/e 175) and 8-bromo-2-methylisoquinolin-1-one m/e 239 and 237). Eluting with dichloromethane yielded a further quantity (50 mg) of bis (N,N-dimethyldithiocarbamato)palladium (II). No other products were isolated by column chromatography.

(e) By reaction of di-μ-chloro-bis (1-thioxo-2-methylisoquinolin-8-yl)dipalladium (II) with N-chlorosuccinimide in dimethylformamide

To a stirred suspension of di-μ-chloro-bis (1-thioxo-2-methylisoquinolin-8-yl)dipalladium (II) (0.50g; 0.79 mmole) in dry dimethylformamide (25 ml) was added N-chlorosuccinimide (0.21g; 1.58 mmole). The reaction mixture was stirred for 24 hours, during which time it became green, initially, and then deep red. Filtration of the reaction mixture yielded the unreacted title complex (0.29g; 58% recovery). The filtrate was evaporated, yielding a deep red gum which was shown by mass spectroscopy to contain succinimide (m/e 99) as the major component and 8-chloro-2-methylisoquinolin-1-one (m/e 195 and 193) as a minor component.

(f) <u>By reaction of di-μ-chloro-bis (1-thioxo-2-methylisoquinolin-8-yl)dipalladium (II) with N-chlorosuccinimide in pyridine</u>

Di-μ-chloro-bis (1-thioxo-2-methylisoquinolin-8-yl) dipalladium (II) (0.50g; 0.79 mmole) was treated with 2 ml (excess) of dry pyridine. The mixture was stirred and a yellow solution formed which then precipitated a bright yellow solid after 1 - 2 minutes. N-chlorosuccinimide (0.21g; 1.58 mmole) was added and the resulting deep green solution was stirred overnight, during which time a green precipitate formed. This solid was filtered off (0.29g), m.p. 125-30°C (d) but could not be identified spectroscopically and decomposed on attempted recrystallisation from chloroform. The mass spectrum of the solid showed ion peaks due to pyridine (m/e 79) and 8-chloro-2-methylisoquinolin-1-one (m/e 195 and 193). Addition of ether to the filtrate precipitated a yellow-green solid which was filtered off (0.28g), m.p. 120-5°C (d). This solid gave the same mass spectrum as the previous product and could not be further characterised by spectroscopic methods. The ethereal filtrate was evaporated and the residual

yellow-orange gum (0.20g) was examined by mass spectroscopy and found to consist mainly of succinimide (m/e 99).

(g) By reaction of di-μ-chloro-bis (1-thioxo-2-methylisoquinolin-8-yl)dipalladium (II) with benzyl triethylammonium chloride followed by treatment with chlorine

To a stirred suspension of di-μ-chloro-bis (1-thioxo-2-methylisoquinolin-8-yl)dipalladium (II) (0.31g; 0.5 mmole) in dichloromethane (25 ml) was added benzyltriethylammonium chloride (1.15g; 5 mmole). The resulting golden-yellow solution was then treated with a solution of chlorine (71 mg; 1 mmole) in carbon tetrachloride (2 ml) forming an intense dark green solution. The reaction mixture was stirred for 4 hours, the solvent was removed, and the residue was extracted with water (50 ml). The extract was then discarded. The yellow-brown solid which remained was filtered off (0.36g), m.p. 100-5°C (d). Owing to its low solubility in organic solvents this compound could not be characterised by spectroscopic methods. Its mass spectrum showed a peak at m/e 175 (2-methylisoquinoline-1-thione). Its elemental analysis was fairly close to that of the co-ordination complex bis (8-chloro-2-methylisoquinoline-1-thione)palladium (II) dichloride.

ANALYSIS: Found: C,41.7%; H,4.0%; N,4.3%

$C_{20}H_{16}Cl_4N_2Pd\ S_2$ requires: C,40.3%; H,2.7%; N,4.7%

(9) ATTEMPTED REPLACEMENT OF PALLADIUM IN CYCLOPALLADATED COMPLEXES BY OXYGEN-OR NITROGEN-CONTAINING GROUPS

REACTION OF 1-THIOXO-2-METHYLISOQUINOLIN-8-YL (N,N-DIISOPROPYL-DITHIOCARBAMATO)PALLADIUM (II) WITH PHENYL IODOSODIACETATE

A stirred solution of the title complex (0.46g; 1 mmole) in ethanol-free chloroform (30 ml) was treated with a solution of phenyl iodosodiacetate (0.32g; 1 mmole) in 5 ml of the same solvent. An orange solution was formed initially and the reaction mixture was stirred overnight, during which time it became deep red in colour and non-oxidising to acidified starch-iodide paper. The reaction flask was then fitted with a condenser and calcium chloride drying tube and the reaction mixture was heated under reflux for 3 hours, during which time a purple precipitate formed. The reaction mixture was cooled and the precipitate was filtered off, (75 mg), m.p.> 300°C. Owing to its involatility and low solubility in organic solvent, this substance could not be characterised. The filtrate was then treated with ether until the precipitation of a yellow solid was complete. The precipitate was filtered off and shown to be bis (N,N-diisopropyldithiocarbamato) palladium (II), (0.20g), m.p.> 300°C. The ethereal filtrate was evaporated and the residual yellow gum (0.45g) was examined by mass spectroscopy. A complex mixture of products was revealed : m/e 233 (8-acetoxy-2-methylisoquinoline-1-thione); m/e 217 (8-acetoxy-2-methylisoquinolin -1-one); m/e 204 (iodobenzene); m/e 191 (8-hydroxy-2-methylisoquinoline-1-thione); m/e 175 (2-methylisoquinoline-1-thione).

REACTION OF 1-THIOXO-2-METHYLISOQUINOLIN-8-YL (N,N-DIISOPROPYL-DITHIOCARBAMATO)PALLADIUM (II) WITH DIBENZOYL PEROXIDE

A stirred solution of the title complex (0.46g; 1 mmole) in ethanol-free chloroform (30 ml) was treated with dibenzoyl peroxide (0.24g; 1 mmole). An orange solution was formed initially and the reaction mixture was stirred overnight, during which time it became red in colour and non-oxidising to acidified starch-iodide paper. The reaction mixture was evaporated, yielding a red solid (0.69g), the mass spectrum of which showed ion peaks believed to be due to (i) bis (N,N-diisopropyldithiocarbamato)palladium (II), (m/e 458 (ii) benzoic anhydride, (m/e 226 and 198), and (iii) benzoic acid, m/e 122, 105 and 77.

The red solid was dissolved in acetone (20 ml) and treated with sodium N,N-diisopropyldithiocarbamate (0.20g; 1 mmole) which precipitated a yellow-orange solid. The solid (0.30g), m.p. 240-50°C (d) was filtered off and was shown by ^{1}H n.m.r. to be a mixture of bis (N,N-diisopropyldithiocarbamato)palladium (II) and the title complex (ratio approximately 1 : 1). The filtrate was evaporated and the residual orange-red gum (0.35g) was examined by mass spectroscopy. Only the three previously mentioned products were found to be present in the gum.

REACTION OF [2-(PHENYLAZO)PHENYL](N,N-DIISOPROPYLDITHIOCARBAMATO) PALLADIUM (II) WITH CHLORAMINE

A stirred solution of the title complex (0.46g; 1 mmole) in ether (150 ml) was treated with a solution of chloramine (52 mg; 1 mmole) in 5 ml of the same solvent. No reaction occurred on admixture of the reactants. After 1 hour the reaction mixture was still oxidising to acidified starch-iodide paper. Irradiation of the reaction mixture with a 500W tungston filament lamp for 2 hours had no effect. After this time, removal of the solvent yielded

the title complex unchanged.

(10) REACTIONS OF THE [1,2,4] DITHIAZOLO[3,4,5 -de] QUINOLIZINYLIUM CATION AND OTHER POTENTIAL PRECURSORS OF CYCLAZINE-LIKE MOLECULES

(a) Reaction with formamidine acetate in methanol and 2-methoxy ethanol

The chloride salt (138mg; 0.61 mmole) and formamidine acetate (63mg; 0.61 mmole) were heated together under reflux in methanol, under nitrogen. After 1.5 hours the reaction mixture became dark red in colour. The reaction was stopped at this stage and a sample of the mixture was examined by mass spectroscopy. The mass spectrum showed a peak at m/e 191. No peak at m/e 169 (desired product) was observed. The solvent was removed from the reaction mixture and was replaced with an equal volume of 2-methoxy ethanol and the mixture was heated under reflux for 1 hour. The reaction mixture was cooled and the solvent was removed yielding a dark red gum which was not amenable to column chromatography and could not be crystallised by trituration with organic solvents. The mass spectrum of this substance showed peaks at m/e 256 (elemental sulphur) and 191. The m/e 191 peak was initially thought to be due to 6-methoxyquinolizine-4-thione but exact mass measurement of this peak was inconclusive.

EXACT MASS MEASUREMENT (m/e 191) :

Found: 191.127633 a.m.u.

$C_{10}H_9N$ O S requires : 191.040483 a.m.u.(error 456 p.p.m.)

(b) Reaction with formamidine acetate in the absence of solvent

The chloride salt (23mg; 0.1 mmole) and formamidine acetate (10mg; 0.1 mmole) were ground together in a small mortar. The finely powdered mixture was then placed in a small glass tube and heated at 100°C under nitrogen for 2 hours, during which time it became dark red in colour. After cooling to room temperature, a sample of the reaction mixture was examined by mass spectroscopy and showed ion peaks at m/e 218(possibly 6-thiocyanatoquinolizine-4-thione), m/e 174 ([1,2,4]thiadiazolo[3,4,5-de] quinolizine), m/e 161 and 117 (quinolizine-4-thione) and m/e 223 (unidentified).

(c) Reaction with triphenylphosphine followed by treatment with acetamidine

The chloride salt (23mg; 0.1 mmole) and triphenylphosphine (26mg; 0.1 mmole) were heated together under reflux with stirring in dry acetonitrile (20 ml), under nitrogen for 1 hour. During this time, no obvious reaction was observed. Acetamidine hydrochloride (10mg; 0.1 mmole) and anhydrous potassium carbonate (14mg; 0.1 mmole) were added and the reaction mixture was heated under reflux for a further hour, during which time a deep red solution formed. The reaction mixture was cooled and filtered. The filtrate was evaporated, yielding a dark red gum, (55mg), from which no pure product could be isolated by trituration with organic solvents. This substance was examined by mass spectroscopy and showed ion peaks at m/e 294 (triphenylphosphine sulphide), m/e 262 (triphenylphosphine) and a peak of nominal m/e 183 splitting into two under high

resolution. Exact mass measurements of the two peaks of mass 183 proved that they were the dibenzophospholylium ion, a normal fragment ion derived from triphenylphosphine, and the desired product 2-methyl [1,3,5] triazino [2,1,6 - de] quinolizine. The ratio of the former peak to the latter was about 30:1.

EXACT MASS MEASUREMENT:

LOW MASS PEAK:	Found:	183.037277 a.m.u.
$C_{12}H_8P$	requires:	183.036361 a.m.u.
		error 5 p.p.m.
HIGH MASS PEAK:	Found:	183.079340 a.m.u.
$C_{11}H_9N_3$	requires:	183.079643 a.m.u.
		error < 2 p.p.m.

(d) Reaction with ethoxycarbonylhydrazine

The perchlorate salt (33mg; 0.11 mmole) and ethoxycarbonylhydrazine (12mg; 0.11 mmole) were heated together with stirring at 100°C in dry dimethylformamide (20 ml), under nitrogen for 3 hours. After cooling, the solvent was removed under high vacuum and the resulting red residue was triturated with a few drops of aqueous sodium bicarbonate solution and was then filtered. The red filter cake was washed with a few drops of water and then dried in vacuo, yielding the perchlorate salt starting material (20mg; 61% recovery). The aqueous filtrate was extracted with ether (50 ml) and the extract was dried over magnesium sulphate. The drying agent was filtered off and the filtrate was evaporated, yielding a yellow oil (10mg). Examination of this substance by mass spectroscopy showed the presence of unreacted ethoxycarbonylhydrazine (m/e 104) and an unidentified substance (m/e 144).

(e) Reaction with triphenylphosphine followed by treatment with ethoxycarbonylhydrazine

The chloride salt (23mg; 0.1 mmole) and triphenylphosphine (26mg; 0.1 mmole) were heated together under reflux with stirring in dry acetonitrile (20 ml), under nitrogen for 1 hour. During this time, no obvious reaction was observed. Ethoxycarbonylhydrazine (11mg; 0.1 mmole) was added and the reaction mixture was heated under reflux for a further 5 hours. The solution was cooled and the solvent was removed yielding an orange-red residue which, when triturated with ether, yielded the chloride salt starting material (17mg; 74% recovery).

(f) Reaction with ammonia in dimethylformamide

The chloride salt (25mg) was dissolved in dry dimethylformamide (20 ml) under a nitrogen atmosphere in a three-necked flask, fitted with a gas inlet tube, condenser and a gas bubbler. The stirred solution was then treated with a gentle flow of ammonia gas for 15 minutes. After this time, only the starting material was present, as was shown by t.l.c. . The reaction mixture was then slowly heated to 100°C and maintained at this temperature for 15 minutes. T.l.c. then showed several yellow spots. The solution was cooled to room temperature, the solvent was removed under high vacuum, and the residual red gum was triturated with water. The water layer was decanted and the water-insoluble gum which remained was extracted with ether (25 ml). The ether extract yielded dark yellow oil (5mg) which was examined by mass spectroscopy and found to contain mainly quinolizine-4-thione (m/e 161 and 117). The ether-insoluble gum which remained was also examined by mass spectroscopy and was shown

to contain the desired product, [1,2,4]thiadiazolo[3,4,5-de]-quinolizine (m/e 174) in addition to quinolizine-4-thione. An attempt to separate the desired product by sublimation *in vacuo* yielded only a tract of yellow sublimate which still contained the m/e 174 material but showed at least 6 spots on a t.l.c. plate, thus suggesting that it was a mixture or was decomposing on the plate (silica gel). An exact mass measurement of the m/e 174 ion was in accord with the proposed structure.

EXACT MASS MEASUREMENT: Found: 174.025701 a.m.u.

$C_9H_6N_2S$ requires: 174.025169 a.m.u.

error < 4 p.p.m.

(g) Reaction with potassium cyanide in dichloromethane in the presence of 18-crown-6

A mixture of the chloride salt (23mg; 0.1 mmole), potassium cyanide (7mg; 0.11 mmole) and 18-crown-6 (0.5mg) was stirred overnight in dichloromethane (25 ml). After this time, t.l.c. showed that no reaction had occurred. The reaction mixture was heated for 5 hours under reflux but still no reaction occurred. The solvent was removed and the residue was extracted with methanol (10 ml). Treatment of the residue with a few drops of perchloric acid precipitated the perchlorate salt of the starting material (18mg; 62% recovery).

(h) Reaction with sodium hydroxide in aqueous methanol

A stirred solution of the chloride salt (0.175g; 0.77 mmole) in methanol (20 ml) was treated with a solution of sodium hydroxide (62mg; 1.55 mmole) in water (5 ml). The resulting deep red solution was stirred for 3 hours. After this time, the solvent was removed and the residue was acidified with dilute

hydrochloric acid and extracted with dichloromethane (50 ml). Evaporation of the dried ($MgSO_4$) extract yielded an orange gum which was chromatographed on silica gel (25g). Eluting with ether-ethanol (1:1) gave yellow coloured solutions which yielded a dark green gum, (0.11g), from which no pure products could be isolated by trituration with organic solvent. Examination of the gum by mass spectroscopy showed at least five components : (i) quinolizine-4-thione (m/e 161 and 117) (ii) 6-hydroxy-quinolizine-4-thione (m/e 177 and 176) (iii) 6-methoxyquinolizine-4-thione (m/e 191) (iv) and (v) hydroxide and methoxide addition products of the starting material (m/e 209, 223).

An exact mass measurement was obtained for 6-hydroxyquinolizine-4-thione

	Found:	177.026097 a.m.u.
$C_9H_7N\ O\ S$	requires:	177.024834 a.m.u.
		error 7 p.p.m.

(i) Reaction with sodium borohydride in the presence of nickel chloride

The chloride salt (0.20g; 0.88 mmole) and nickel chloride hexahydrate (0.10g; 0.42 mmole) were dissolved in water (25 ml). To the stirred solution at 0°C was added dropwise a solution of sodium borohydride (17mg; 0.44 mmole) in water (5 ml). A deep purple precipitate formed immediately and, after the addition of reducing agent was complete, the reaction mixture was allowed to warm to room temperature and was stirred for 3 hours. The precipitate was filtered off, washed with ethanol, and dried *in vacuo* yielding bis (6-thioxoquinolizine-4-thiolato)nickel (II), (0.17g; 87%), m.p.200-5°C (d) as a deep purple solid.

I.R. SPECTRUM: νmax 1605, 1550, 1345, 1285, 1200, 1185, 1160, 1110, 870, 800, 775, 735 cm^{-1}

MASS SPECTRUM: at 200°C : m/e 256 (S_8) and breakdown peaks S_7, etc.
at 230°C : m/e 378 (Ni), 160, 117

ANALYSIS: Found: C,48.6%; H,2.6%; N,6.2%

$C_{18}H_{12}N_2NiS_4$ requires: C,48.8%; H,2.7%; N,6.3%

REACTION OF DI-μ-CHLORO-BIS (4-THIOXOQUINOLIZIN-6-YL)DIPALLADIUM(II) WITH ZINC

The title complex (0.50g; 0.83 mmole) and activated zinc powder* (0.11g; 1.66 mmole) were ground together in a mortar. The finely ground mixture was then placed in a sublimation tube and heated to 300°C under vacuum. The resulting dark yellow sublimate, (25mg), m.p. 86-90°C, was shown by mass spectroscopy and ^1H n.m.r. to be quinolizine-4-thione. The involatile residue, a black solid, (0.53g), was intractable and could not be characterised.

* Prepared by washing zinc powder several times with 5% hydrochloric acid and then washing in turn with water, methanol and ether.

REACTION OF DI-μ-CHLORO-BIS (4-THIOXOQUINOLIZIN-6-YL)DIPALLADIUM (II) WITH COPPER

The title complex (0.50g; 0.83 mmole) and activated copper metal* (0.11g; 1.66 mmole) were ground together in a mortar. The finely ground mixture was then placed in a sublimation tube and heated to 300°C under vacuum. The resulting dark yellow, sticky sublimate was extracted with dichloromethane and the extract was evaporated to a red gum, (85mg) which was shown by mass spectroscopy and ^1H n.m.r. to be quinolizine-4-thione. The involatile residue, a black solid, (0.52g), was intractable and could not be characterised.

* Prepared by washing copper bronze with a 2% solution of iodine in

acetone.

REACTION OF QUINOLIZINE-4-SELONE WITH TRIPHENYLPHOSPHINE

Quinolizine-4-selone (0.21g; 1 mmole) and triphenylphosphine (0.26g; 1 mmole) were mixed together and heated at 120° for 2 hours under nitrogen, during which time a black molten mass formed. After this time, the reaction mixture was chromatographed on alumina (50g). Eluting with light petroleum and then with ether yielded triphenylphosphine selenide as a white solid, (80mg), m.p. 180-2°C [lit. m.p.[90] 184-5°C]. Eluting with chloroform yielded quinolizine-4-selone as an orange solid, (0.10g), m.p. 93-96°C. No other products were isolated by column chromatography.

(11) PREPARATION OF STARTING MATERIALS

1,2-dihydro-2-methylisoquinolin-1-one

This compound was prepared by an adaption of the method of Perkin and Robinson.[91]

2-methylisoquinolinium iodide (30g; 0.11 mole) and potassium ferricyanide (85g; 0.25 mole) were mixed together in water (1 litre) in a 3 litre separating funnel. Ether (1 litre) was added, followed by small portions of a solution of potassium hydroxide (31g; 0.55 mole) in water (300 ml) with shaking. After the addition of base was complete the mixture was shaken for a further 15 minutes. The layers were separated and the aqueous

layer was re-extracted with ether (1 litre). The combined organic extracts were washed with water and dried over magnesium sulphate. The drying agent was filtered off and the extract was evaporated yielding a dark red oil.

Distillation under reduced pressure yielded 1,2-dihydro-2-methylisoquinolin-1-one as a yellow oil (10.0g; 57%), b.p. 160-4° C/0.1 mm, [lit. b.p.[92] 161-5°C/3mm].

1,2-dihydro-2-methylisoquinoline-1-thione

This compound was prepared from the corresponding isoquinolone and phosphorus pentasulphide in 43% yield, m.p. 110-111° C [lit. m.p.[93] 112°C].

4,7-Dichloro-1-methylquinolinium iodide

A stirred solution of 4,7-dichloroquinoline (3.96g; 0.02 mole) and dimethyl sulphate (3.02g; 0.024 mole) in dimethylformamide (25 ml) was heated at 100°C for 30 minutes. The solvent was removed under high vacuum and the residual yellow oil was treated with a solution of potassium iodide (6.7g; 0.04 mole) in water (10 ml). The resulting yellow precipitate was filtered off, washed with a little water and then with ether, and dried in vacuo yielding 4,7-dichloro-1-methylquinolinium iodide, (4.45g; 65%), m.p. 196-202°C (d), [lit. m.p.[94] 200-7°C (d)].

7-Chloro-1, 4-dihydro-1-methylquinoline-4-thione

Solutions of 4,7-dichloro-1-methylquinolinium iodide (6.80g; 0.02 mole) in ethanol (400 ml) and of sodium sulphide (7.20g; 0.03 mole) in water (40 ml) were mixed and heated under reflux with stirring for 3 hours, during which time a yellow solution formed. The reaction mixture was reduced to small volume, whereupon a bright yellow solid precipitated. The mixture was filtered and the filter

cake was washed with a little water and dried in vacuo. Recrystallisation from ethanol yielded 7-chloro-1,4-dihydro-1-methylquinoline-4-thione (2.62g; 63%), m.p. 203-5°C (d).

I.R. SPECTRUM: ν max 1605, 1595, 1525, 1515, 1360, 1230, 1170, 1140, 1090, 1030, 960, 865, 825, 810 cm^{-1}

^1H n.m.r. SPECTRUM: ($CDCl_3$) δ 8.80 [d, ($^3J_{HH}$ = 8Hz), 1H, H-5]; δ 7.4-7.1 (m, 4 aromatic protons); δ 3.78 (s, 3H, NCH_3)

MASS SPECTRUM: m/e 209 (M^+), 165

ANALYSIS: Found: C,57.0%; H,3.7%; N,6.3%

$C_{10}H_8ClNS$ requires: C,57.3%; H,3.8%; N,6.7%

ACRIDONE

This compound was prepared from N-phenylanthranilic acid and concentrated sulphuric acid in 76% yield, m.p. > 300°C, [lit. m.p.[86] 350°C] by the method of Albert.[86]

9,10-Dihydro-10-methylacridin-9-one

A stirred suspension of acridone (3.12g; 0.016 mole) in dry dimethylformamide (50 ml) was treated with sodium hydride (0.38g; 0.016 mole). The mixture was heated to 100°C, resulting in the formation of a golden-yellow solution. Dimethyl sulphate (25 ml) was added and the mixture was heated at 100°C for 1 hour. The mixture was cooled and the solvent was removed under high vacuum. The residue was triturated with water and the water-insoluble material was recrystallised from ethanol, yielding 9,10-dihydro-10-methylacridin-9-one as a pale yellow solid, (2.85g; 85%), m.p. 196-8°C, [lit. m.p.[86] 199°C].

9,10-dihydro-10-methylacridine-9-thione

This compound was prepared from the corresponding acridone by reaction with phosphoryl chloride followed by treatment with

sodium thiosulphate, in 70% yield, m.p. 268-70°C (d), [lit. m.p.[95] 267°C].

Quinolizin-4-one

A solution of ethyl 2-pyridylacetate (55g; 0.33 mole) and diethyl ethoxymethylenemalonate (80g; 0.37 mole) in absolute ethanol (250 ml) was treated with a solution of sodium ethoxide in absolute ethanol [from sodium (10g; 0.43 mole) and ethanol (125 ml)] . The mixture was kept for 24 hours and the green precipitate of 1,3-di(ethoxycarbonyl)quinolizin-4-one (54g) was filtered off. The filtrate was reduced to small volume and acidified with dilute hydrochloric acid, whereupon a further 22g of partially hydrolysed ester precipitated and was filtered off.

The two reaction products were combined and heated under reflux in concentrated hydrochloric acid (600 ml) for 2 hours. The reaction mixture was cooled on ice and neutralised with solid sodium carbonate and then extracted with chloroform (600 ml). The extract was dried with magnesium sulphate and evaporated, yielding an orange oil. Distillation under reduced pressure yielded quinolizin -4-one as a yellow, hygroscopic solid (21.5g; 44%), m.p. 72-3°C, [lit. m.p.[96] 72-3°C].

4-Chloroquinolizinium perchlorate

This compound was prepared by reaction of quinolizin-4-one with phosphoryl chloride followed by treatment with perchloric acid in 83% yield, m.p. 300-5°C (d) [lit. m.p.[97] 310°C (d)] by the method of Van Aller and Reynolds.[97]

Quinolizine-4-thione

This compound was prepared by reaction of 4-chloroquinolizinium perchlorate with sodium sulphide in 64% yield, m.p. 98-99°C

[lit. m.p.[98] 98-100°C] by the method by Van Allen and Reynolds.[97]

Quinolizine-4-selone

To a stirred solution of 4-chloroquinolizinium perchlorate (2.64g; 0.01 mole) in water (250 ml) was added dropwise, under nitrogen, a solution of sodium hydrogen selenide (1.13g; 0.011 mole) in water (20 ml), prepared by the method of Klayman.[99] An orange solution resulted immediately and a yellow-orange solid was then precipitated. The reaction mixture was stirred for 2 hours, and the precipitate was filtered off and dried *in vacuo* (yield 1.25g). The aqueous filtrate was extracted with dichloromethane (200 ml), the extract reduced to small volume, and chromatographed on alumina (50g). Eluting with dichloromethane yielded a further quantity of product.(0.47g). The two samples of the product were combined together and recrystallised from benzene under nitrogen yielding quinolizine-4-selone as a yellow-orange solid, (1.25g; 60%), m.p. 115-6°C (sealed tube).

I.R. SPECTRUM: ν max 1635, 1580, 1570, 1280, 1260, 1205, 1160, 1105, 1080, 1025, 970, 795, 775, 750 cm^{-1}

^1H n.m.r.:($CDCl_3$) δ 10.75 [d,($^3J_{HH}$=7Hz), 1H, H-6]; δ 8.45 (m, 1H, H-3); δ 7.9-7.3 (m, 5 aromatic protons).

MASS SPECTRUM: m/e 209 (M^+), 117

ANALYSIS:	Found:	C,51.8%;	H,3.4%;	N,6.6%
C_9H_7NSe	requires:	C,52.0%;	H,3.4%;	N,6.7%

Thioxanthenethione

This compound was prepared from thioxanthenone and phosphorus pentasulphide in 64% yield, m.p. 167-9°C [lit. m.p.[100] 172-5°C].

2-Phenylthiochromen-4-one

This compound was prepared by reaction of thiophenol with ethyl benzoylacetate in 42% yield, m.p. 122-3°C [lit. m.p.[101] 125°C] by the method of Bossert.[102]

2-Phenylthiochromen-4-thione

This compound was prepared from 2-phenylthiochromen-4-one and phosphorus pentasulphide in 72% yield, m.p. 111-112°C [lit. m.p.[103] 112-3°C].

Benzylideneaniline

This compound was prepared from benzaldehyde and aniline in 66% yield, m.p. 48-50°C [lit. m.p.[104] 48°C].

3-phenyl-1,2-benzisothiazole

2-aminobenzophenone (19.7g; 0.1 mole) was heated in concentrated hydrochloric acid (60 ml) until a white paste formed. Water (60 ml) was added and the mixture was cooled to 0°C. The mixture was diazotised at this temperature with sodium nitrite (7.2g; 0.105 mole) in water (50 ml). After the addition of sodium nitrite was complete, the mixture was allowed to stand for 20 minutes, after which time, excess sodium nitrite was removed by the addition of a small amount of urea. The diazonium solution was then added dropwise to a stirred mixture of sodium acetate (100g), potassium thiocyanate (10.6g; 0.12 mole) and cuprous thiocyanate (12.2g; 0.12 mole) in water (250 ml) at 0-5°C over a period of 20-30 minutes. The mixture was stirred for 1 hour at room temperature after the addition of the diazonium solution was complete. The reaction mixture was filtered and the filter cake was washed with ether (1000 ml). The ether layer was separated from the aqueous layer, washed with water (500 ml), and then dried over magnesium sulphate. The drying agent was

filtered off and the filtrate was evaporated yielding a red oil. The crude product was chromatographed on alumina (500g). Eluting with ether yielded 2-thiocyanatobenzophenone as a red oil (16.7g; 70%) which was sufficiently pure for further reaction.

The thiocyanate (16.7g) was stirred in liquid ammonia (500 ml) - ethanol (25 ml) for 5 hours. After this time the solution was decanted and allowed to evaporate yielding a deep red gum. The crude product was chromatographed on silica gel (400g). Eluting with ether - light petroleum (1:3) yielded a yellow oil (7.45g) which was triturated with light petroleum at acetone-solid CO_2 temperature and yielded 3-phenyl-1,2-benzisothiazole as a white solid, (3.0g; 14%), m.p. 65-67°C [lit. m.p.[105] 71°C].

Triphenylphosphine-N-p-tolylimide

To a stirred solution of triphenylphosphine (3.9g; 0.015 mole) in sodium dried ether (50 ml) was added dropwise a solution of p-tolyl azide (1.99g; 0.015 mole, under nitrogen, over a period of 5 minutes. The reaction mixture was stirred for 1 hour, during which time a pale yellow precipitate formed. The solution was reduced to small volume and filtered yielding triphenylphosphine-N-p-tolylimide, (3.72g; 67%), m.p. 133-5°C [lit. m.p.[106] 132-4°C].

Di(4-morpholinyl)disulphide

This compound was prepared by reaction of morpholine with disulphur dichloride in 83% yield, m.p. 124-5°C, [lit. m.p.[88] 124-125°C] by an adaption of the method of Danen and Newkirk.[69]

Di(N-phthalimidyl)disulphide

This compound was prepared by reaction of potassium phthalimide with disulphur dichloride in 43% yield, m.p. 220-3°C,

[lit. m.p.[107] 228-30°C] by the method of Kalnins.[107]

Chlorocarbonylsulphenyl chloride

This compound was prepared by reaction of trichloromethanesulphenyl chloride with sulphuric acid in 68% yield by the method of Kuhle.[73]

n-Butoxycarbonylsulphenyl chloride

This compound was prepared by reaction of chlorocarbonylsulphenyl chloride with n-butanol in 47% yield, b.p. 60-64°C / 1 mm, [lit. b.p.[73] 84°C / 15 mm] by the method of Kuhle.[73]

Morpholine-N-sulphenyl chloride

A stirred solution of di(4-morpholinyl)disulphide (4.72g; 0.02 mole) in dry carbon tetrachloride (25 ml) at 0-5°C was treated with a gentle flow of chlorine gas for 2 minutes. Excess chlorine was removed from the mixture under reduced pressure at the rotary evaporator for 5 minutes at room temperature. The solvent was then removed at the rotary evaporator at 30-40°C. The residual light orange oil was then distilled under reduced pressure yielding morpholine-N-sulphenyl chloride as a yellow oil, (2.94g; 48%), b.p. 80°C / 0.1 mm, [lit. b.p.[73] 58-60°C / 0.6 mm]

Chloramine

A solution of chloramine in ether was prepared by reaction of aqueous ammonia with sodium hyprchlorite by the method of Hauser.[108]

Phenyl iodosodiacetate

This compound was prepared from iodobenzene in 26% yield, m.p. 157-9°C, [lit. m.p.[104] 160.5°C] by the method outlined in Vogel's Handbook.[109]

Thiocyanogen

Solutions of thiocyanogen in chloroform were prepared by reaction of lead (II) thiocyanate with bromine by the method outlined in "Organic Reactions".[110]

Sodium N,N-diisopropyldithiocarbamate

This compound was prepared by reaction of diisopropylamine with carbon disulphide in aqueous sodium hydroxide in 51% yield by the method of Klopping.[111]

Tetraethylammonium N,N-dimethyldithiocarbamate

This compound was prepared by reaction of tetraethylammonium chloride with sodium dimethyldithiocarbamate in 92% yield by the method of Davis.[44]

Tetraethylammonium N,N-diisopropyldithiocarbamate

Tetraethylammonium chloride (1.84g; 0.01 mole) and sodium diisopropyldithiocarbamate (2.00g; 0.01 mole) were stirred together in ethanol (40 ml) for 1 hour. The precipitate of sodium chloride was filtered off. Removal of the solvent left a pale green oil. The oil was dissolved in a small volume of acetone and ether was added until the precipitation of cream coloured solid was complete. The precipitate was filtered off, yielding tetraethylammonium diisopropyldithiocarbamate (1.70g; 55%). The compound was hygroscopic and was stored in a desiccator over calcium chloride.

Tetraethylammonium O,O-diethyl dithiophosphate

A solution of sodium ethoxide prepared from sodium (0.175g; 7.6 mmole) and ethanol (10 ml) was added to O,O-diethyl hydrogen dithiophosphate (1.41g; 7.6 mmole). Tetraethylammonium chloride (1.40g; 7.6 mmole) in ethanol (20 ml) was added and the

mixture was stirred for 10 minutes. The mixture was filtered to remove the precipitate of sodium chloride and the filtrate was evaporated yielding a pale orange solid. The crude product was recrystallised from acetone, yielding tetraethylammonium diethyl dithiophosphate as white needles, (1.61g; 67%), m.p. 130-2°C.

Bis(N,N-diisopropyldithiocarbamato)palladium (II)

A solution of sodium tetrachloropalladate (0.294g; 1 mmole) in methanol (20 ml) was added dropwise to a stirred solution of sodium N,N-diisopropyldithiocarbamate (0.80g; 4 mmole) in methanol (40 ml). The resulting yellow precipitate was filtered off and dried *in vacuo* yielding bis (N,N-diisopropyldithiocarbamato) palladium (II), (0.41g; 89%), m.p.> 300°C. Recrystallisation from benzene gave the analytically pure product.

I.R. SPECTRUM: ν max 1495, 1335, 1190, 1145, 1035, 935, 905, 840, 795 cm^{-1}

MASS SPECTRUM: m/e 458 (M^+,Pd), 282 (Pd)

ANALYSIS: Found: C,36.9%; H,6.2%; N,6.2%

$C_{14}H_{28}N_2Pd\ S_4$ requires: C,36.7%; H,6.1%; N,6.1%

Bis (p-perthiotoluato)zinc (II)

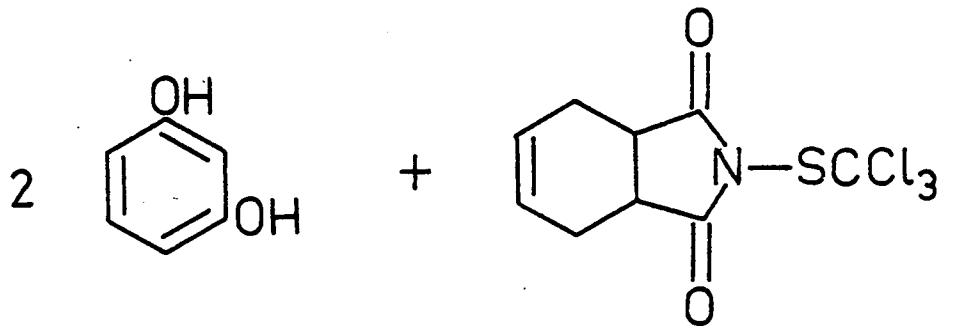
This compound was prepared by reaction of p-tolualdehyde and ammonium disulphide followed by treatment with zinc chloride in 26% yield, m.p. 190-2°C [lit. m.p.[70] 192-3°C] by the method of Fackler.[70]

Palladium acetate

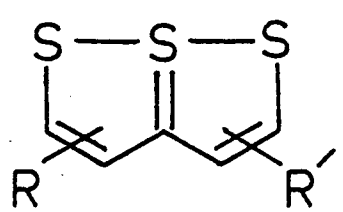
This compound was prepared from precipitated palladium metal in 68% yield, decomp. 205°C, [lit.[112] decomp.205°C], by the method of Wilkinson.[112]

Methanolic sodium or lithium tetrachloropalladate solution

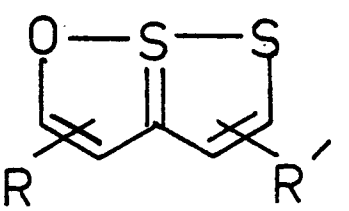
Methanolic solutions were prepared by heating under reflux a suspension of sodium or lithium chloride (2 molar equivalents) and palladium chloride (1 molar equivalent) in methanol until a homogeneous dark brown solution formed.



(272)



(273)



(274)

Appendix I

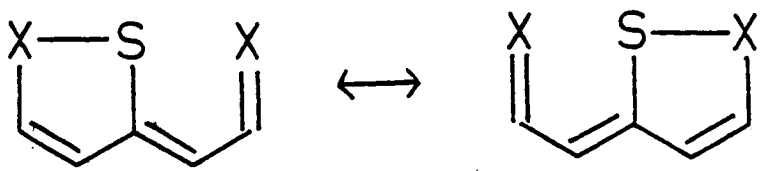
Attempted Syntheses of 1,6-Dioxa-6a-Thiapentalenes from 1,3-Disubstituted Allenes

The first synthesis of a dioxathiapentalene was reported in 1969 by Pomerantz et al[113a] who obtained a yellow solid from the reaction of resorcinol with Captan [N-(trichloromethylthio)-4-cyclohexene-1,2-dicarboxamide]. The structure of this product was later established[113b] as [1,2]benzoxathiolo[2,3-b][1,2]-benzoxathiole-6-S^{IV} -3,9-diol (272).

The dioxathiapentalenes and their earlier known structural analogues, the trithiapentalenes (273) and oxadithiapentalenes (274), have attracted considerable attention over the years since the bonding in these compounds is of an unusual type. The first views[114] on the bonding in such systems involved the concept of single-bond - no bond resonance, e.g. (275) ↔ (276). There has been no proof of such contributing resonance structures, or even of a rapid equilibrium between valence isomers, and perhaps the best explanation of the bonding in these systems, taking 1,6,6aλ^4 - trithiapentalene as a typical example is the following:

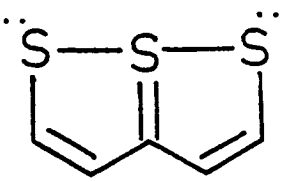
Each sulphur atom retains two unshared 3s electrons. The terminal sulphur atoms contribute two electrons to σ -bonds and two to the π -system, and the central sulphur atom contributes three electrons to σ -bonds and one to the π -system. Together with the five π -electrons from the carbon atoms, the π -electrons from the sulphur atoms form a 10 π - electron system which may be represented by the structures (277) or (278).

The σ -bonding in the linear three sulphur sequence is

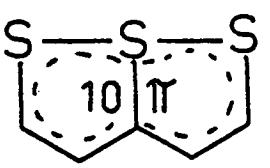


(275) (276)

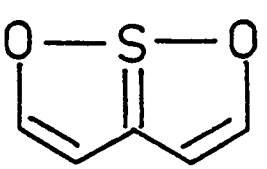
X = O or S



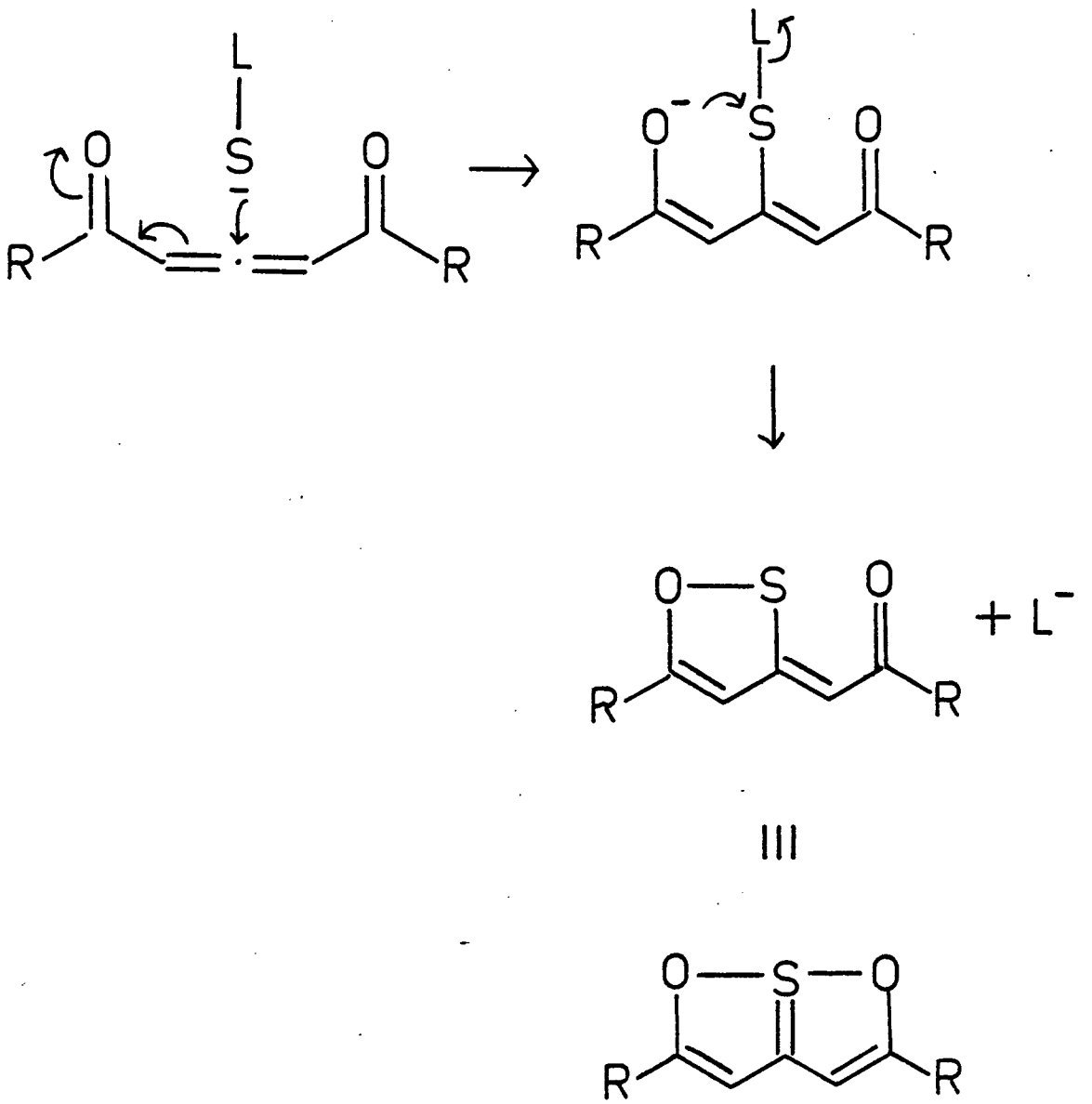
(277)



(278)



(279)

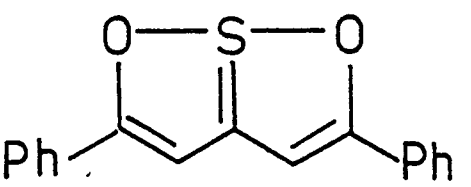


L = leaving group

Scheme (xviii)

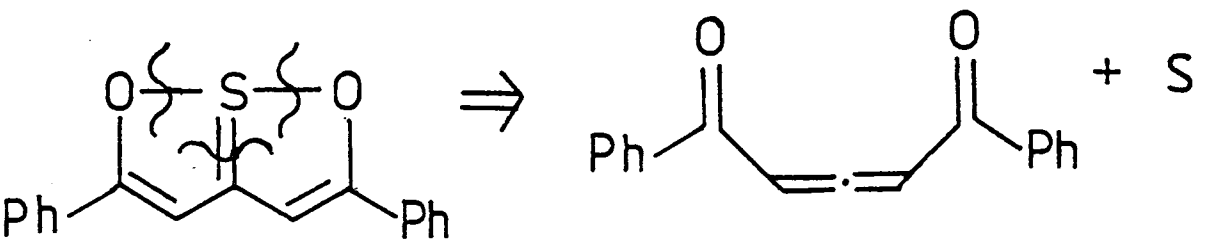
(Scheme XVIII).

Preliminary studies by Leaver and Munro[119] have demonstrated the feasibility of this scheme as exemplified in a synthesis of 2,5-diphenyl-1,6-dioxa-6a λ^4 -thiapentalene (283) from 1,3-dibenzoylallene. In the following discussion, an account is given of further investigations which were carried out in this field.

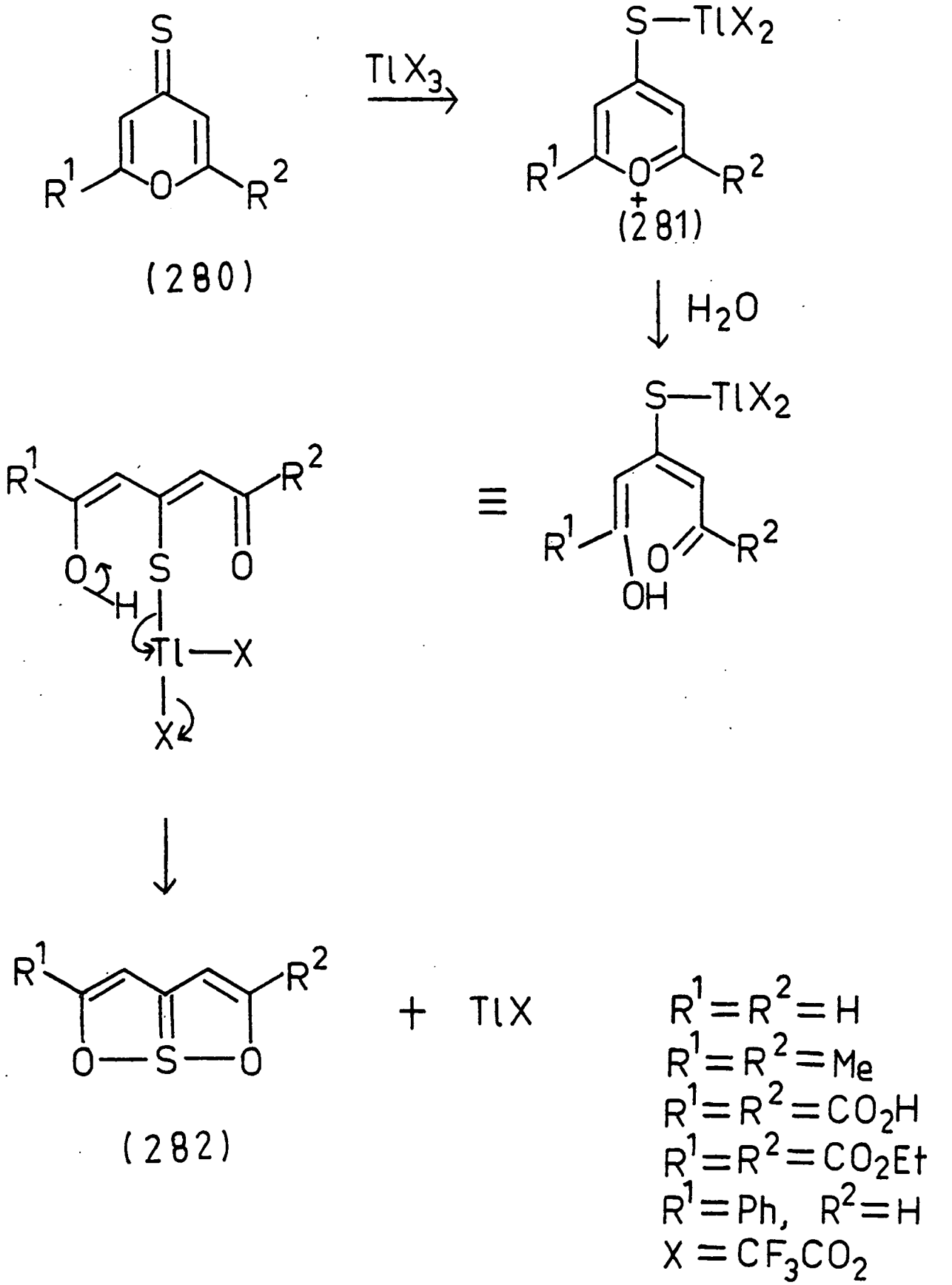


(283)

By a simple disconnection of 2,5-diphenyl-1,6-dioxa-6a λ^4 -thiapentalene (283), it is seen that in principle it would be possible to synthesise this molecule from 1,3-dibenzoylallene and elemental sulphur.



(283)


S
TlX_3
S—TlX_2
R^1
R^2
O
+
(280)
(281)
H_2O
S—TlX_2
OH
≡
H
Tl—X
X
(282)
+ TlX
$R^1=R^2=H$
$R^1=R^2=Me$
$R^1=R^2=CO_2H$
$R^1=R^2=CO_2Et$
$R^1=Ph,\ R^2=H$
$X=CF_3CO_2$

Scheme (xvii)

generally believed to be of a rather unusual type, analogous to that in the I_3^- ion. There are three σ -orbitals, one bonding, one non bonding and one antibonding, and since four electrons are available, this system is described as an "electron-rich three-centre bond.[115]

Pedersen et al[116] have presented microwave spectroscopic evidence that the structure of 1,6-dioxa-6aλ^4-thiapentalene (279) is of the same type. Their observations indicated that it was a planar molecule with C_{2v} symmetry.

Complementary evidence for the C_{2v} symmetry of this molecule has been obtained recently from ^1H n.m.r. studies in a nematic phase.[117]

Apart from the synthesis of dioxathiapentalenes via fusion of resorcinol and captan, the only other route to these compounds is via reaction of 4H-pyran-4-thiones (280) with thallium (III) trifluoroacetate[118] (Scheme (XVII)).

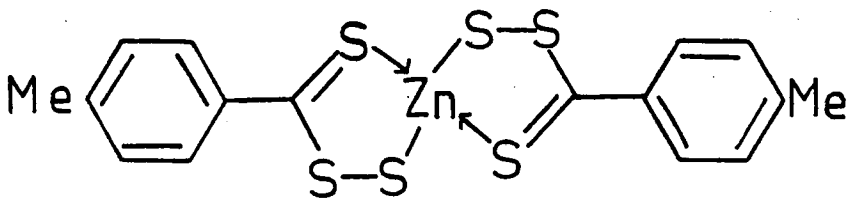
The pyrylium salt (281) formed in the reaction is ring-opened by water and the resulting intermediate then eliminates thallium (I) trifluoracetate, to yield the dioxathiapentalene (282). However, a limitation of this method is that it is not applicable to the synthesis of 2,5-diaryl substituted products.

One synthetic method which has not been investigated involves the reaction of sulphur nucleophiles with 1,3-disubstituted allenes containing carbonyl groups in both terminal positions. In this synthesis one can envisage attack on the central carbon of the allene by the nucleophile with transfer of the negative charge from the nucleophile to the oxygens and displacement of a good leaving group from the nucleophile

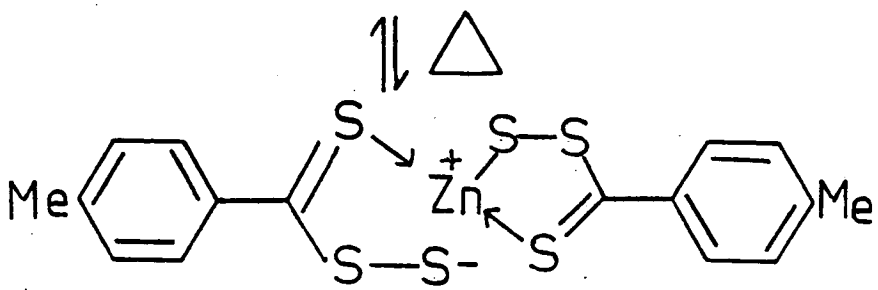
This attractive synthesis is ruled out on consideration of the reaction conditions which would be required for such a transformation. In order for elemental sulphur to act as a nucleophile, opening of the S_8 ring would have to occur, thus generating an intermediate of the type $\overset{+}{S}-S_6-\overset{-}{S}$ (or a diradical). This ring opening would not occur at temperatures low enough to compete with the known[120,121] dimerisation of 1,3-dibenzoylallene which occurs even at moderate temperatures. It was therefore essential, in order that sulphur be transferred to the allene, that the chosen reagent should attack the allene under very mild conditions (eg., at room temperature), otherwise the dimer would be the reaction product.

In confirmation of the preliminary work of Leaver and Munro,[119] it was found that the sulphur-rich complex bis (p-perthiotoluato)zinc (II) (204) [70,71] was effective in inserting a sulphur atom into dibenzoylallene. Reaction occurred upon warming a two-fold excess of the allene with the zinc complex in benzene, forming 2,5-diphenyl-1-6-dioxa-6aλ^4thiapentalene in 15% yield. No improvement in yield was obtained upon doubling the concentration of zinc complex. Satisfactory spectroscopic and analytical data were obtained for the dioxathiapentalene. The mechanism of this reaction is likely to involve chelate ring opening in the complex to generate the nucleophilic sulphur species (284) which then attacks the central carbon of the allene, leading ultimately to the dioxathiapentalene (Scheme XIX).

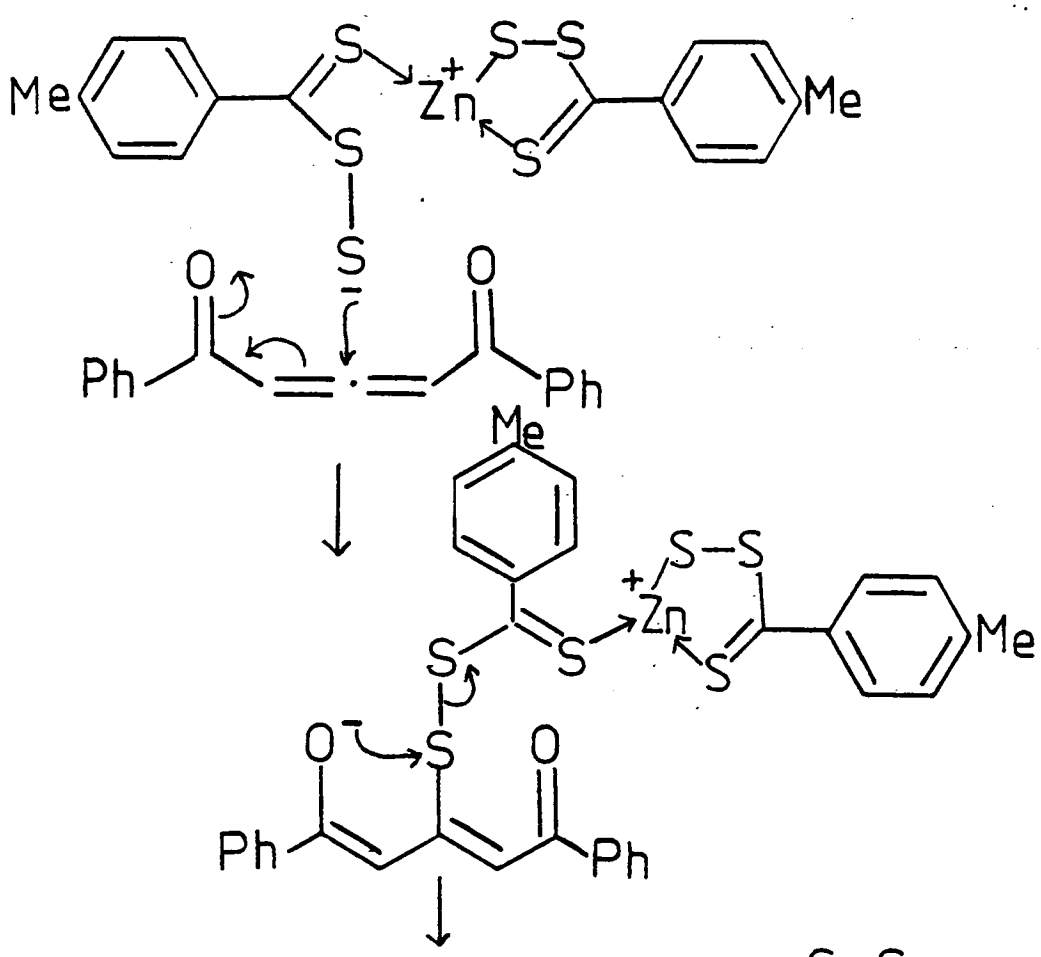
An alterative route to the 1,6-dioxa-6aλ^4-thiapentalene (283), in principle capable of extension to the synthesis of its dioxaselena-analogue was investigated. It was envisaged that the

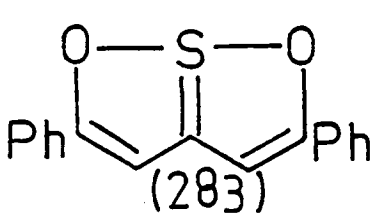


(204)



(284)





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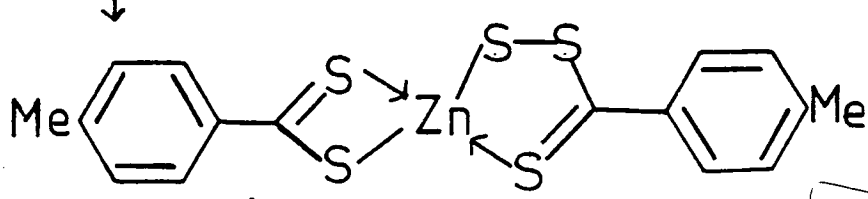
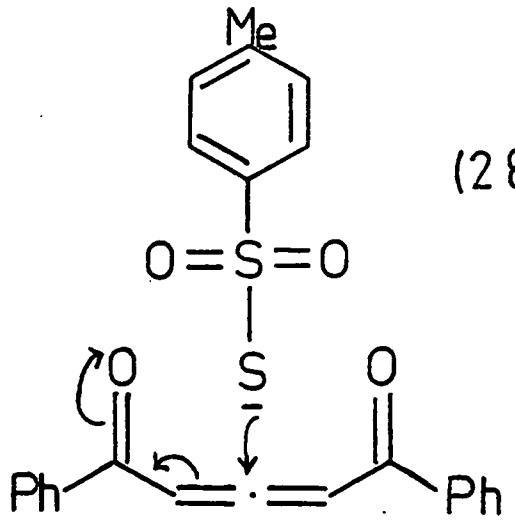
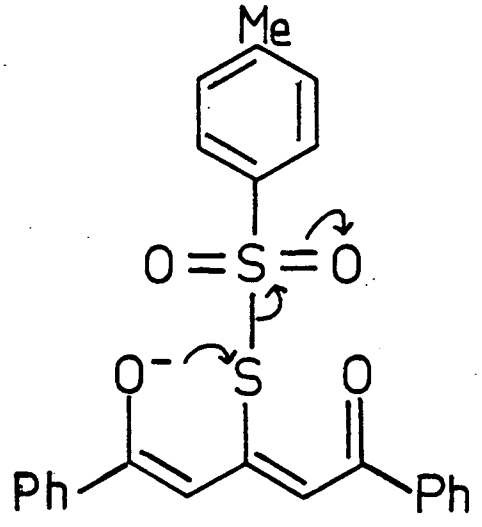


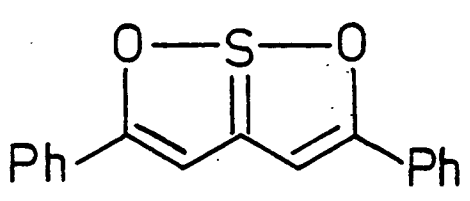
Scheme (xix)



(285)



(286)



(283)

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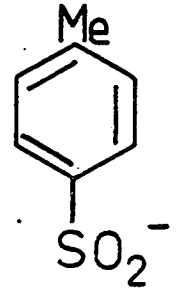
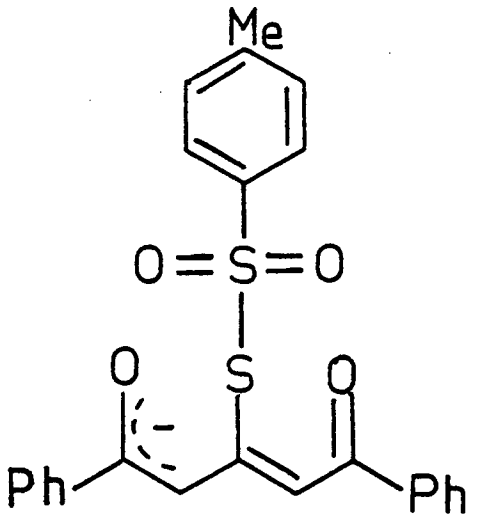


Scheme (xx)



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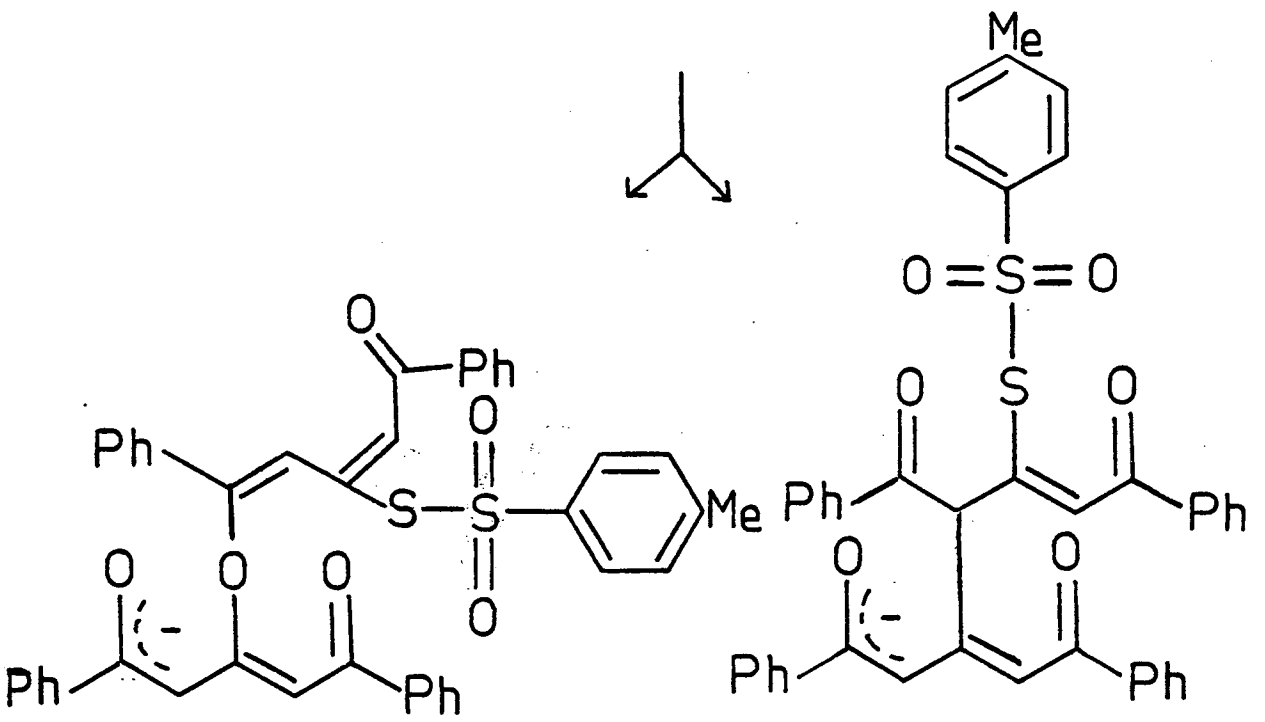


polymer

polymer

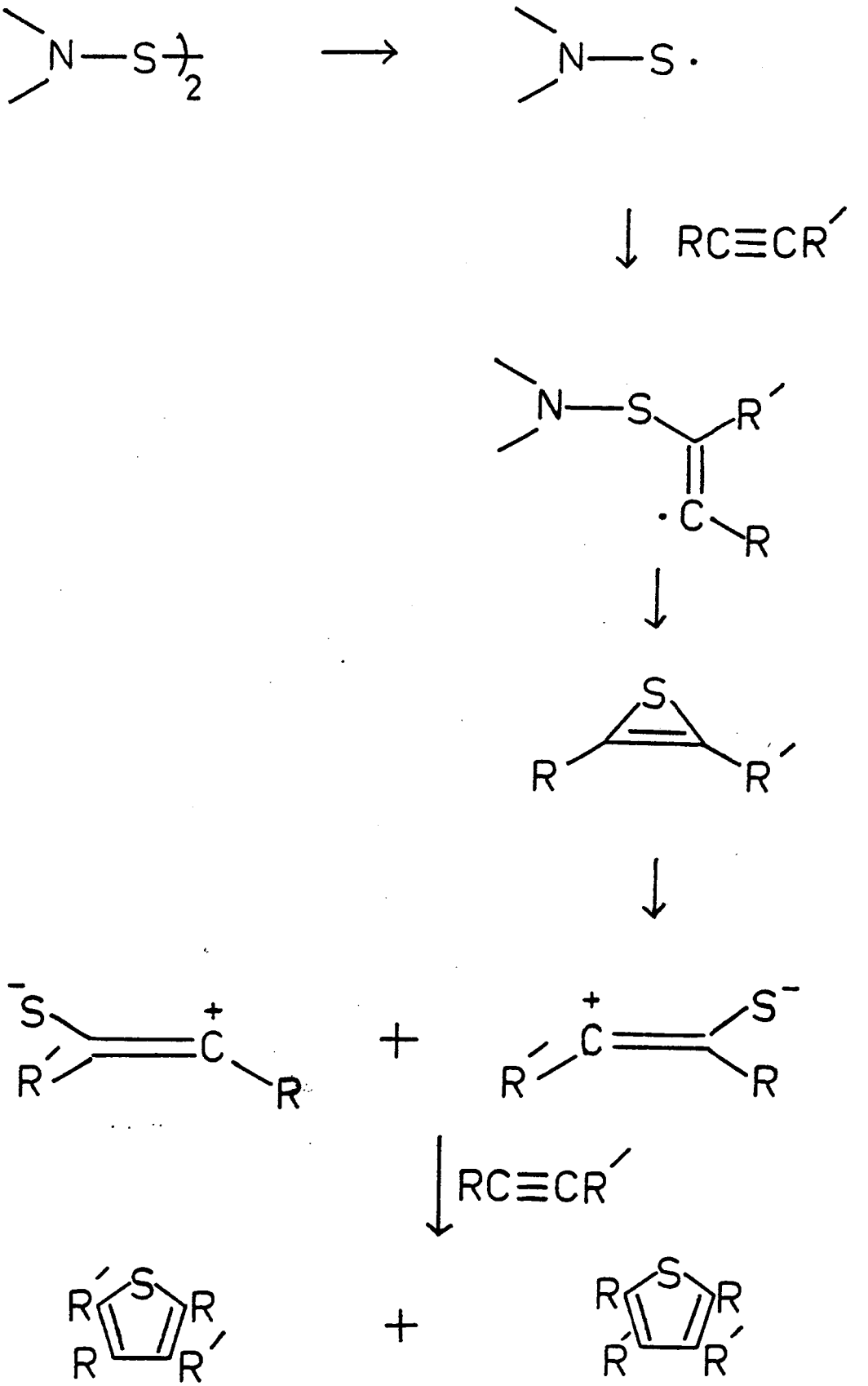
Scheme (xxi)

p-toluenethiosulphonate anion (285) would act as the nucleophile and that a p-toluenesulphinate anion would be expelled as the leaving group (Scheme XX).

The tetraethylammonium salt of (285) was chosen since it was soluble in aprotic solvents, particularly chlorinated hydrocarbons. However, it was found that admixture of the reactants in chloroform resulted in the immediate formation of a dark brown tar. A possible explanation of this result might be that the p-toluenesulphinate leaving group is not ejected from the intermediate (286) and that polymerisation then occurs by further reaction of this intermediate with dibenzoylallene. Since (286) is a delocalised enolate type anion, bond formation could occur on either oxygen or carbon (Scheme XXI).

A similar type of reaction of dibenzoylallene with potassium thiocyanate was attempted. In this case the transfer of sulphur and elimination of cyanide ion was envisaged. However, as in the previous reaction, a brown tar was formed immediately upon admixture of the reactants in the presence of 18-crown-6 in chloroform. In view of the failure of the reactions of dibenzoylallene with anionic sulphur transfer reagents, the feasibility of sulphur transfer via a radical species was investigated.

The formation of thionitroxyl radicals in the thermolysis of bis-amine disulphides has been detected by e.s.r.[69] Such radicals are capable of transferring sulphur to acetylenes, presumably to generate thiirene intermediates, which then react further with the acetylene to yield thiophenes[68] (Scheme XXII). In an attempt to utilise bis-amine disulphides in the synthesis of

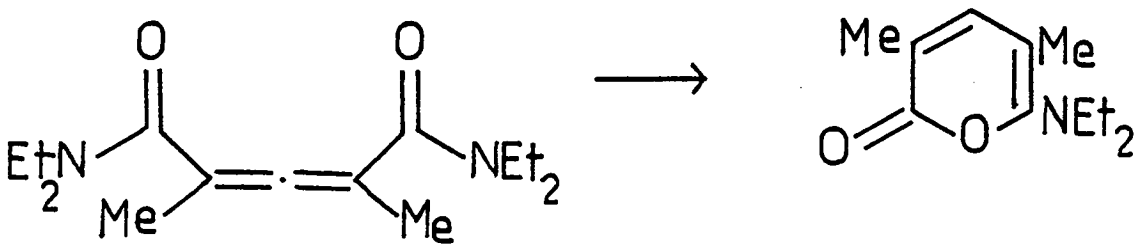


Scheme (xxii)

dioxathiapentalenes, the reagents di(N-morpholinyl)disulphide, di (N-pyrrolidinyl)disulphide and di(N-phthalimidyl)disulphide were prepared and allowed to react with dibenzoylallene in benzene.

It was found that in each case the expected 2,5-diphenyl-1,6-dioxa-6aλ^4-thiapentalene was formed, but only in traces, as detected by mass spectroscopy. Apart from polymeric material, the only other substances recovered from these reaction mixtures were sulphur and unreacted bis-amine disulphide. The failure of the disulphides to transfer a sulphur atom to dibenzoylallene in acceptable yield was attributed to the dimerisation of dibenzoylallene which occurred in preference to the desired reaction. The thermal instability of dibenzoylallene evidently rendered it unsuitable for use in reactions with sulphur-transfer reagents and therefore prompted investigations into the reactions of these reagents with more thermally stable allenes.

In contrast to dibenzoylallene, N,N,N',N'-tetraethyl-2,4-dimethylpenta-2,3-dienediamide (287)[122] is much more thermally stable and is converted into the α-pyrone (288) only at temperatures above 180°C.[123]



(287) (288)

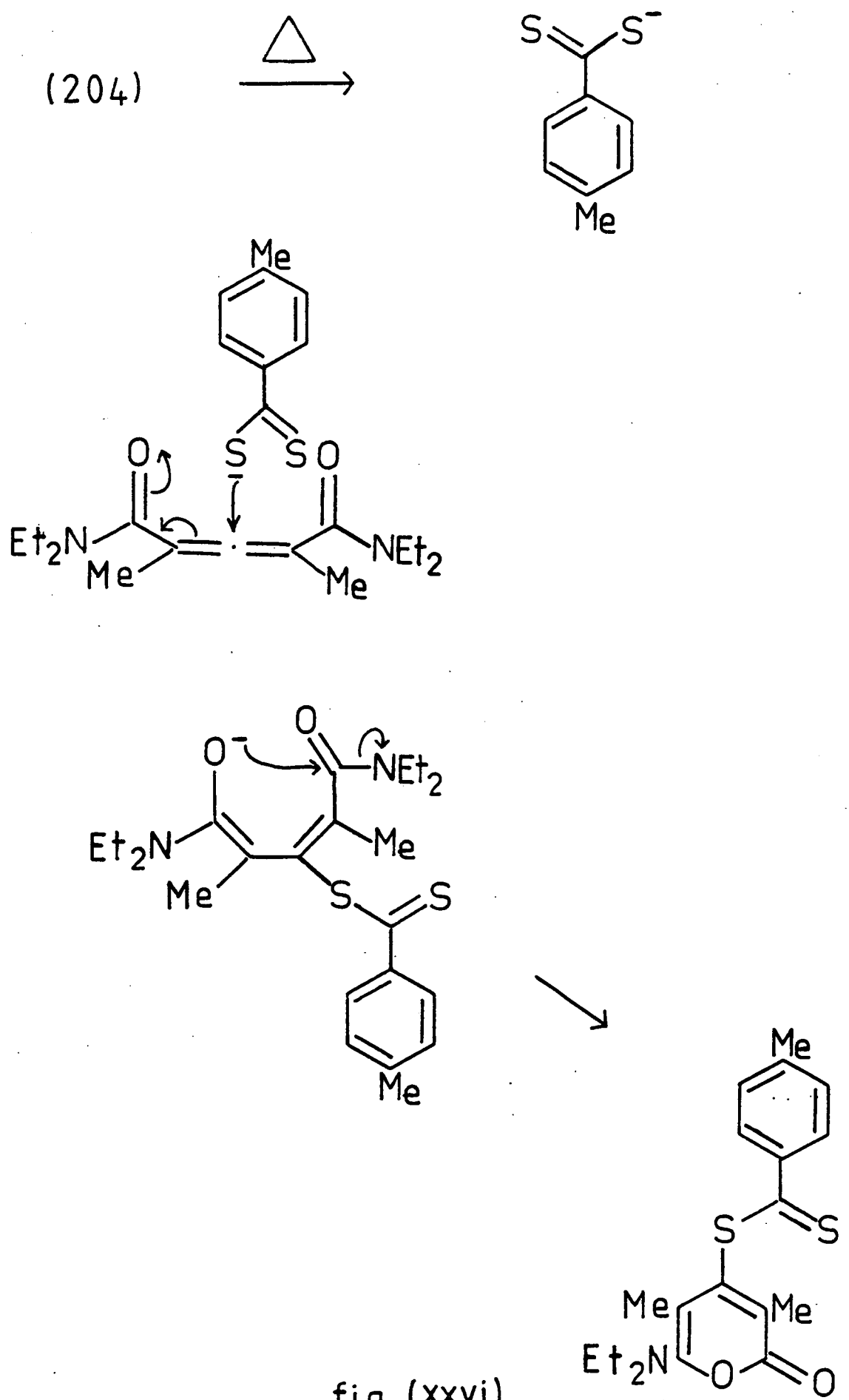
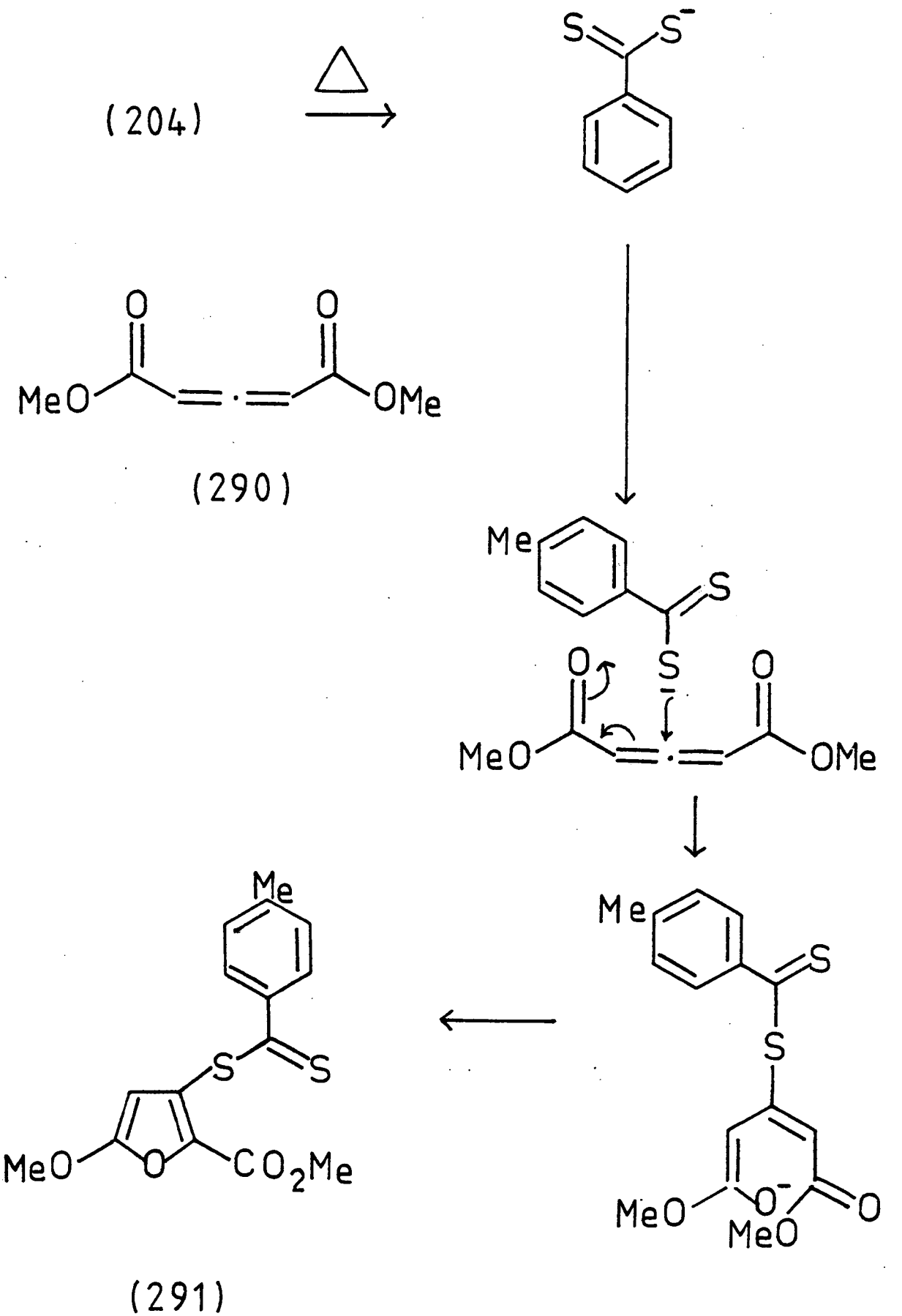

(204)
Δ
S
S⁻
Me
Me
O
S
S
O
Et2N
Me
Me
NEt2
O⁻
O
NEt2
Et2N
Me
Me
S
S
Me
Me
S
S
Me
Me
Et2N
O
O
(289)

fig (xxvi)

Surprisingly the allene diamide did not react in the expected manner with bis (p-perthiotoluato)zinc (II). Upon heating the reactants together in boiling benzene for 6 hours, the allene diamide was recovered in 85% yield. The zinc complex had decomposed somewhat after this time to an unidentified orange-red solid, the mass spectrum of which showed the presence of the perthiotoluato ligand. More interestingly, a small amount of a substance was isolated which, on the basis of its mass spectrum, was thought to have the α-pyrone structure (289), [m/e 361 (M^+); 261 (M^+-Et_2NCO); 135 (p-$MeC_6H_4CS^+$)]. A possible mechanism for the formation of the pyrone is shown in figure (XXVI).

The greatest contrast in behaviour between the allene diamide and dibenzoylallene was observed in the reaction of the former with tetraethylammonium p-toluenethiosulphonate. The allene diamide was recovered in 60% yield after heating with the thiosulphonate in boiling 1,1,2-trichloroethane (115°C) for 5 hours. Partial decomposition of the thiosulphonate occurred to yield a small amount of a substance, which on the basis of its mass spectrum was thought to be di-p-tolyl disulphide [m/e 236 (M^+), 123, 91].

As further evidence to illustrate the inertness of the allene diamide towards nucleophilic attack, it was found that heating the allene and sulphur together in boiling xylene had no effect. Both reactants were recovered almost quantitatively. The inertness of this allene towards nucleophilic attack is presumably a consequence of the less electrophilic nature of the central carbon of the allene, electron withdrawal from this centre by amide carbonyl groups being much less effective than by ketonic carbonyl groups as in dibenzoylallene.



(291)

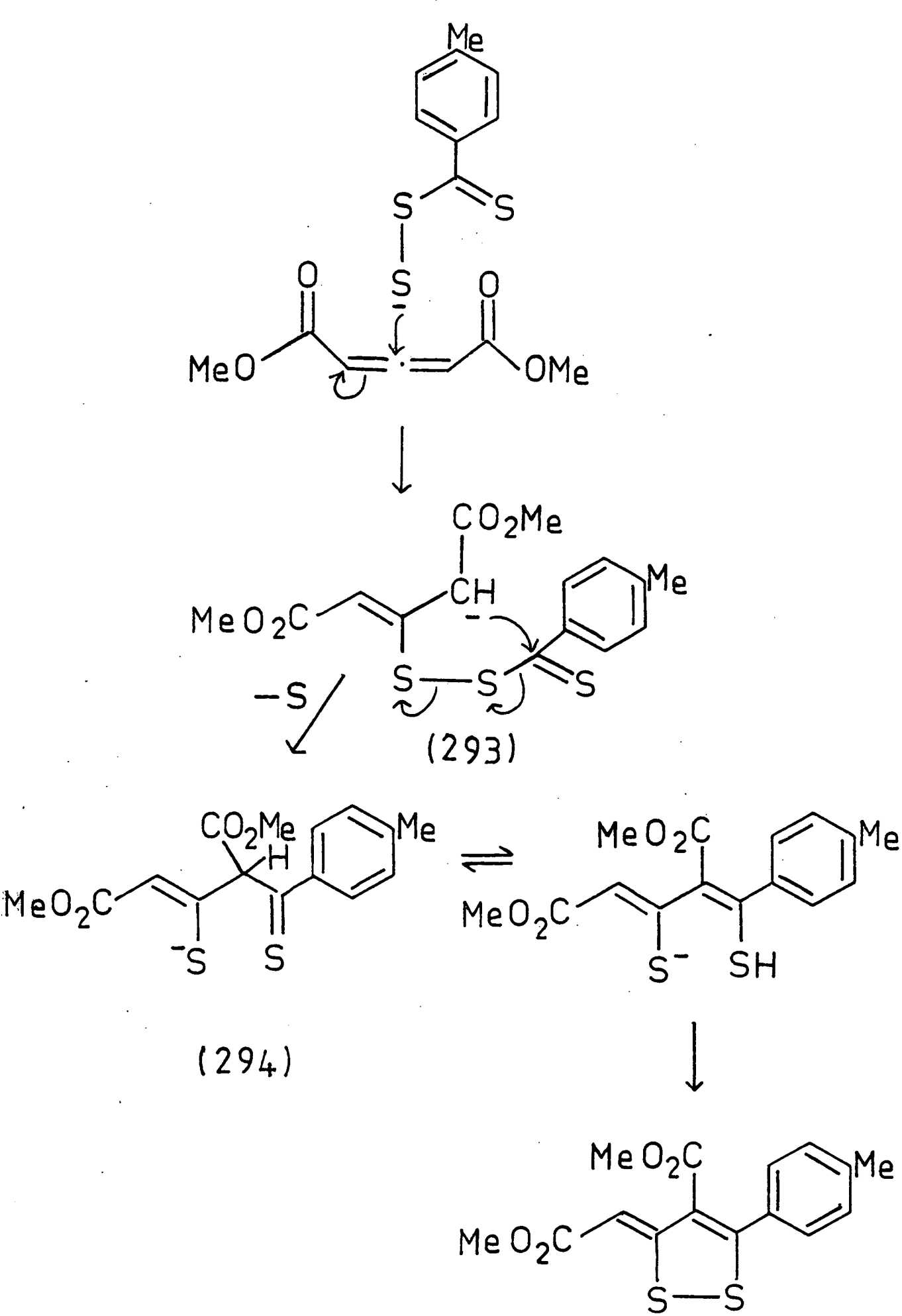
fig (xxvii)

The electron withdrawing effect of an ester carbonyl group is generally thought to be intermediate between that of its ketone and amide counterparts. It was thought, therefore, that an allene diester might react with a sulphur-transfer reagent in the desired manner, hopefully in acceptable yield. For this purpose, 1,3-dimethoxycarbonylallene (290) was prepared and treated with bis (p-perthiotoluato)zinc (II).

Upon heating the reactants together in benzene for 3 hours, an orange insoluble solid was formed, presumably a zinc complex. The filtered reaction mixture was chromatographed to yield a yellow solid, the mass spectrum of which showed ion peaks at m/e 322, 291 (M^+-MeO), 265/264, and 135 ($p\text{-}MeC_6H_4CS^+$), indicating that the desired product had not been formed.

It was initially thought that this product might be 2-methoxycarbonyl-3-p-methylthiobenzoylthio)-5-methoxyfuran (291). A possible mechanism for the formation of this compound is shown in figure (XXVII). The oxidative cyclisation (a formal elimination of hydride ion) shown in the last stage of the reaction sequence might be facilitated by the presence of free sulphur.

However, the ^1H n.m.r. spectrum of the compound was not in accord with the furan structure since the expected downfield shift of the ortho-aryl protons (as a consequence of electron withdrawal by the thiocarbonyl group) was not observed. The observed closely spaced multiplet in the aromatic region (almost a broad singlet) suggested that no thiocarbonyl group was present. In the aliphatic region of the spectrum, two three-proton singlets (OMe) were observed at δ 3.77 and δ 3.62 in addition to an aryl methyl signal at δ 2.38. On the basis of these facts, an alternative structure



Scheme (xxiii) (292)

(292) was proposed for the reaction product. This product, 3-methoxycarbonylmethylene-4-methoxycarbonyl-5-p-tolyl-1,2-dithiole, was thought to be formed according to Scheme (XXIII). A perthio-anion attacks the central carbon of the allene. The carbanion (293) thus generated then attacks the thiocarbonyl unit to form the intermediate (294) via loss of a sulphur atom. Enolisation of (294) is then followed by oxidative cyclisation to the dithiole (292).

Complementary evidence for the structure (292) was obtained from ^{13}C n.m.r. studies. The key features of the spectrum (apart from the aryl carbon signals) were peaks due to two ester methyl carbons at 52.3 and 51.6 p.p.m. and a methine (=CH—) carbon at 101.6 p.p.m. All but two quaternary carbons were observed. Presumably the signals due to C-4 and C-5 were missing on account of there being no hydrogens near to these nuclei. The absence of a thiocarbonyl carbon (which is generally observed in the region of 200 p.p.m.) was further evidence against the initially proposed furan structure.

In conclusion, in view of the lack of success of these reactions, there would seem to be little point in pursuing further the reactions of electrophilic allenes with sulphur-transfer reagents.

Experimental

Reactions of dibenzoylallene

(a) with bis(p-perthiotoluato)zinc(II)

Dibenzoylallene (1.0g; 0.004 mole) in dry benzene (10 ml) was added to a stirred suspension of bis (p-perthiotoluato)zinc (II) (0.93g; 0.002 mole) in dry benzene (40 ml) under nitrogen. The reaction mixture was then heated slowly to the boiling point. After being allowed to cool, the solution was filtered and the dark yellow precipitate was collected. Recrystallisation from ethyl acetate yielded 2,5-diphenyl-1,6-dioxa-6a λ^4-thiapentalene as a yellow solid (0.11g; 10%) m.p. 226-229°C. Chromatography on alumina of the filtered reaction mixture eluting with toluene yielded a further 55mg of product, m.p. 225-8°C. (Combined yield = 15%).

I.R. SPECTRUM: ν max 1535, 1180, 1090, 770, 695 cm^{-1}

^1H n.m.r. SPECTRUM: (d_6-Me_2SO) δ 8.0-7.9 (m,4H, ortho-phenyl protons); δ 7.58 (s, 2H,H-3/H-4); δ 7.55-7.45 (m,6H, meta-and para-phenyl protons).

MASS SPECTRUM: m/e 280 (M^+), 252 (M^+-CO), 105, ($PhCO^+$), 77 (Ph^+)

ANALYSIS: Found: C,72.8%; H,4.3%

$C_{17}H_{12}O_2S$ requires: C,72.8%; H,4.3%

(b) with tetraethylammonium p-toluenethiosulphonate

A solution of dibenzoylallene (0.50g; 0.002 mole) in chloroform (10 ml) was added to a solution of tetraethylammonium p-toluenethiosulphonate (0.64g; 0.002 mole) in chloroform (10 ml), resulting in the immediate formation of a deep red solution. The reaction mixture was heated under reflux for 4 hours, during which time, no further chemical reaction was observed. Evaporation of

the solvent yielded a dark brown oil which could not be crystallised and was not amenable to chromatography.

(c) with potassium thiocyanate

Dibenzoylallene (0.30g; 0.0012 mole) was added to a stirred mixture of potassium thiocyanate (0.12g; 0.0012 mole) and 18-crown-6 (0.01g) in chloroform (25 ml). A deep red solution formed immediately. The reaction mixture was then heated under reflux for 1 hour, during which time, no further chemical reaction was observed. Evaporation of the solvent yielded a dark brown oil which could not be crystallised and was not amenable to chromatography.

(d) with di(N-morpholinyl)disulphide

Dibenzoylallene (0.5g; 0.002 mole) and di(N-morpholinyl) disulphide (0.48g; 0.002 mole) were stirred together in benzene (20 ml) under nitrogen. The reaction mixture was then slowly heated to the boiling point and maintained under reflux for 5 hours. The evaporated reaction mixture was chromatographed on alumina. Eluting with ether yielded a yellow solid (12 mg), m.p. 120-5°C which was shown by mass spectroscopy to contain the dioxathiapentalene (m/e 280) and elemental sulphur. Further chromatography yielded di(N-morpholinyl)disulphide (0.15g) and small quantities of brown oils which could not be purified.

(e) with di(N-pyrrolidinyl)disulphide

This reaction was carried out on the same scale and under the same conditions as those of the preceding reaction. Chromatography on alumina, eluting with light petroleum - ether (7 : 3), yielded a sticky yellow-brown solid (38 mg) which was shown by mass spectroscopy to contain the dioxathiapentalene (m/e 280) and

elemental sulphur. Further chromatography yielded only small quantities of brown oils which could not be purified.

(f) with di(N-phthalimidyl)disulphide

This reaction was carried out on the same scale and under the same conditions as those of reaction (d). The reaction mixture was worked up after heating under reflux for 2 hours. Chromatography on alumina, eluting with light petroleum - ether (1 : 1) yielded a red-brown gum (5 mg) which was shown by mass spectroscopy to contain the dioxathiapentalene (m/e 280). Further chromatography yielded only small quantities of brown oils which could not be purified.

Reactions of N,N,N'N' -tetraethyl-2,4-dimethylpenta-2,3-dienediamide

(a) with bis (p-perthiotoluato)zinc(II)

A stirred suspension of the allene (1.0g; 0.0038 mole) and bis (p-perthiotoluato)zinc(II) (0.87g; 0.0019 mole) in dry benzene (50 ml), under nitrogen, was heated slowly to the boiling point, and maintained under reflux for 6 hours. The reaction mixture was cooled and filtered to yield an orange-red solid (0.12g), m.p. 80-4°C, the mass spectrum of which showed ion peaks at m/e 135 (p-thiotoluoyl) and 199 (p-thiotoluoyldithio). The filtrate was evaporated and the residue was chromatographed on alumina. Eluting with dichloromethane yielded an orange-red gum (30 mg), the mass spectrum of which showed ion peaks at m/e 361, 261, 234 and 135. Continued elution with dichloromethane-methanol yielded the unreacted allene (0.85g).

(b) with tetraethylammonium p-toluenethiosulphonate

The allene (0.20g; 0.75 mmole) and tetraethylammonium p-toluenethiosulphonate (0.24g; 0.75 mmole) were heated together, under

reflux, in 1,1,2-trichloroethane (20 ml), under nitrogen for 5 hours. The reaction mixture was evaporated and the residue was chromatographed on alumina. Eluting with ether yielded a dark yellow gum (30 mg), the mass spectrum of which showed ion peaks at m/e 246, 123 and 91. Continued elution with ethyl acetate yielded the unreacted allene (0.12g).

(c) with elemental sulphur

The allene (0.30g; 1.2 mmole) and sulphur (0.29g; 1.2 mmole) were heated together in refluxing xylene (25 ml), under nitrogen, for 4 hours. The reaction mixture was evaporated and the residue was treated with acetone and filtered to yield sulphur (0.28g). The filtrate yielded the allene quantitatively upon evaporation.

Reaction of 1,3-dimethoxycarbonylallene with bis (p-perthiotoluato) zinc(II)

The allene (0.25g; 1.6 mmole) and bis (p-perthiotoluato) zinc(II) (0.37g; 0.8 mmole) in dry benzene (25 ml) were slowly heated to the boiling point, under nitrogen, and kept under reflux for 3 hours. The reaction mixture was cooled and filtered to yield an orange solid (25 mg), m.p. 125-8°C. The solid was washed with ethyl acetate and the washings were combined with the reaction mixture filtrate. The combined organic solutions were evaporated and the residue was chromatographed on alumina. Eluting with ether - light petroleum (1 : 1) yielded 3-methoxycarbonyl-methylene-4-methoxycarbonyl-5-p-tolyl-1,2-dithiole as yellow needles, (30 mg; 5%), m.p. 125-8°C (from benzene).

I.R. SPECTRUM: ν max 1720 (C= O), 1640, 1320, 1190, 800, 720 cm^{-1}

^1H n.m.r. SPECTRUM: ($CDCl_3$) δ 7.3 - 7.1 (m,4H, aryl ring protons);

δ 6.34 (s, 1H, 1 olefinic proton); δ 3.77 (s, 3H, 3 methoxycarbonyl protons); δ 3.62 (s, 3H, 3 methoxycarbonyl protons); δ 2.38 (s, 3H, $ArCH_3$)

^{13}C n.m.r. SPECTRUM: ($CDCl_3$) 170.1, 165.5, 164.5 (3 quaternary carbons); 140.9, 129.4, 127.7, 125.2 (4 aryl ring carbons); 101.6 ($-\underline{C}H=$); 52.3, 51.6 (2 X $CO_2\underline{C}H_3$); 21.3 ($ArCH_3$).

MASS SPECTRUM: m/e 322 (M^+), 291 (M^+-MeO), 265, 264, 135 ($\underline{p}$-$MeC_6H_4CS^+$)

ANALYSIS: Found: C,56.1%; H,4.3%

$C_{15}H_{14}O_4S_2$ requires: C,55.9%; H,4.3%

1,3-Dibenzoylallene was prepared from 1,5-diphenylpent-2-yne-1,5-diol in 36% yield, m.p. 81-3°C (d), [lit. m.p.[120] 84°C (d)] by the method of Bardone - Gaudemar.[120]

N,N,N',N'-Tetraethyl-2,4-dimethylpenta-2,3-dienediamide was prepared from 1-(N,N-diethylamino)propyne in 63% yield, b.p. 140-5°C / 0.1 mm, by the method of Ficini.[122]

1,3-Dimethoxycarbonylallene was prepared from diethyl acetone-1,3-dicarboxylate in 41% yield b.p. 120°/0.2 mm, [lit. b.p.[124] 58°/ 0.02 mm], by the method described in "Organic Synthesis".[124]

Bis (p-perthiotoluato)zinc(II) was prepared by the method of Fackler.[70]

Di(N-morpholinyl)disulphide was prepared by an adaption of the method of Danen and Newkirk.[69]

Di(N-pyrrolidinyl)disulphide was prepared from pyrrolidine and disulphur dichloride in 33% yield, m.p. 48-9°C, [lit. m.p.[69] 50-1°C], by the method of Danen and Newkirk.[69]

Di(N-phthalimidyl)disulphide was prepared by the method of Kalnins.[107]

Tetraethylammonium p-toluenethiosulphonate

Sodium p-toluenethiosulphonate (6.3g; 0.03 mole), prepared by the method of Hayashi et al,[125] was dissolved in hot absolute alcohol (100 ml) and added to a solution of tetraethylammonium chloride monohydrate (5.4g; 0.03 mole) in absolute alcohol (10 ml). The mixture was then refluxed for 1.5 hr. Filtration of the reaction mixture, followed by removal of the solvent and trituration of the oily product from light petroleum, gave the tetraethylammonium salt as a white solid (8.97g; 95%). The anhydrous product was obtained by drying in a desiccator to constant weight.

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CYCLOPALLADATION AS A ROUTE TO CATIONIC CONDENSED RING SYSTEMS CONTAINING ISOTHIAZOLE OR 1,2-DITHIOLE NUCLEI

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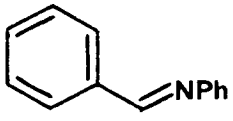
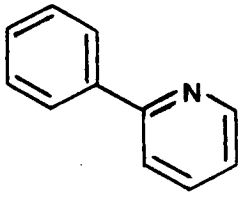
Abstract. Isothiazolium and 1,2-dithiolylium salts containing fused rings have been synthesised from cyclometalated palladium complexes.

The process of cyclometalation in transition metal complexes has recently been reviewed[1] and its potential as a route to metal-free heterocycles has been realised in the synthesis of indazolones,[2,3] dihydroisoindolones,[3] quinolones,[4] dihydrobenzo[c]thiophenones,[5] and cyclopenta[c]cinnolines.[6] Hitherto, however, the formation of such heterocycles has involved a replacement of the transition metal atom by one or more carbon atoms derived from carbon monoxide[2,3,4,5] isocyanides,[7] hexafluorobut-2-yne,[4] or cyclopentadiene.[6] We now report two variants of a general procedure for the replacement of palladium, in cyclopalladated complexes, by sulphur, thus providing a route to a series of novel isothiazolium and 1,2-dithiolylium salts containing condensed ring systems. The organic starting materials used in this work are shown in formulae (A)-(G) which may be represented collectively by the general formula (1)[8] where the atom (X) is nitrogen or sulphur.



(A)



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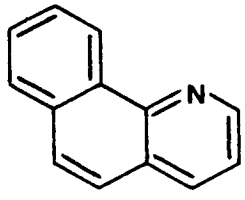
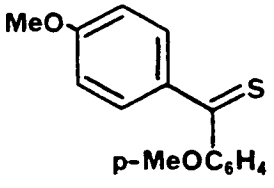
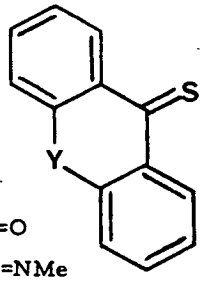


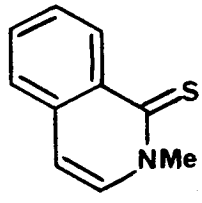
(C)



(D)

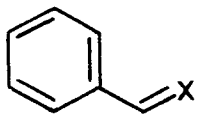


(E): Y=O
(F): Y=NMe

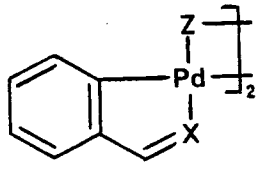


(G)

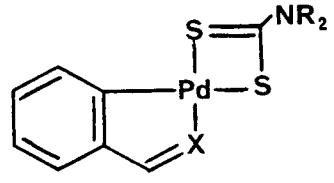
Reaction of substrates (A)[9]-(C) with palladium acetate or of (D)[10]-(G) with sodium or lithium tetrachloropalladate gave the dimeric complexes (2; Z=OAc or Cl)[11] but these, for various reasons, did not react cleanly with reagents considered likely to introduce sulphur. For efficient replacement of palladium, it was necessary first to convert the dimeric complexes (2) into monomeric dithiocarbamato-complexes (3; R=Me or iPr)[12] by reaction with a tetraethylammonium N,N-dialkyldithiocarbamate in chloroform [for (2; Z=OAc)] or with the corresponding sodium salt in N,N-dimethylformamide [for (2; Z=Cl)]. The complexes (3A-E; R=Me) reacted with thiocyanogen, in chloroform, to give the thiocyanato-compounds (4A-E),[13] which remained in solution, together with the highly insoluble dimeric palladium complex, $[Pd(Me_2NCS_2)SCN]_2$. Treatment of the thiocyanates (4) with perchloric acid gave the isothiazolium perchlorates (5A-C) and the 1,2-dithiolylium perchlorates (5D and 5E) (Table).



(1)



(2)



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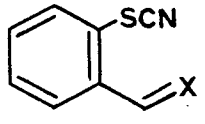
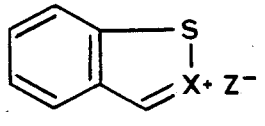


(4)



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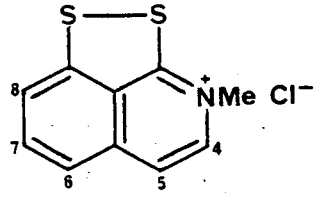

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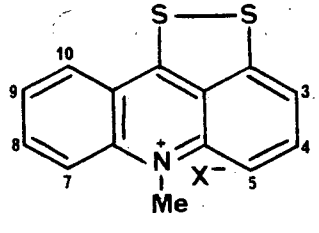

(7)

The complexes (3F) and (3G) reacted with thiocyanogen to give products, not yet completely identified, in which the heterocyclic ligand remained bound to palladium. In these cases, however, the salts (6) and (7) (Table) were obtained by slowly adding solutions of the dithiocarbamato-complexes (3F and 3G; R=iPr), in chloroform, to a two-fold excess of morpholine-N-sulphenyl chloride[14] in the same solvent. Removal of the chloroform by

Table: Data for the Salts (5)

Compound[a]	Yield[b] (%)	M. p. (°C)	δ ^{1}H (ppm)[c]
(5A; Z=ClO_4)	34	212° (dec)	7.7-8.2 (7H, m) 8.34 (1H, d) 8.58 (1H, d) 9.74 (1H, s)
(5B; Z=ClO_4)	25	168-169°	7.8-8.2 (4H, m) 8.40-8.62 (2H, m) 8.80 (1H, dd) 9.26 (1H, d)
(5C; Z=ClO_4)	58	140° (dec)	8.1-8.7 (7H, m) 9.54 (1H, dd)
(5D; Z=ClO_4)	90	220° (dec)	4.01 (3H, s) 4.16 (3H, s) 7.30 (2H, d) 7.54 (1H, dd) 7.84 (1H, d) 7.88 (2H, d) 8.34 (1H, d)
(5E; Z=ClO_4)	48	235° (dec)	7.65-8.5 (m)
(6)	91	decomp. 230-235°	4.16 (3H, s) 7.86 (1H, d, H-5) 7.92 (1H, d, H-8) 8.18 (1H, t, H-7) 8.30 (1H, d, H-6) 8.35 (1H, d, H-4)
(7; X=ClO_4)	81	266-268° (dec)	4.36 (3H, s) 7.82 (1H, t, H-9) 8.07 (1H, d, H-3) 8.17 (1H, d, H-5) 8.31 (1H, td, H-8) 8.34 (1H, t, H-4) 8.44 (1H, d, H-7) 8.47 (1H, d, H-10)

[a] Satisfactory elemental analyses were obtained in all cases. [b] Overall yields from the dithiocarbamato-complexes (3). [c] Spectra of (5A-E) measured in CF_3CO_2H at 100 MHz; spectra of (6) and (7) in Me_2SO-d_6 at 360 MHz.

evaporation left solid residues containing the chloride salt (6) or (7), di(N-morpholinyl) sulphide, and the dimeric palladium complex, $[Pd(iPr_2NCS_2)Cl]_2$. Treatment of these mixtures with pyridine, in dichloromethane, converted the dimeric complex into the soluble monomeric derivative, $Pd(iPr_2NCS_2)(C_5H_5N)Cl$, leaving the salts as the only insoluble products.

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References and Notes

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8. Products derived from these substrates are specified by using both a numeral and a letter. For example, (2A) indicates the complex of type (2) derived from substrate (A).
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11. The substrates (B) and (C) were known to give chloride-bridged complexes (see ref. 1) but the corresponding acetate-bridged complexes are new. Substrates (E)-(G) had not previously been cyclopalladated. Yields of dimeric complexes (2) were 75-95% and satisfactory elemental analyses were obtained for those that are new.
12. Satisfactory elemental analyses were obtained for all dithiocarbamato-complexes (3) and ^1H n. m. r. and mass spectrometric data were consistent with the assigned structures. Yields of these complexes were 50-80%.
13. Satisfactory elemental analyses were obtained for the thiocyanato-compounds (4B) and (4C). The other thiocyanates, being less stable, were characterised by i. r. and mass spectrometry (M^+ and strong M^+-CN fragment) before being converted into the salts (5). Accurate mass measurements (M^+) were obtained for (4A) and (4E).
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PARTICIPATION OF N-METHYL GROUPS IN THE CYCLOPALLADATION OF N,N-DIMETHYLTHIOBENZAMIDES.

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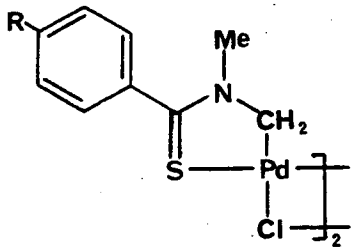
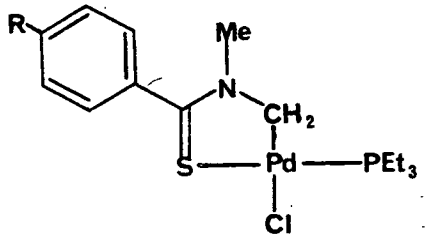
Edinburgh EH9 3JJ.

The process of metal-carbon σ-bond formation in cyclometallation (1) usually occurs at an aromatic ring. Less commonly, C-methyl groups may be involved, as in the cyclopalladation reactions of 8-methylquinoline (2), N,N-dimethyl-o-toluidine (3), and the oxime and N,N-dimethylhydrazone of 3,3-dimethylbutan-2-one (4). N-Methyl groups have not hitherto been observed to participate in cyclometallation but we now report the first example of such a reaction in the cyclopalladation of tertiary thiobenzamides.

N,N-Dimethylthiobenzamide and its p-methyl derivative reacted with methanolic sodium tetrachloropalladate at room temperature to give brown precipitates, probably co-ordination complexes, which were converted, after .5 hr at reflux, into the pale yellow or grey cyclopalladated complexes (I) (Table 1).



(I)



(II)

a: R = H

b: R = Me

These highly insoluble halogen-bridged dimers were not themselves amenable to spectroscopic investigation but they reacted with triethylphosphine (2 mol. equiv.), in dichloromethane, to give monomeric derivatives (colourless needles, after chromatography on alumina and recrystallisation from benzene), the structures (II) of which were established by ^{1}H and ^{13}C n.m.r. (Table 2). The CH_2-Pd-P structural unit was revealed by the

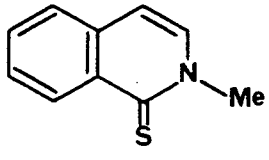
TABLE 1

Yields, Melting Points, and Analyses

Compound	Yield (%)	M. p. (°C)	Found (Calcd.) (%) C	H	N
Ia	81	273-274 (dec)	35.1 (35.3)	3.3 (3.3)	4.5 (4.6)
Ib	87	dec. 275-280	37.5 (37.5)	3.9 (3.8)	4.2 (4.4)
IIa	62	178-179	42.3 (42.5)	5.8 (5.9)	3.7 (3.3)
IIb	82	200-201	43.9 (43.9)	6.1 (6.2)	3.2 (3.2)

presence of a two-proton doublet ($^3J_{PH}$ ca. 4Hz) at δ 4.15 in the ^1H spectra and of a ^{13}C signal near δ 55 which was a doublet ($^2J_{PC}$ ca. 4Hz) in the fully proton-decoupled spectra and became a triplet of doublets under SFORD conditions. In the light of previously reported (5) values for cis- and trans-$^2J_{P\text{-}Pd\text{-}C}$, the small value observed here points to a cis-configuration for the CH_2-Pd-P unit. The presence of four aromatic ^{13}C resonances in the spectra of complexes (II) is further evidence for the presence of a non-palladated benzene ring.

The behaviour of these thiobenzamides in cyclopalladation contrasts sharply with that of the closely related N-methyl-1,2-dihydroisoquinoline-1-thione (III) which is cyclopalladated exclusively in the benzene ring (C-8) (6). We suggest that when the two competing reaction sites (NMe and aromatic CH) are held approximately equidistant from the coordinating centre (S) of the ligand, as in the rigid bicyclic structure (III), cyclopalladation is preferred at the sp^2-centre. Since the constraint of a thiolactam ring is absent in the thiobenzamides, it is probable that steric interaction during the initial act of coordination to palladium causes the aryl group to rotate out of the plane of the thiocarbonyl group. Cyclopalladation then occurs at the more accessible N-methyl group which remains close to the coordination site because of resonance-enforced planarity in the thioamide linkage.



(III)

TABLE 2

^{1}H (100 MHz), ^{13}C (20 MHz) and ^{31}P (24.2 MHz) N.m.r. Spectra[a]

Compound	Nucleus	C=S	Ar	NCH_2	NCH_3	PEt_3
IIa	^{1}H [b]		7.2-7.5 (5H, m)	4.15 (2H, d)	3.12 (3H, s)	1.82 (6H) 1.15 (9H)
	^{13}C [b,c]	194.5s	137.0s, 130.2d 128.5d, 126.7d	55.4td	45.4q	14.3td 8.0q
	^{31}P [d]					+20.2
IIb	^{1}H [b]		7.2 (4H, br. s) 2.35 (3H, s, Me)	4.15 (2H, d)	3.16 (3H, s)	1.85 (6H) 1.18 (9H)
	^{13}C [b]	194.6	140.7, 134.2 129.1, 126.8 21.2 (Me)	55.1	45.4	14.2 7.9
	^{31}P [d]					+20.2

a) Solvent $CDCl_3$. b) p.p.m. from TMS. c) Multiplicities are those observed with single frequency off-resonance decoupling. d) p.p.m. from H_3PO_4 (external); positive to high frequency.

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