The Dithiole Series. Part 8.[1] Synthesis of Ring-fused 1,2-Dithiolylium and Isothiazolium Salts from Complexes containing Cyclopalladated Ligands

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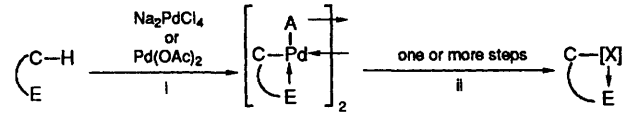
Ring-fused 1,2-dithiolylium or isothiazolium salts were obtained by substitution of a sulphur atom for the grouping (R_2NCS_2Pd) in various cyclopalladated complexes [$Pd(R_2NCS_2)L$] derived from ligands (LH) containing Ar–C=S or Ar–C=N– substructures. This process was accomplished by reaction of the complexes with: (*a*), thiocyanogen (yielding an intermediate metal-free thiocyanato-compound) followed by perchloric acid, or (*b*), morpholine-*N*-sulphenyl chloride.

In forming complexes with transition metals, many aromatic and heteroaromatic compounds undergo cyclometallation, a process in which a σ-bond is created between the metal and a carbon atom close to (usually γ to) the principal ligating (electron-pair donor) atom (Scheme 1, step i). When the metal is palladium, this process (cyclopalladation) is of particularly wide generality and can provide a starting point for the synthesis of various metal-free heterocycles (Scheme 1, step ii), as described

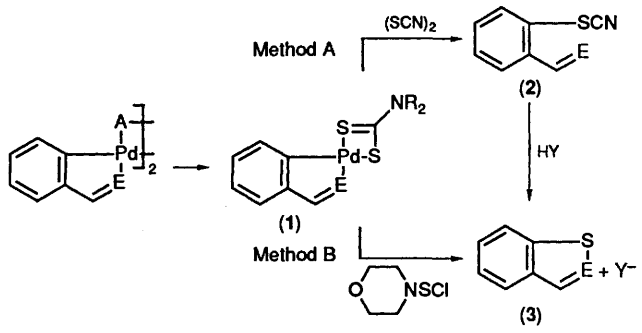


Scheme 1. A = Cl or OAc; [X] = non-metallic atom or group.

in a recent review.[2] Most of the previous applications of this strategy have involved replacement of palladium by carbon but the potential for wider use is obvious and we chose to investigate the replacement of palladium by sulphur. The finally successful procedures, which provide routes (Scheme 2) to hitherto unknown or unusual types of isothiazolium and 1,2-dithiolylium salts, have been outlined in a preliminary communication[3] and the syntheses of the required cyclopalladated complexes have been reported in detail elsewhere.[4] We now give details of the reactions of these complexes that led to the final metal-free products.

Results

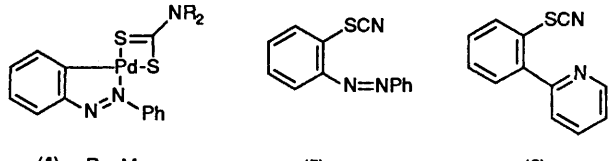
In the search for a reagent that would replace a carbon–palladium by a carbon–sulphur bond, much of the exploratory work was carried out on cyclopalladated complexes of the readily available ligand, azobenzene (Hazb). The chloride-bridged complex[5] [{Pd(azb)Cl}$_2$], being of very low solubility in most inert solvents, was not a satisfactory substrate but the more soluble acetato-bridged complex[6] [{Pd(azb)(OAc)}$_2$] and the dithiocarbamato complex (**4a**)[4] were considered to offer better opportunities for reaction. These complexes were treated, under various conditions, with compounds containing reactive S–N,[7] S–S, or S–Cl bonds but the desired replacement of palladium by sulphur occurred in only one reaction—that of the complex (**4a**) with thiocyanogen in chloroform at room temperature. 2-Thiocyanatoazobenzene (**5**), identical with a specimen prepared by the method of Burawoy,[8] was thus obtained from the solution and most of the palladium was recovered in the form of an insoluble yellow solid, thought to be mainly [{$Pd(Me_2NCS_2)(SCN)$}$_2$] (see below).



Scheme 2.

Method A (*Scheme* 2).—After this initial success, the reaction with thiocyanogen was applied to other dithiocarbamato complexes of the type (**1**) and conditions were found for the conversion of the resulting thiocyanato compounds (**2**) into salts of the type (**3**).

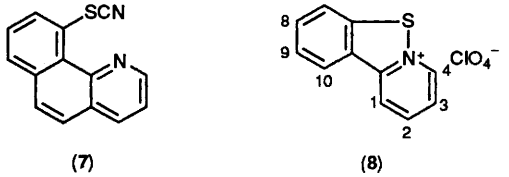
2-(2-Thiocyanatophenyl)pyridine (**6**) and 10-thiocyanato-



(**4**) **a**; R = Me
b; R = Pr^i

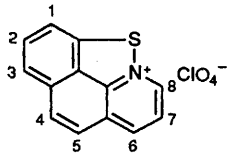
(**5**)

(**6**)



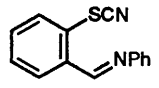
(**7**)

(**8**)

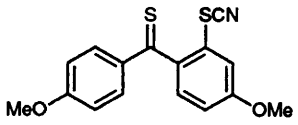


(**9**)

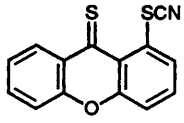
benzo[*h*]quinoline (**7**) were obtained as analytically pure, crystalline solids and the former was converted into the benzisothiazolopyridinium salt (**8**) by reaction with bromine followed by perchloric acid. The initial use of bromine was, however, almost certainly unnecessary, the related isothiazolobenzo[*h*]quinolinium salt (**9**) being obtained by treatment of



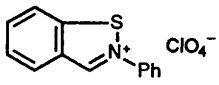
(**10**)



(**11**)

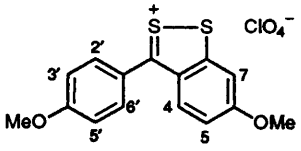


(**12**)

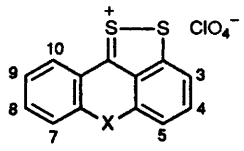


(**13**)

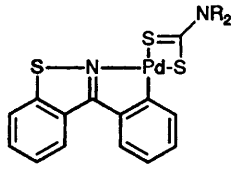
the thiocyanato compound (**7**) with perchloric acid alone. Other thiocyanato compounds (**10**), (**11**), and (**12**), being somewhat unstable, were not obtained analytically pure. They were characterised mass spectrometrically [M^+ and prominent $(M - CN)^+$] and converted directly into the corresponding salts (**13**), (**14**), and (**15**) by treatment with perchloric acid (Table). Unlike its oxygen analogue (**15**), the dithiolothioxanthylium salt (**16**) could not be obtained pure by this procedure.



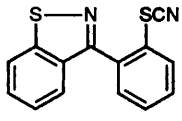
(**14**)



(**15**) X = O
(**16**) X = S



(**17**) **a**; R = Me
b; R = Pr^i



(**18**)

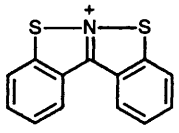
The reaction of the benzisothiazole complex (**17a**) with thiocyanogen yielded a crystalline, though somewhat unstable thiocyanato compound (**18**), the mass spectrum of which showed the expected molecular ion at *m/z* 268 and a prominent fragment ion at *m/z* 242 (*M* − CN), possibly due to the isothiazoloisothiazolium ion (**19**). It was disappointing, therefore, that treatment of the thiocyanate (**18**) with perchloric acid did not yield an isolable salt. The linkage of two sulphur atoms to the same quaternary nitrogen would have been an unique and interesting feature of this heteroaromatic ring system (**19**).

In all the foregoing examples, addition of thiocyanogen to the cyclopalladated complexes (**1**) in chloroform led to the appearance of a deep-red colour or to the darkening of an already reddish solution. After this initial change, the dark colour faded

Table. Ring-fused 1,2-dithiolylium and isothiazolium salts prepared according to Scheme 2.

Salt[a]	R in complex (1)	Method	Yield (%)[b]
(**8**)	Me	A	25[c]
(**8**)	Pr^i	B	84
(**9**)	Me	A	58
(**13**)	Me	A	34
(**14**)	Me	A	83
(**15**)	Me	A	44
(**15**) Cl^-	Pr^i	B	39[c]
(**16**) Cl^-	Pr^i	B	61
(**22**) Cl^-	Pr^i	B	91
(**24**) Cl^-	Pr^i	B	81
(**25**) Cl^-	Pr^i	B	16[c]
(**26**) Cl^-	Pr^i	B	66
(**27**) Cl^-	Pr^i	B	76
(**28**)	Pr^i	B	54

[a] Perchlorate unless otherwise stated. [b] Overall yield from (**1**). [c] Yield not optimised.

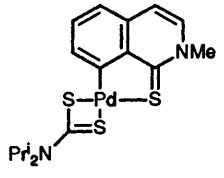


(**19**)

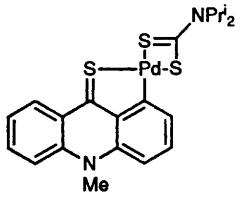
and a yellow solid containing most of the palladium was precipitated. The metal-free thiocyanato compound (**2**) could then be obtained by filtration and evaporation of the solution. These changes are consistent with an initial oxidative addition of thiocyanogen, forming an unstable palladium(IV) complex, followed by reductive elimination, as shown[9] or suggested[10] for several related reactions of palladium(II) complexes.

Stoicheiometric considerations and IR evidence [bands near 2 100 (SCN) and 1 540 cm^{-1} (R_2NCS_2)] suggested that the precipitated solids probably contained the thiocyanato-bridged dimer [{Pd(R_2NCS_2)(SCN)}$_2$] as a major component, though minor variations in the IR spectra were apparent in solids obtained from different cyclopalladated starting materials. One such solid, on treatment with triethyl- or triphenyl-phosphine, yielded the complexes [Pd(SCN)(Me_2NCS_2)(PR_3)], expected from bridge-splitting of the dimer.

In contrast to the behaviour described above was that of complexes, such as [Pd(miqt)(Pr$^i_2$NCS$_2$)]* (**20**) and (**21**),



(**20**)



(**21**)

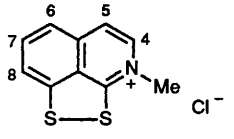
containing a cyclopalladated, benzo-fused pyridinethione substructure. During the reaction of these complexes with thiocyanogen, an initial darkening of colour followed by fading was again observed but no metal-free thiocyanato compounds were formed. The heterocyclic ligands appeared largely in the precipitated palladium complexes which showed IR absorptions near 2 100 cm^{-1} (SCN) and elemental compositions close to

* The abbreviation miqt indicates the cyclopalladated *N*-methylisoquinolinethione ligand.

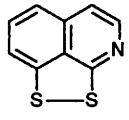
those required for thiocyanato-bridged dimeric complexes such as [{Pd(miqt)(SCN)}$_2$]. Consequently, the thiocyanogen procedure (method A) was not applicable to the preparation of condensed ring dithiolylium salts from heterocycles containing a pyridinethione substructure.

Method B (*Scheme* 2).—In the search for a more generally applicable alternative to the thiocyanogen procedure, the isoquinolinethione complex (**20**) was chosen as the most easily accessible test substrate. The initial exploratory work was centred upon the use of other disulphides (dibenzoyl, *N,N'*-dimorpholinyl[11] and *N,N'*-diphthalimidyl[12] disulphides) as possible replacements for thiocyanogen. In practice, however, the complex (**20**) was unchanged by these reagents, even at temperatures (boiling toluene or 1,1,2-trichloroethane) sufficient to cause decomposition of the disulphides.

Attention was then turned to reactions of (**20**) with the more strongly electrophilic sulphenyl chlorides, choosing examples with easily removable *S*-substituents. Butoxycarbonylsulphenyl chloride (BuO_2CSCl)[13] reacted rapidly with the complex (**20**) in chloroform but gave only the chloride-bridged dimer[4] [{Pd(miqt)Cl}$_2$] (82%) as a yellow precipitate. Another precipitate, similar in general appearance, was obtained when morpholine-*N*-sulphenyl chloride[13] (1 mol equiv.) was added to a solution of the complex (**20**) in chloroform. In this case, however, two other products, di-*N*-morpholinyl sulphide and the dithiocarbamate [Pd($Pr^i_2NCS_2$)$_2$], were isolated from the solution. Moreover, the IR spectrum of the precipitated solid showed peaks due to another product in addition to all major peaks characteristic of the dimer [{Pd(miqt)Cl}$_2$]. The mass spectrum of this mixture of insoluble products showed, *inter alia*, ion peaks at *m/z* 191 and 50/52 (3:1 doublet characteristic of CH_3Cl) suggesting the presence of the salt (**22**), thermal decomposition of which (in the mass spectrometer) could have generated chloromethane and the dithioloisoquinoline (**23**)



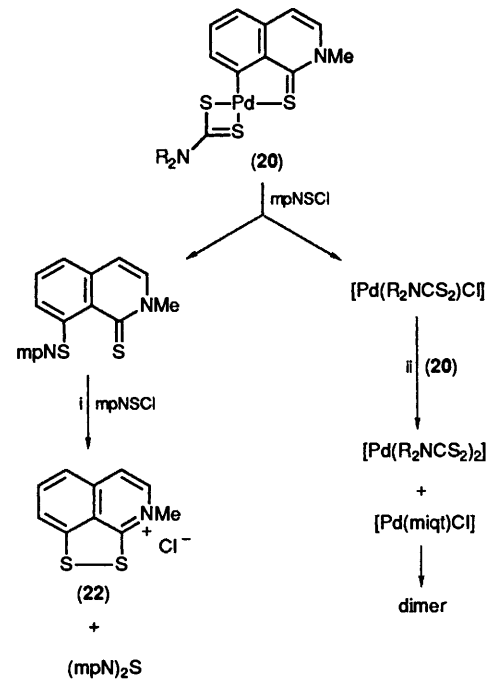
(**22**)



(**23**)

(M = 191). Thus four products from this reaction of the complex (**20**) with morpholine-*N*-sulphenyl chloride had been at least partially identified and, although reliable yields had not been determined, a tentative reaction scheme was proposed to account for their formation (Scheme 3).

According to this hypothetical scheme, reaction path i leading to the salt (**22**) ought to be maximised by using 2 mol equiv. of morpholinesulphenyl chloride per mol equiv. of the complex (**20**) and the ligand-exchange process [reaction path (ii)] ought to be minimised by keeping the concentration of the starting complex (**20**) low throughout the reaction. These conditions were achieved by slowly adding a solution of the complex (**20**) to morpholinesulphenyl chloride (2 mol equiv.) in chloroform and, as predicted from Scheme 3, three products were formed in high yields: the dithioloisoquinolinium chloride (**22**) (91%), *N,N'*-dimorpholinyl sulphide (88%), and the dimeric dithiocarbamato complex [{Pd($Pr^i_2NCS_2$)Cl}$_2$] ($\geqslant$ 78%). These products, obtained as a mixture by evaporation of the chloroform, were separated by extraction with diethyl ether [to remove $(mpN)_2S$] followed by treatment of the diethyl ether-insoluble fraction with pyridine in dichloromethane; the salt (**22**) remained as an insoluble solid and the monomeric complex [Pd($Pr^i_2NCS_2$)Cl(C_5H_5N)] (78%) was recovered from the solution, thus confirming the presence of the chloride-bridged



Scheme 3. R = Pr^i; mpN = *N*-morpholinyl.

dimer [{Pd($Pr^i_2NCS_2$)Cl}$_2$] as the third component of the initial mixture of products.

This procedure (method B), occasionally modified in minor detail, proved to be generally applicable and usually superior to method A for the conversion of cyclopalladated complexes of the type (**1**) into isothiazolium or 1,2-dithiolylium salts (Table). The di-isopropyldithiocarbamato ligand was preferable to its dimethyl analogue since it confers higher solubility on the starting complexes (**1**). For ease of purification, it was usually convenient to convert the initially-formed chloride salts into perchlorates. Despite its general success, method B failed to yield an isolable product from the benzisothiazole complex (**17b**).

In principle, it would seem possible to simplify method B, as shown below for the preparation of the salt (**22**), by using sulphur dichloride (1 mol equiv.) in place of morpholinesulphenyl chloride. Although this method was indeed shown to

$$[Pd(miqt)(Pr^i_2NCS_2)] + SCl_2 \longrightarrow (\mathbf{22}) + \tfrac{1}{2}[\{Pd(Pr^i_2NCS_2)Cl\}_2]$$

be viable, it gave a lower yield (75%) of product (**22**) than the corresponding reaction with morpholinesulphenyl chloride. Possibly this is due to the fact that SCl_2 is difficult to obtain pure, being susceptible to partial disproportionation into S_2Cl_2 and Cl_2.

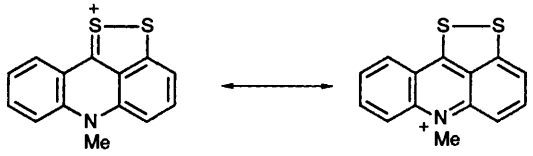
The suspected thermal decomposition of the salt (**22**) was confirmed by heating a specimen in a sublimation apparatus under reduced pressure. A yellow sublimate which collected was identified as [1,2]dithiolo[3,4,5-*ij*]isoquinoline (**23**) by ^{1}H NMR and high resolution mass spectrometry. Being unstable in air, it was not obtained analytically pure.

Discussion

The samples listed in the Table are sufficiently varied to establish the wide generality of these procedures for the synthesis of hitherto unknown or uncommon isothiazole and 1,2-dithiole ring systems.

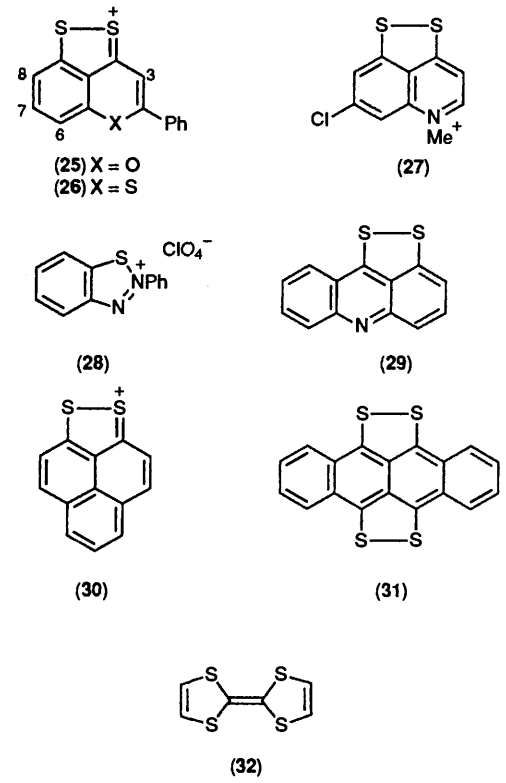
Among the isothiazolium salts described here, compound (**9**) is the parent member of a new ring system incorporating the isothiazolo[2,3-*a*]pyridinium[14] substructure. The parent benzo derivative (**8**) of this bicyclic cation is also new and, since many substituted 2-arylpyridines have been successfully cyclopalladated,[15] our route to the benzo-fused system should be more widely applicable than that of Abramovitch and his co-workers[16] which requires the presence of an electron-withdrawing substituent in the benzene ring. Similarly, many variously substituted derivatives of the 2-phenyl[1,2]benzisothiazolium ion (**13**) should be available by our procedure *via* cyclopalladation[17] of Schiff bases.

With the exception of the acridinium salt (**24**), which is a quaternary derivative of the previously known[18] dithiolo-acridine (**29**), all of the [*cd*]-fused dithiole derivatives listed in the Table are representatives of new ring systems. These compounds are delocalised cations in which the positive charge is present partially in the 1,2-dithiole ring and partially in the other heterocyclic substructure [*e.g.* (**24a**)↔(**24b**)]. They are,



(**24a**) (**24b**)

therefore, analogous to the phenaleno[1,9-*cd*]dithiolylium cation[19] (**30**) which has been synthesised for testing as a possible component of organic metals. 1,2-Dithiolylium cations lacking fused rings have also been tested[20] for this purpose and various polycyclic compounds [*e.g.*, (**31**)] containing one or two 1,2-dithiole rings [*cd*]-fused[21] to a naphthalene, anthracene, or tetracene nucleus are highly effective electron donors, comparable to the better known bis-(1,3-dithioles) [*e.g.*, TTF (**32**)], for the construction of organic metals.[22] It is possible, therefore, that the procedures described in this communication could have applications in the synthesis of such electro-active materials.



(**25**) X = O
(**26**) X = S
(**27**)
(**28**)
(**29**)
(**30**)
(**31**)
(**32**)

Experimental

NMR data refer to solutions in deuteriochloroform (unless otherwise stated) and chemical shifts are ppm to high frequency from tetramethylsilane. Mass spectrometric data were obtained by electron impact ionisation. For complexes, the reported values of M^+ are *m/z* of the ion containing ^{106}Pd. Alumina for chromatography (Laporte type UG) was deactivated by addition of water (0.05–0.1 cm^3 per g alumina). For use as a reaction solvent, chloroform was freed from ethanol by passage through activated alumina. Light petroleum refers to the fractions of b.p. 40–60 °C (for chromatography) and 60–80 °C (for recrystallisation). Ether refers to diethyl ether. Solutions of thiocyanogen in chloroform (ethanol-free) were obtained by treatment of lead(II) thiocyanate with bromine according to the method of Wood.[23] Such solutions were assumed to contain a quantitative yield of thiocyanogen and were used when freshly prepared. The preparation of dithiocarbamato complexes [type (**1**)] has been described elsewhere.[4]

Hazard Warnings.—(*a*) In one preparation of morpholine-*N*-sulphenyl chloride, vigorous decomposition occurred during distillation. The kugelrohr glassware was filled with charred material and the pressure increased sufficiently to disconnect the ST joint leading to the rotary vacuum pump. As in a previously recorded[24] case, the incident was thought to be due to contamination of the crude sulphenyl chloride with *N*-chloromorpholine. It is important, therefore, to start with carefully purified dimorpholinyl disulphide, free from morpholinium chloride. As a further precaution it is prudent to avoid distillation of the sulphenyl chloride on a larger scale or at a higher temperature than indicated below.

(*b*) The hazards involved and the precautions required in handling perchloric acid and perchlorates are well documented.[25] As a further precaution, preparations of perchlorates were carried out on a small scale ($\leq$1.5 mmol) and with low working concentrations (<0.25M) of perchloric acid.

*Morpholine-*N*-sulphenyl Chloride.*—Di(4-morpholinyl) disulphide[11a] was prepared from morpholine and disulphur dichloride in ether.[26] It was washed with water to remove morpholinium chloride and recrystallised from light petroleum (b.p. 80–100 °C).

Chlorine was passed through a solution of the disulphide (4.72 g) in dry carbon tetrachloride (25 cm^3) at 0–5 °C until the solution showed the yellow colour of free Cl_2 (*ca.* 2 min). The excess of chlorine was removed under reduced pressure (rotary evaporator for 5 min at room temperature) and the solvent was evaporated at 30–40 °C. The residual oil was distilled at 0.1 mmHg in a kugelrohr (oven temperature 80 °C) to yield the sulphenyl chloride (2.94 g, 48%) (lit.,[13] b.p. 58–60 °C at 0.6 mmHg) as a pale yellow oil. Storage in a freezer is recommended.

Method A, Procedure (*i*)*: Preparation of Thiocyanato Compounds.*—A stirred solution of the appropriate dithiocarbamato complex [type (**1**)] in chloroform was treated dropwise with a chloroform solution (*ca.* 0.1M; 1 mol equiv.) of thiocyanogen. A deep red colour, produced initially, began to fade after 5–10 min and a yellow solid was precipitated. Unless otherwise stated (below), stirring was continued for *ca.* 16 h. The yellow solid was filtered off and the filtrate was evaporated to obtain the crude thiocyanato compound which, if sufficiently stable, was purified by chromatography on alumina (elution with ether, dichloromethane–ether, or toluene–ether, as appropriate) and by re-

crystallisation. Thiocyanates that decomposed during attempted purification were characterised mass-spectrometrically and the crude products were used in procedure (ii). Details of individual experiments and of products obtained by procedure (i) are given below. All these products showed a molecular ion and a strong fragment ion due to $(M - CN)^+$ in their mass spectra.

(*a*) The azobenzene complex (**4a**) (0.41 g in 25 cm^3 $CHCl_3$) yielded 2-thiocyanatoazobenzene (**5**) (0.10 g, 42%) as orange needles, m.p. 97–99 °C (from light petroleum) (lit.,[8] m.p. 99 °C), IR and ^1H NMR spectra identical with those of an authentic specimen prepared by the method of Burawoy.[8]

(*b*) *N,N*-Dimethyldithiocarbamato[2-(2-pyridyl)phenyl-*N*']-palladium(II) (0.5 g in 25 cm^3 $CHCl_3$) yielded 2-(2-*thiocyanatophenyl*)*pyridine* (**6**) (0.10 g, 50%), m.p. 102–103 °C (from pentane–ether) (Found: C, 67.9; H, 3.8; N, 13.2. $C_{12}H_8N_2S$ requires C, 67.9; H, 3.8; N, 13.2%); δ_H(60 MHz) 7.1–7.5 (3 H, m), 7.55–8.05 (4 H, m), and 8.60 (1 H, dd, 6-H).

(*c*) Benzo[*h*]quinolin-10-yl-*N*-(*N,N*-dimethyldithiocarbamato)palladium(II) (1.42 g in 100 cm^3) yielded 10-*thiocyanatobenzo*[h]*quinoline* (**7**) (0.56 g, 68%), m.p. 173–174 °C (decomp.) (from ethanol) (Found: C, 70.9; H, 3.3; N, 11.8. $C_{14}H_8N_2S$ requires C, 71.2; H, 3.4; N, 11.9%).

(*d*) *N,N*-Dimethyldithiocarbamato[2-(*N*-phenylformimidoyl)phenyl-*N*']palladium(II) (0.55 g in 20 cm^3 $CHCl_3$) yielded *N*-(2-thiocyanatobenzylidene)aniline (**10**) [0.10 g, 48% (86% in a later preparation)] as a yellow oil, turning brown in air (Found: M^+ 238.055. $C_{14}H_{10}N_2S$ requires *M*, 238.056); δ_H(60 MHz) 6.9–7.9 (9 H, m) and 8.40 (1 H, s, CH=N).

(*e*) *N,N*-Dimethyldithiocarbamato[5-methoxy-2-(4-methoxythiobenzoyl)phenyl-*S*']palladium(II) (0.97 g in 50 cm^3 $CHCl_3$) yielded a crude sample of 4,4'-dimethoxy-2-thiocyanatothiobenzophenone (**11**) (0.5 g, 89%) as a red-brown solid, m.p. 102–105 °C (decomp.); ν_{max} 2 095 cm^{-1} (C≡N); *m/z* 315 (M^+) and 289 ($M^+ - CN$). The product decomposed during attempted recrystallisation.

(*f*) *N,N*-Dimethyldithiocarbamato(9-thioxoxanthen-1-yl-*S*)-palladium(II) (0.51 g in 250 cm^3 $CHCl_3$) yielded a crude sample of 1-thiocyanatoxanthene-9-thione (**12**) (0.2 g, 64%) as a red-brown solid, m.p. 143–145 °C (decomp.) that decomposed during attempted recrystallisation (Found: M^+, 268.9973. $C_{14}H_7NOS_2$ requires *M*, 268.9969).

(*g*) The benzisothiazole complex (**17a**) (0.25 g in 30 cm^3 $CHCl_3$ stirred with thiocyanogen for 1 h; product chromatographed on alumina in ether) yielded 3-(2-thiocyanatophenyl)-1,2-benzisothiazole (**18**) (0.14 g, 87%) as a solid, m.p. 100–101 °C, that decomposed during attempted recrystallisation [Found: M^+, 268.0126; ($M^+ - CN$) 242.0087. $C_{14}H_8N_2S_2$ requires *M*, 268.0129; (M − CN) 242.0098]; δ_H(100 MHz) 7.4–8.1 (3 complex m).

Method A, Procedure (*ii*)*: Conversion of Thiocyanato Compounds into Isothiazolium and* 1,2-*Dithiolylium Perchlorates.*—The thiocyanato compound (*x* g) was dissolved in ethanol or acetic acid and treated with 70% aqueous perchloric acid (approx *x* cm^3). The solution was stirred for 0.5–1 h at room temperature, cooled in ice, and (if necessary) diluted with ether to enhance crystallisation of the product. The resulting perchlorate was filtered off and recrystallised from acetic acid containing a trace of perchloric acid. Details of individual experiments and of products obtained by procedure (ii) are given below.

(*a*) 10-Thiocyanatobenzo[*h*]quinoline (**7**) (0.10 g in 35 cm^3 EtOH) yielded 8a-*azonia*-9-*thiacyclopenta*[def]*phenanthrene perchlorate* (**9**) (0.11 g, 85%), explosive decomp. 140 °C (Found: C, 50.2; H, 2.9; N, 4.4. $C_{13}H_8ClNO_4S$ requires C, 50.4; H, 2.6; N, 4.5%); δ_H(100 MHz; CF_3CO_2H) 8.1–8.7 (7 H, m) and 9.54 (1 H, dd, 8-H).

(*b*) *N*-(2-Thiocyanatobenzylidene)aniline (**10**) (0.12 g in 5 cm^3 AcOH) yielded 2-*phenyl*-1,2-*benzisothiazolium perchlorate* (**13**) (0.062 g, 40%) as plates, m.p. 212 °C (decomp.) (Found: C, 49.9; H, 3.1; N, 4.4. $C_{13}H_{10}ClNO_4S$ requires C, 50.1; H, 3.2; N, 4.5%); δ_H(100 MHz; CF_3CO_2D) 7.7–8.0 (6 H, m, 5-H and Ph), 8.12 (1 H, td, 6-H), 8.31 (1 H, br d, 7-H), 8.55 (1 H, br d, 4-H), and 9.74 (1 H, s, 3-H).

(*c*) The thiocyanatothione (**11**) (0.20 g in 35 cm^3 AcOH) yielded 6-*methoxy*-3-(4-*methoxyphenyl*)*benzo*1,2-*dithiolylium perchlorate* (**14**) (0.23 g, 93%) as orange needles, m.p. 220 °C (decomp.) (Found: C, 46.1; H, 3.3. $C_{15}H_{13}ClO_6S_2$ requires C, 46.3; H, 3.4%); δ_H(100 MHz; CF_3CO_2H) 4.01 (3 H, s, OMe), 4.16 (3 H, s, OMe), 7.30 (2 H, d, 3'-H and 5'-H), 7.54 (1 H, dd, 5-H), 7.84 (1 H, br s, 7-H), 7.88 (2 H, d, 2'-H and 6'-H), and 8.34 (1 H, d, 4-H).

(*d*) The thiocyanatoxanthenethione (**12**) (0.10 g in 75 cm^3 AcOH) yielded [1,2]*dithiolo*[3,4,5-kl]*xanthenylium perchlorate* (**15**) (0.09 g, 68%) as orange needles, m.p. 235–236 °C (decomp.) (Found: C, 45.5; H, 2.1. $C_{13}H_7ClO_5S_2$ requires C, 45.6; H, 2.1%); λ_{max}(EtOH–$HClO_4$) 222, 235sh, 254sh, 263, 295, 334, and 503 nm (log ε 3.97, 3.88, 3.79, 3.84, 3.66, 3.92, and 3.79); δ_H[360 MHz; $(CD_3)_2CO$] 7.84 (1 H, ddd, *J* 8.2, 7.3, and 1.1 Hz, 9-H), 7.95 (1 H, dd, *J* 8.2 and 0.6 Hz, 5-H), 8.04 (1 H, dd, ^3J 8.7 Hz, 7-H), 8.31 (1 H, ddd, *J* 8.7, 7.3, and 1.5 Hz, 8-H), 8.45 (1 H, dd, *J* 8.2 and 0.6 Hz, 3-H), 8.55 (1 H, t, *J* 8.2 Hz, 4-H), and 8.64 (1 H, ddd, *J* 8.2, 1.5, and 0.4 Hz, 10-H).

[1,2]*Benzisothiazolo*[2,3-a]*pyridinium Perchlorate* (**8**).—A solution of 2-(2-thiocyanatophenyl)pyridine (**6**) (0.15 g) and bromine (0.13 g) in ethanol (22 cm^3) was heated under reflux for 30 min. The solvent was evaporated and the residue was heated with perchloric acid (0.15 cm^3, 70%) in ethanol (15 cm^3). After being filtered and cooled, the solution deposited the *perchlorate* (**8**) (0.10 g, 51%) as needles, m.p. 168–169 °C (Found: C, 46.2; H, 2.7; N, 4.7. $C_{11}H_8ClNO_4S$ requires C, 46.3; H, 2.8; N, 4.9%); δ_H(100 MHz; CF_3CO_2H) 7.8–8.2 (4 H, m), 8.4–8.6 (2 H, m), 8.80 (1 H, dd), and 9.26 (1 H, dd, 4-H).

Characterisation of the Yellow Solid obtained in Method A, Procedure (*i*).—The solid (0.28 g) was stirred with a solution of triethylphosphine (0.12 g) in dichloromethane (30 cm^3) for 30 min. Evaporation of the solvent, trituration with ether, and recrystallisation from acetone yielded N,N-*dimethyldithiocarbamato*(*thiocyanato*)(*triethylphosphine*)palladium(II) (0.30 g, 75%) as yellow needles, m.p. 150 °C (Found: C, 30.0; H, 5.3; N, 7.0%; M^+, 402. $C_{10}H_{21}N_2PPdS_3$ requires C, 29.9; H, 5.2; N, 6.9%; *M*, 402); ν_{max} 2 080 (C≡N) and 1 550br cm^{-1} (Me_2NCS_2). A similar reaction with triphenylphosphine yielded N,N-*dimethyldithiocarbamato*(*thiocyanato*)(*triphenylphosphine*)-*palladium*(II) as orange prisms, m.p. 232–233 °C (from acetonitrile–chloroform) (Found: C, 48.5; H, 3.9; N, 5.2. $C_{22}H_{21}N_2PPdS_3$ requires C, 48.2; H, 3.9; N, 5.1%); ν_{max} 2 080 and 1 540 cm^{-1}; δ_H(80 MHz) 3.22, 3.33 (6 H, 2s, Me_2N) and 7.3–7.7 (15 H, m, Ph).

Reaction of N,N-*Di-isopropyldithiocarbamato*(1-*thioxo*-2-*methylisoquinolin*-8-*yl*-S)*palladium*(II) (**20**) *with Morpholine*-N-*sulphenyl Chloride.*—A solution of the complex (**20**) (0.46 g, 1 mmol) in chloroform (30 cm^3) was added dropwise during 15 min to a stirred solution of morpholine-*N*-sulphenyl chloride (0.31 g, 2 mmol) in chloroform (10 cm^3). A yellow precipitate formed immediately. After continued stirring for 3 h, the solvent was evaporated and the solid residue was extracted with ether (25 cm^3). Evaporation of the filtered ethereal solution yielded *N,N'*-dimorpholinyl sulphide (0.18 g, 88%), m.p. 125–126 °C (from light petroleum) (lit.,[11a] 125–126 °C) (Found: C, 46.8; H, 7.9; N, 13.3%; M^+, 204. Calc. for $C_8H_{16}N_2O_2S$: C, 47.1; H, 7.8; N, 13.7%; *M*, 204).

The ether-insoluble product was stirred vigorously for 15 min

with a solution of pyridine (1 cm^3) in dichloromethane (40 cm^3) and the remaining insoluble material was filtered off, washed (CH_2Cl_2), and dried to yield 3-*methyl*[1,2]*dithiolo*[3,4,5-ij]-*isoquinolinium chloride* (**22**) (0.22 g, 91%) as a yellow powder, m.p. 269–270 °C (partial decomposition from *ca.* 230 °C) (Found: C, 49.5; H, 3.2; N, 5.6. $C_{10}H_8ClNS_2$ requires C, 49.7; H, 3.3; N, 5.8%); *m/z* 191 ($M^+ - CH_3Cl$) and 52/50 (CH_3Cl^+); λ_{max}(EtOH) 253, 335, and 419 nm (log ε 4.15, 3.56, and 3.97); δ_H[360 MHz, $(CD_3)_2SO$] 4.16 (3 H, s, CH_3), 7.86 (1 H, d, *J* 7 Hz, 5-H), 7.92 (1 H, d, *J* 8 Hz, 6-H or 8-H), 8.18 (1 H, t, *J* 8 Hz, 7-H), 8.30 (1 H, d, *J* 8 Hz, 8-H or 6-H), and 8.35 (1 H, d, *J* 7 Hz, 4-H).

Evaporation of the dichloromethane solution and recrystallisation of the residue from dichloromethane–light petroleum yielded *chloro*(N,N-*di-isopropyldithiocarbamato*)(*pyridine*)*palladium*(II) (0.31 g, 78%) as an orange solid, decomp. 155–160 °C (Found: C, 36.3; H, 4.7; N, 6.8. $C_{12}H_{19}ClN_2PdS_2$ requires C, 36.3; H, 4.8; N, 7.1%); δ_H(100 MHz) 1.40, 1.45 (12 H, 2d, CH_3), 4.5 (1 H, br m, Me_2CH), 7.35 (2 H, m, 3- and 5-PyH), 7.80 (1 H, br t, 4-PyH), and 8.75 (1 H, br d, 2- and 6-PyH).

Method B, General Procedure.—A solution of the appropriate dithiocarbamato complex [type (**1**; R = Pr^i)] (0.5–1.5 mmol) in chloroform (volume stated below for individual experiments) was added dropwise during 15 min to a stirred solution of morpholine-*N*-sulphenyl chloride (2 mol equiv.) in chloroform (10 cm^3). After 1–2 h, the precipitate which had formed was filtered off and resuspended in dichloromethane (20 cm^3). Pyridine (1 cm^3) was added, the suspension was stirred vigorously for 15 min, and the required chloride salt, which remained undissolved, was filtered off, washed with dichloromethane, and dried. For easier purification, the chloride was generally converted into the corresponding perchlorate by treatment of a hot solution, in methanol or acetic acid, with a few drops of 70% aqueous perchloric acid. The perchlorate crystallised immediately or on cooling. Details of individual experiments and of products obtained by this procedure (modified where stated) are given below.

(*a*) *N,N*-Di-isopropyldithiocarbamato[2-(2-pyridyl)phenyl-*N*]palladium(II) (1 mmol in 25 cm^3 $CHCl_3$) yielded [1,2]benzisothiazolo[2,3-*a*]pyridinium chloride (84%), m.p. 220–223 °C, which was converted into the corresponding perchlorate (**8**), m.p. 168–169 °C, IR and ^1H NMR spectra identical with those of the specimen prepared by method A.

(*b*) *N,N*-Di-isopropyldithiocarbamato(9-thioxoxanthen-1-yl-*S*)palladium(II) (1.5 mmol in 50 cm^3 $CHCl_3$) yielded [1,2]-dithiolo[3,4,5-*kl*]xanthenylium chloride (39%), *m/z* 243 ($C_{13}H_7OS_2^+$), which was converted into the corresponding perchlorate (**15**), m.p. 235–236 °C (decomp.) (from methanol), IR spectrum identical with that of the specimen prepared by method A.

(*c*) *N,N*-Di-isopropyldithiocarbamato(9-thioxothioxanthen-1-yl-*S*)palladium(II) (1 mmol in 25 cm^3 $CHCl_3$) yielded a chloride (61%), *m/z* 259 ($C_{13}H_7S_3^+$), which was converted into [1,2]*dithiolo*[3,4,5-kl]*thioxanthenylium perchlorate* (**16**), purple needles, m.p. 220–222 °C (decomp.) (from methanol) (Found: C, 43.7; H, 2.0. $C_{13}H_7ClO_4S_3$ requires C, 43.5; H, 2.0%); λ_{max}(EtOH–$HClO_4$) 238, 254, 288, 314, 330, 375, and 570 nm) log ε 3.98, 4.11, 3.87, 4.00, 3.87, 3.39, and 3.91); δ_H([360 MHz; $(CD_2)_2CO$] 7.92 (1 H, ddd, *J* 8.3, 7.1, and 1.1 Hz, 9-H), 8.15 (1 H, br t, 8-H), 8.27 (1 H, br dd, ^3J 8.3 Hz, 7-H), 8.3–8.4 (2 H, m, 4-H and 5-H), 8.56 (1 H, br d, *J* 8.8 Hz, 3-H), and 8.78 (1 H, br d, *J* 8.3 Hz, 10-H).

(*d*) The dithiocarbamato complex (**21**) (0.6 mmol in 350 cm^3 $CHCl_3$) yielded a chloride (81%), m.p. 250–253 °C (decomp.), *m/z* 241 ($M^+ - CH_3Cl$) and 52/50 (CH_3Cl^+), which was converted into 6-*methyl*[1,2]*dithiolo*[3,4,5-kl]*acridinium perchlorate* (**24**), a red–purple solid, m.p. 266–268 °C (decomp.) (from acetic acid) (Found: C, 47.1; H, 2.8; N, 3.8. $C_{14}H_{10}ClNO_4S$ requires C, 47.3; H, 2.8; N, 3.9%); λ_{max}(EtOH–$HClO_4$) 245, 257sh, 279, 305, 340, 520sh, and 548 nm (log ε 4.37, 4.16, 4.25, 4.40, 3.46, 4.0, and 4.10); δ_H[360 MHz, $(CD_3)_2SO$] 4.36 (3 H, s, CH_3), 7.82 (1 H, br t, 9-H), 8.07 (1 H, d, *J* 8.6 Hz, 3-H or 5-H), 8.17 (1 H, d, *J* 7.9 Hz, 5-H or 3-H), 8.31 (1 H, ddd, *J* 9.1, 7.0, and 1.5 Hz, 8-H), 8.34 (1 H, t, 4-H), 8.44 (1 H, br d, *J* 9.1 Hz, 7-H), and 8.47 (1 H, br d, *J* 8.2 Hz, 10-H).

(*e*) *N,N*-Di-isopropyldithiocarbamato(2-phenyl-4-thioxochromen-5-yl-*S*)palladium(II) (1 mmol in 25 cm^3 $CHCl_3$) yielded a chloride (16%), m.p. 158 °C, *m/z* 269 ($C_{15}H_9OS_2^+$), which was converted into 4-*phenyl*[1,2]*dithiolo*[3,4,5-de]-*chromenylium perchlorate* (**25**), red crystals, m.p. 189–190 °C (from methanol) (Found: C, 48.7; H, 2.65 $C_{15}H_9ClO_5S_2$ requires C, 48.85; H, 2.5%); λ_{max} 259, 310, 354, and 480 nm (log ε 3.72, 3.64, 4.00, and 3.90); δ_H(360 MHz) 7.71 (2 H, m, 3′- and 5′-Ph protons), 7.82–7.84 (2 H, d + m, 6-H or 8-H and 4′-Ph proton), 7.98 (1 H, d, 8-H or 6-H), 8.14 (1 H, s, 3-H), 8.21 (2 H, m, 2′- and 6′-Ph protons), and 8.27 (1 H, t, 7-H).

(*f*) *N,N*-Di-isopropyldithiocarbamato(2-phenyl-4-thioxothiochromen-5-yl-*S*)-palladium(II) (1 mmol in 25 cm^3 $CHCl_3$) yielded a chloride (66%), m.p. 263–264 °C (decomp.), *m/z* 285 ($C_{15}H_9S_3^+$), which was converted into 4-*phenyl*[1,2]*dithiolo*[3,4,5-de]*thiochromenylium perchlorate* (**26**), red–purple crystals, m.p. 182–184 °C (from methanol) (Found: C, 47.0; H, 2.4. $C_{15}H_9ClO_4S_3$ requires C, 46.8; H, 2.3%); λ_{max}(EtOH–$HClO_4$) 250, 289, 348, and 532 nm (log ε 4.12, 4.06, 4.24, and 4.24); δ_H(360 MHz, $CDCl_3$–CF_3CO_2H) 7.68 (2 H, m, 3′- and 5′-Ph protons), 7.79 (1 H, m, 4′-Ph proton), 7.88 (2 H, m, 2′- and 6′-Ph protons), 8.03–8.13 (3 H, m, 6-H, 7-H, and 8-H), and 8.25 (1 H, s, 3-H).

(*g*) *N,N*-Di-isopropyldithiocarbamato(7-chloro-1,4-dihydro-1-methyl-4-thioxoquinolin-5-yl-*S*)palladium(II) (1 mmol in 25 cm^3 $CHCl_3$) yielded a chloride (76%), m.p. 289–292 °C (decomp.), *m/z* 227/225 ($M^+ - CH_3Cl$), which was converted into 7-*chloro*-5-*methyl*[1,2]*dithiolo*[3,4,5-de]*quinolinium perchlorate* (**27**), a yellow solid, m.p. 295–298 °C (decomp.) (from methanol) (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%); λ_{max}(EtOH–$HClO_4$) 268, 297, and 440 nm (log ε 4.21, 3.90, and 4.16); δ_H[100 MHz, $(CD_3)_2SO$] 4.09 (3 H, s, CH_3), 7.82 (1 H, d, *J* 7 Hz, 3-H), 7.87 (1 H, d, *J* 1.5 Hz, 6-H or 8-H), 8.10 (1 H, d, *J* 1.5 Hz, 8-H or 6-H), and 8.71 (1 H, d, *J* 7 Hz, 4-H).

(*h*) *N,N*-Di-isopropyldithiocarbamato(2-phenylazophenyl-*N*)palladium(II) (**4b**) (1 mmol in 15 cm^3 $CHCl_3$) was added to morpholine-*N*-sulphenyl chloride (2 mmol) as in the general procedure. After 2 h, the solution was evaporated and the solid residue was washed with ether (50 cm^3), resuspended in dichloromethane (20 cm^3), and treated with pyridine (1 cm^3). After being stirred vigorously for 15 min, the suspension was diluted with ether (20 cm^3) and the insoluble yellow chloride (89%) was filtered off. A solution of the chloride in methanol (5 cm^3) was treated with perchloric acid to yield 2-phenylbenzo-1,2,3-thiadiazolium perchlorate (**28**) (54% overall) as yellow needles, m.p. 213–215 °C (decomp.) [lit.,[8] m.p. 214–216 °C (decomp.)] (Found: C, 46.2; H, 2.9; N, 8.9. Calc. for $C_{12}H_9ClN_2O_4S$: C, 46.1; H, 2.9; N, 9.0%).

Reaction of the Complex (**20**) *with Sulphur Dichloride.*—A solution of the complex (**20**) (0.46 g, 1 mmol) in chloroform (25 cm^3) was added dropwise, during 15 min, to a stirred solution of freshly distilled sulphur dichloride (0.11 g, 1 mmol) in chloroform (10 cm^3). The solution immediately became red and, after 3 h, it had deposited a brown solid which was filtered off and resuspended in dichloromethane (20 cm^3). Pyridine (1 cm^3) was added, the suspension was stirred vigorously for 15 min, and the remaining solid was filtered off, washed with dichloromethane, and dried. The product (0.18 g, 75%) was a yellow solid which, despite having a lower m.p. [252–255 °C

(decomp.)], gave an IR spectrum identical with that of the chloride (**22**) prepared from (**20**) by reaction with morpholine-*N*-sulphenyl chloride.

Thermolysis of 3-*Methyl*[1,2]*dithiolo*[3,4,5-ij]*isoquinolinium Chloride* (**22**).—The chloride (0.1 g) was heated to 250 °C in an evacuated (*ca.* 0.1 mmHg) sublimation apparatus and the resulting yellow–orange sublimate (0.07 g), m.p. 83–87 °C (decomp.), was chromatographed on alumina. Elution with chloroform yielded [1,2]*dithiolo*[3,4,5-ij]*isoquinoline* (0.03 g) as a yellow solid, m.p. 87–89 °C (decomp.) (Found: M^+ 190.9867. $C_9H_5NS_2$ requires 190.9863); δ_H(100 MHz) 7.05 (1 H, d, *J* 6 Hz, 5-H), 7.2–7.5 (3 H, m, 6-H, 7-H, and 8-H), and 8.02 (1 H, d, *J* 6 Hz, 4-H). The compound was unstable in air and became less pure on attempted recrystallisation.

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