Highly Conjugated π-Electron Donors for Organic Metals: Synthesis and Redox Chemistry of New 1,3-Dithiole and 1,3-Selenathiole Derivatives

Adrian J. Moore and Martin R. Bryce*
Department of Chemistry, University of Durham, South Road, Durham, DH1 3LE, UK

The bis(1,3-dithiolium) dication salts 8a–c have been synthesised in three steps (31–51% overall yields) starting from 1,4-bis(bromomethyl)naphthalene, 9,10-bis(chloromethyl)anthracene and 4,4'-bis(chloromethyl)biphenyl, respectively. The bis(halogenomethyl) compounds 5 were converted into the dipiperidiniumbis(dithiocarboxylate) salts 6, which on alkylation with 3-chlorobutan-2-one yielded bis(dithioesters) 7; cyclisation of 7 occurred on treatment with concentrated sulphuric acid to give dication salts 8. Dimethyl 1,3-dithiol-2-ylphosphonate 20, dimethyl 4,5-dimethyl-1,3-dithiol-2-ylphosphonate 21 and dimethyl 1,3-selenathiol-2-ylphosphonate 22 were treated with butyl-lithium in the presence of a range of carbonyl compounds and quinones, e.g., cyclopentanone, cyclohexanone, benzophenone, acetophenone, benzaldehyde, thioxanthen-9-one, anthraquinone, bianthrone and naphthacene-5,12-quinone to yield Wittig-Horner products, e.g., alkenes 26–34 and the anthracenediylidene derivatives 35, 36, 40–43 and 53. Unsymmetrical derivatives 37–39 were prepared in two steps as follows: anthrone reacted with 2-methylthio-1,3-dithiolium iodides 45 and 46 in pyridine–acetic acid to yield ketones 48 and 49 which were then treated with the Wittig–Horner reagents 23–25. Cyclic voltammetric data for the new tetrathiafulvalene, selenatrithiafulvalene and diselenadithiafulvalene derivatives 35–43 and 53, show that these systems undergo two-electron redox behaviour which is observed as a single wave. Complexes of these donors with electron acceptors, e.g. 7,7,8,8-tetracyano-p-quinodimethane (TCNQ), have been obtained, some of which are organic semiconductors.

There is presently keen interest in organic materials that possess special solid state properties, notably high electrical conductivity. A large number of organic metals has been spawned by the progenitor complex TTF 1–TCNQ.[1] These complexes and salts crystallise with segregated stacks of cations and anions which results in strongly anisotropic transport properties; hence they are termed 'one-dimensional metals'. The field has been reviewed regularly over the last few years[2] and monographs[3] and detailed conference proceedings[4] have been published.

Much synthetic effort has been devoted to systematically varying the structure of TTF, 1, with consequential changes to the ionisation potential, symmetry and size of the donors. The incorporation of selenium and tellurium atoms into the ring system has been a prominent theme.[2,4] The present work concerns derivatives of TTF in which there is a cyclic, conjugated, π-framework between the 1,3-dithiole rings. Some analogous selenium-containing derivatives are also described. These molecules are designed to undergo multistage redox reactions with relatively low oxidation potentials; extending conjugation in this manner is known to stabilise the dication state, relative to TTF, by reducing the intramolecular Coulombic repulsion energy.[5] Therefore, the salts of these donors may show electronic and magnetic properties quite different from the salts of TTF.
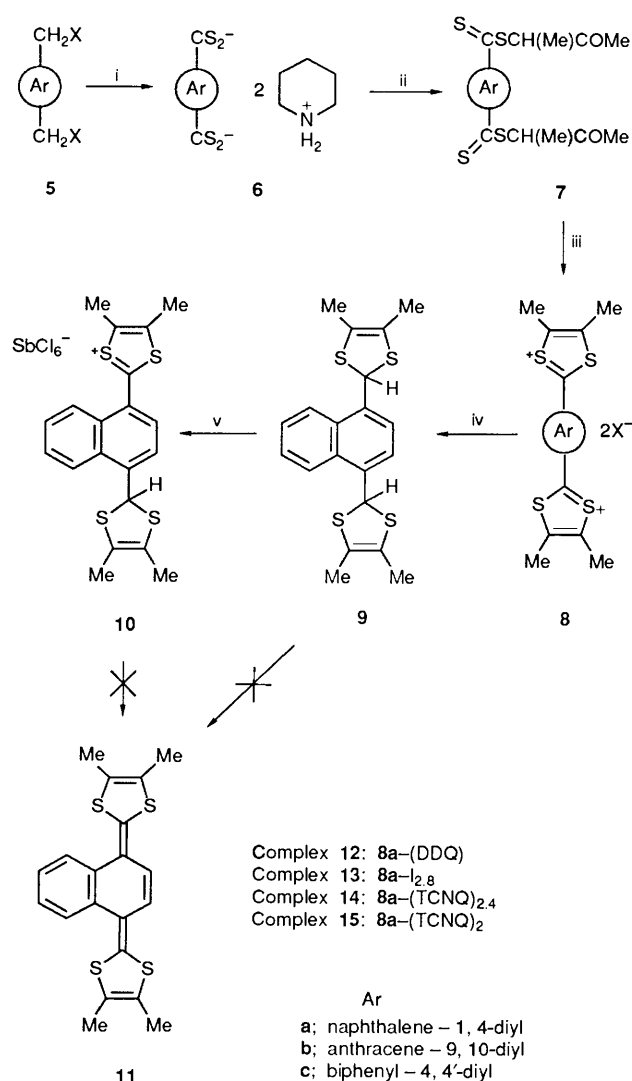
Our initial targets were systems 8a–c in which the linking group is 1,4-naphthalene, 9,10-anthracene and 4,4'-biphenyl, respectively. These molecules 8a–c were expected to be isolable in their oxidised (dication) redox states, in which the bridging ring is aromatic,[6] with added stability for the dication state being provided by the aromaticity of the 1,3-dithiolium rings.[7] At the outset of the present work,[8] only a few extended bis(1,3-dithiolium) dications containing cyclic linking groups were known,[5c] and a new derivative has been reported subsequently.[9] Other extended TTF derivatives of current interest, that are related to our targets, include molecules 2[5b,10] and 3[11] (prepared in the reduced form) and molecule 4 (prepared in the oxidised form).[12] As pointed out by Yoshida et al.[12] for the

1

2

3

4
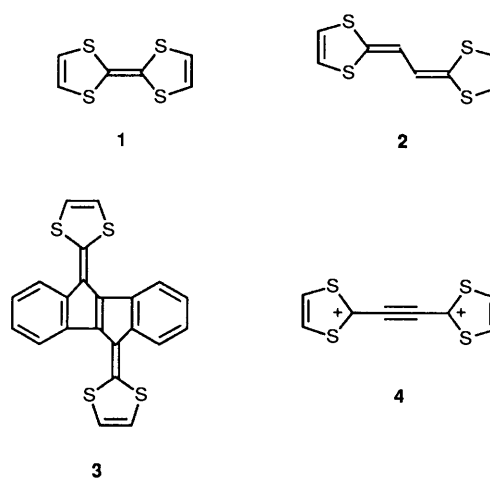
formation of crystalline organic conductors it is desirable to obtain the more rigid structures that result from insertion of cyclic groups between the 1,3-dithiole rings, rather than the more flexible structures of vinylogous derivatives, e.g., 2.

Results and Discussion

Synthesis of Bis(1,3-dithiolium) Dication Salts.—Many diverse routes are now available for the synthesis of TTF derivatives and their selenium and tellurium analogues.[13] The methodology we have used to prepare the three dications 8a–c is outlined in Scheme 1. The 1,3-dithiolium ring is constructed by a three-step elaboration of a halogenomethyl group, using an approach which dates back to the work of Leaver et al.[14] The 4,5-dimethyl-1,3-dithiolium ring is far easier to synthesise by this route than the unsubstituted ring, because the use of chloroacetaldehyde, instead of 3-chlorobutan-2-one, is not straightforward.[15] Bis(halogenomethyl) compounds 5a–c were

Complex 12: 8a–(DDQ)
Complex 13: 8a–I$_{2.8}$
Complex 14: 8a–(TCNQ)$_{2.4}$
Complex 15: 8a–(TCNQ)$_2$

Ar

a; naphthalene – 1, 4-diyl
b; anthracene – 9, 10-diyl
c; biphenyl – 4, 4′-diyl

Scheme 1 *Reagents and conditions:* i, elemental sulphur, sodium methoxide, refluxing methanol, followed by HCl, then piperidine; ii, 3-chlorobutan-2-one, dichloromethane, 20 °C; iii, conc. sulphuric acid, − 10 °C; iv, sodium borohydride, ethanol, 20 °C; v, triphenylcarbenium hexachloroantimonate, refluxing dichloromethane

treated with a mixture of elemental sulphur and sodium methoxide,[16] followed by acidification, to yield the corresponding, pungent, bis(dithiocarboxylic) acids which were isolated as their crystalline dipiperidinium salts 6a–c.[17] The CS$_2$⁻ group was identified in the IR spectra of 6a–c as a band at v_{max}/cm⁻¹ *ca.* 1010. Alkylation of salts 6a–c with 3-chlorobutan-2-one yielded the α-oxoalkyl dithioesters 7a–c. The key cyclisation step, which followed, was brought about by the dissolution of the dithioesters 7 in conc. sulphuric acid under carefully controlled conditions; it was important to add compounds 7a–c to the acid portionwise while maintaining the temperature of the mixture at − 10 °C; the reaction is exothermic and at higher temperatures intractable tars are formed. The resulting bis(4,5-dimethyl-1,3-dithiolium) dications were isolated as either the bis(hydrogen sulphate) or bis(hexafluorophosphate) salts 8a–c which were stable to storage. The overall yields for the sequence 5→8 were 31–51%. ¹H NMR spectra of salts 8 showed a singlet peak at δ$_H$ 2.93–3.01, characteristic of methyl group protons on a 1,3-dithiolium ring,[5c.12] which are shifted downfield from the normal value for Me–C=C protons (*cf.* compound 36 considered below, δ$_H$ 1.91).

The dication 8a reacted smoothly with 2 equiv. of sodium borohydride at C-2 of the heterocyclic ring to yield the dihydro

compound 9 (58% yield), which is a potential precursor of the fully conjugated, reduced TTF analogue 11. Hydride abstraction, followed by deprotonation, of bis(1,3-benzodithiolium) dications, analogous to 9, is known to yield neutral, quinonoid systems,[18] although this procedure does not seem to have been reported for bis(1,3-dithiolium) systems. Reaction of compound 9 with 1 equiv. of triphenylcarbenium hexachloroantimonate gave the monocation salt 10 (75% yield). However, attempts to further convert cation salt 10 into the neutral system 11 by reaction with an excess of triethylamine gave a complex mixture of products from which nothing could be isolated. Attempted dehydrogenation of compound 9 with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) did not yield 11; instead, a highly insoluble brown powder, identified as complex 12 was obtained (20% yield). Elemental analysis of complex 12 clearly supports a 1:1 stoicheiometry; the IR spectrum shows no carbonyl absorption from DDQ, but, instead, a very strong phenoxyl radical band is observed at v_{max}/cm⁻¹ 1566 and a broad charge-transfer band is present at v_{max}/cm⁻¹ 3400–3000. Also a strong singlet is observed in the solid state ESR spectrum of complex 12 at *g* 2.0003, indicative of an organic free radical. Similar data have been used previously to identify quinol complexes of bis(1,3-dithiole) systems.[5c.18a] The oxidation state of the bis(1,3-dithiole) system 8a in complex 12 is not clear. Taken together, the analytical and spectroscopic data are consistent with the molecules being present in the radical cation form. However, based on cyclic voltammetric data for the dication 8a, and other solid state data for related complexes (see Table 2 and discussions below), it is more likely that the radical cation disproportionates and there is a mixture of the dicationic and neutral forms, 8a and 11, respectively, in complex 12. The formation of complex 12 can be explained by the initial dehydrogenation of compound 9 to yield donor molecule 11 which then forms a charge-transfer complex *in situ* with a second DDQ molecule.[18a] Complex 12 is an electrical insulator σ$_{rt}$/S cm⁻¹ 2 × 10⁻⁸; only a very few examples of conducting salts formed by the DDQ radical anion are known.[19]

In situations where the neutral donor is not obtainable from its dication salt, complexes of the donor with iodine or TCNQ can often be obtained by metathesis reaction of the dication salt with either lithium iodide or the lithium salt of TCNQ (Li⁺ TCNQ·⁻). Such reactions have been rationalised by initial single electron transfer from I⁻, or TCNQ·⁻, to the bis(1,3-dithiolium) dication, followed by aggregation of the iodine or TCNQ moiety.[20] In this way, non-stoicheiometric, conducting, charge-transfer complexes have been isolated. On addition of dication salt 8a to a boiling solution of an excess of lithium iodide in acetone, the solution immediately darkened and a fine red powder precipitated on cooling (95% yield). The ratio donor:iodine for the isolated complex 13 was estimated to be 1:2.8 from elemental analysis. Conductivity measurements on a powdered sample showed the material to be an insulator (σ$_{rt}$/S cm⁻¹ *ca.* 1 × 10⁻¹², two-probe compressed pellet measurement). The dication salt 8a reacted in a similar manner with an excess of Li⁺TCNQ·⁻ in boiling acetonitrile–acetone to give a blue–black solid on cooling, which was identified from elemental analysis as complex 14 (45% yield). The stoicheiometry of complex 14 was 1:2.4 (donor:TCNQ) and this analysis was highly reproducible on several samples. The dication salt 8c also reacted with Li⁺TCNQ·⁻ in acetone to give complex 15 (40% yield) for which analytical data suggested 1:2 stoicheiometry. The extreme insolubility of dication salt 8b precluded the characterisation of any of its complexes *via* metathesis reaction.

Physical data for TCNQ complexes 14 and 15 are summarised in Table 1. Both complexes 14 and 15 exhibit two-probe compaction conductivities in the semiconductor regime, indicative of a segregated stacking motif and a partially-filled

Table 1 Physical properties of TCNQ complexes

Complex	Stoicheiometry[a]	$\sigma_{rt}/S\ cm^{-1}$	$\nu(C\equiv N)/cm^{-1\ d}$	λ_{max}/nm
14	1:2.4	$1 \times 10^{-3\ b}$	2177	880, 835, 780, 380[e]
15	1:2	$6 \times 10^{-2\ b}$	2183	895, 835, 780, 385[e]
54	1:4	$4 \times 10^{-3\ b}$	2185, 2155	842, 746, 395, 200[f]
55	1:4	$1 \times 10^{-2\ b}, 60^{c}$	2209, 2187, 2158	843, 744, 394, 200[f]
56	1:4	$3 \times 10^{-3\ b}$	2180, 2158	847, 740, 380, 195[f]

[a] Dication: TCNQ, deduced from elemental analysis. [b] Two-probe compaction measurement. [c] Four-probe single crystal measurement. [d] FT-IR (KBr disc). [e] Solid-state (Nujol, CaF_2 plates). [f] Solution (MeCN).
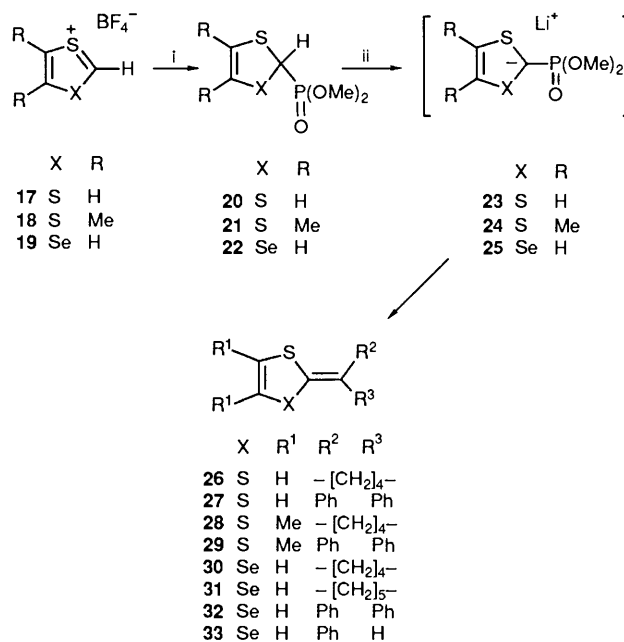
energy band on the TCNQ stack. The relatively high conductivity value suggests that the stoicheiometry of complex **15** is not exactly 1:2. A complex of this stoicheiometry with the donor present in the dication form should be a Mott Hubbard insulator.[2a] The IR spectra of both complexes **14** and **15** show broad peaks, characteristic of an organic conductor; the charge-transfer band is observed at 3450–3000 cm^{-1} and the cyanide absorptions are appropriate for anionic TCNQ.[21] Solid state UV–visible spectra of the complexes **14** and **15** show characteristic transitions of $TCNQ^0$ and $TCNQ^{\cdot-}$ consistent with the complexes being mixed valence.[22] The existence of charge-transfer in complex **14** was further confirmed by the detection of a strong ESR signal with a g-value of 2.0003.

Wittig–Horner Reactions of 1,3-Dithiole and 1,3-Selenathiole Carbanions: Synthesis of Extended Tetrathiafulvalene Derivatives and Selenium-containing Analogues.—Alongside our investigations into the bis(4,5-dimethyl-1,3-dithiolium) dications **8a–c**, we pursued a completely different approach that


16
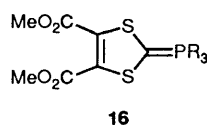
has yielded extended quinonoid donors e.g., **35–43** in the neutral (reduced) form.[23] The key step is Wittig–Horner reactions of the heterocyclic carbanions **23–25** (Scheme 2). Although Wittig reactions of the ylide **16** have been used on several occasions to yield TTF analogues,[5b,24] only scant attention has been given to the dimethyl- and dihydro-1,3-dithiolium anions **23** and **24**; compound **24** was initially studied by Akiba et al., who established the superiority of the phosphonate ester **24** over the corresponding phosphorane, in Wittig reactions.[25] More recently, reactions of **23** and **24** have been reported by Lerstrup et al.[26] and by Yamashita et al.[27] We now report new reactions of the anions **23** and **24**, along with the generation and in situ trapping of the hitherto unknown 1,3-selenathiole carbanion **25**. All these species **23–25** are highly reactive nucleophiles, partly due to their 8π potentially anti-aromatic nature.

The cations **17–19** were prepared using literature procedures, and they reacted rapidly with trimethyl phosphite in the presence of an equimolar amount of sodium iodide in acetonitrile at room temperature to give the phosphonate esters **20–22** in >90% yields. The esters **20–22** were isolated, after column chromatography, as hygroscopic red oils, and identified by NMR, IR, mass spectroscopic data and elemental analysis. The instability of ester **22** meant it was best used in subsequent reactions immediately after isolation. The esters **20–22** were easily deprotonated with 1 mol equiv. of butyllithium in tetrahydrofuran (THF) at −78 °C; an instant colour change from red to yellow–orange was observed on dropwise addition of the base to solutions of the ester. To establish that carbanions **23–25** were thus being formed, we added a range of simple carbonyl compounds, e.g., cyclopentanone, cyclohexanone,
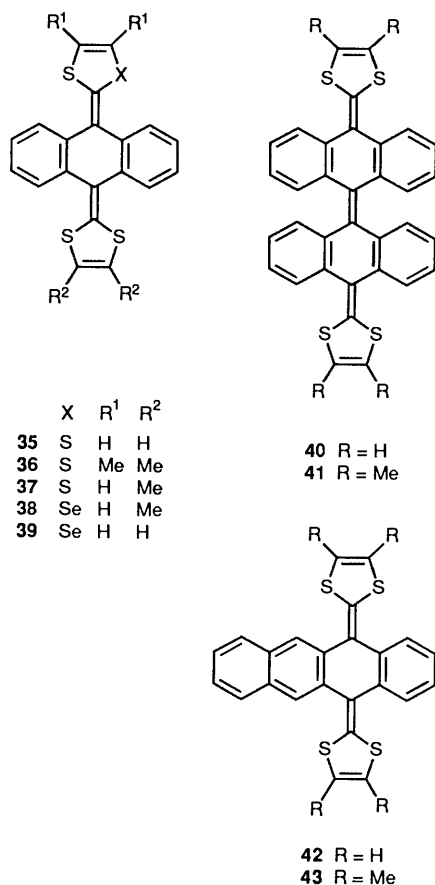
	X	R
17	S	H
18	S	Me
19	Se	H

	X	R
20	S	H
21	S	Me
22	Se	H

	X	R
23	S	H
24	S	Me
25	Se	H

	X	R^1	R^2	R^3
26	S	H		$-[CH_2]_4-$
27	S	H	Ph	Ph
28	S	Me		$-[CH_2]_4-$
29	S	Me	Ph	Ph
30	Se	H		$-[CH_2]_4-$
31	Se	H		$-[CH_2]_5-$
32	Se	H	Ph	Ph
33	Se	H	Ph	H

Scheme 2 *Reagents and conditions:* i, trimethyl phosphite, sodium iodide, acetonitrile, 20 °C; ii, butyllithium, THF, −78 °C, followed by carbonyl compound

benzophenone, acetophenone and benzaldehyde, to these solutions and obtained the expected new products of Wittig–Horner reaction, viz. alkenes **26–33**, typically in 60–70% yields (Scheme 2). Thioxanthen-9-one reacted similarly with the carbanion **24** to afford product **34**.
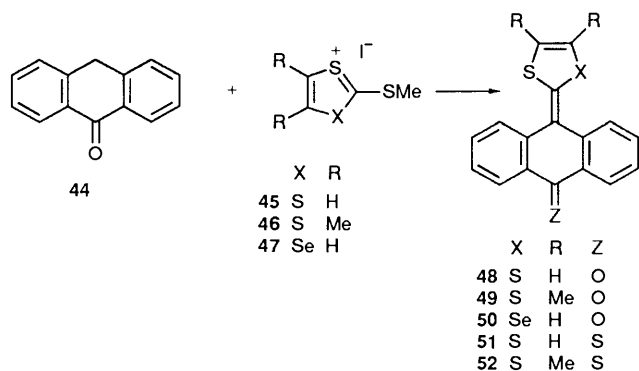

34
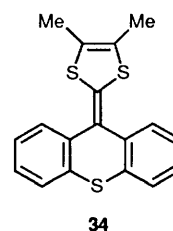
We next trapped 1,3-dithiole carbanions **23** and **24** with anthraquinone, bianthrone and naphthacene-5,12-quinone to give the extended tetrathiafulvalene derivatives **35**, **36**, **40–43** which were isolated in good yields as air-stable, orange crystalline solids.* Compound **36** is the reduced form of dication **8b**, the isolation of which has been described above. A second, minor product which was always present alongside the TTF derivative, was identified by mass spectral evidence as the corresponding half-substituted quinone. These minor products were difficult to separate completely from unchanged starting quinone, so only two of these ketones, viz. compounds **48** and **49**

* The results of a single crystal X-ray analysis of compound **36** will be reported elsewhere.[28]

	X	R¹	R²
35	S	H	H
36	S	Me	Me
37	S	H	Me
38	Se	H	Me
39	Se	H	H

40 R = H
41 R = Me

42 R = H
43 R = Me

The solution UV–visible spectra of the extended donors 35–43 all show the expected large bathochromic shifts relative to TTF 1 (*e.g.*, TTF: 1 λ_{max}/nm 317; compounds 35 and 40: λ_{max}/nm 415 and 438, respectively). This is consistent with a lowering of the $\pi \rightarrow \pi^*$ excitation energy as a result of the increase in conjugation between the 1,3-dithiole rings. It is noteworthy that the UV spectra of ketones 48 and 49 (λ_{max}/nm 467 and 481, respectively) are red-shifted further than their corresponding anthracenediylidene derivatives 35 and 36,

48a R = H
49a R = Me
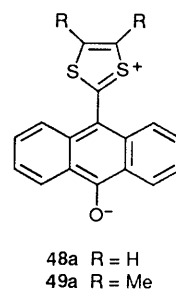
respectively. This may be rationalised by a resonance contribution from the aromatic dipolar structures 48a and 49a to the excited states of 48 and 49, which would reduce the n→π* excitation energy. However, the contribution of these dipolar structures to the ground states of 48 and 49 is minimal as judged by ¹H NMR spectra; the chemical shift values for the methyl protons of 36 and 49 are virtually identical, which strongly supports canonical form 49 for the ketone [*viz.* δ_H(CDCl₃) 1.91 for 36 and 1.98 for 49]. A methyl substituent on a cationic 1,3-dithiolium ring, *e.g.*, structure 49a, should occur at δ_H 2.90–3.05 (*cf.* dications 8a–c discussed earlier). Similar dipolar structures have been considered previously for 1,3-benzodithiolylidene derivatives.[25b]

The isomeric *cis* and *trans* diselenadithiafulvalene derivatives 53a and 53b with a bridging anthracenediylidene group,

Complex 54: 35–(TCNQ)₄
Complex 55: 36–(TCNQ)₄
Complex 56: 37–(TCNQ)₄

53a   53b
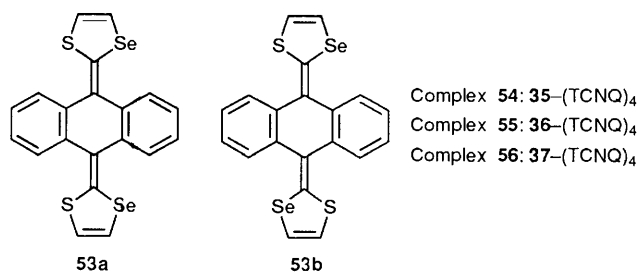
were obtained as an inseparable mixture by reaction of anthraquinone with 2 equiv. of the anion 25. The ¹H NMR spectrum of the product mixture exhibited two distinct AB coupling patterns with equal integration, for 4-H and 5-H of the 1,3-selenathiole rings, indicating a 1:1 mixture of the *cis* and *trans* isomers 53a and 53b. These isomers were thermally stable; their NMR signals did not coalesce on heating to 85 °C and there was no change in the NMR spectrum after heating at 150 °C in dimethyl sulphoxide for 10 h. Diselenadithiafulvalene has previously been obtained as an inseparable mixture of *cis* and *trans* isomers.[31]

Donors 35–37 yield conducting 1:4 complexes 54–56 with TCNQ which were isolated in 32–48% yields from mixtures of the neutral donor and acceptor molecules in acetonitrile solution. Donor 36 also forms an insulating 1:2 complex with 2,5-dibromo-TCNQ. Data for the complexes are given in Table 1. The single crystal X-ray structure and variable temperature conductivity and magnetic susceptibility data for complex 55 will be reported elsewhere.[28]

were purified. However, an alternative route, *viz.* the reaction of anthrone 44 with 2-thiomethyl-1,3-dithiolium iodides 45 and 46 in refluxing pyridine–acetic acid, cleanly afforded compounds 48 and 49, respectively, in *ca.* 85% yields (Scheme 3). These reaction conditions were based on those developed previously

	X	R
45	S	H
46	S	Me
47	Se	H

	X	R	Z
48	S	H	O
49	S	Me	O
50	Se	H	O
51	S	H	S
52	S	Me	S

Scheme 3 *Reagents and conditions:* i, pyridine–acetic acid, reflux

by Gompper and Kutter for analogous reactions of the 1,3-benzodithiolium system.[29] A similar procedure yielded the 1,3-selenathiole derivative 50 (86% yield). Ketones 48 and 49 were converted into the corresponding thioketones 51 and 52 by reaction with phosphorous pentasulphide in pyridine (*ca.* 70% yield). The reaction of the ketones 48–50 with 1 equiv. of the appropriate carbanion 23, 24 or 25 afforded the unsymmetrical derivatives 37–39 (58–74% yield). This two-step methodology, starting from anthrone, provides an attractive route to unsymmetrical electron donors and avoids the problems usually encountered in the preparation of unsymmetrical TTF derivatives by cross-coupling methods, *viz.* the formation of complex product mixtures.[13a,b,30]

Table 2 Cyclic voltammetric data recorded *versus* Ag/AgCl, Pt button electrode, scan rate 100 mV s^{-1}, 5 × 10^{-5} mol dm^{-3} compound, 0.1 mol dm^{-3} Bu$_4$N$^+$ ClO$_4^-$ in acetonitrile. Data for compounds **8a** and **8c** were obtained with an initial reduction scan, while data for compounds **35–43** and **53** were obtained with an initial oxidative scan.

Compound	E_{ox}/V	E_{red}/V
8a	+0.06	+0.03
8c	+0.13	+0.10
35	+0.40	+0.20
36	+0.42	+0.07
37	+0.36	+0.19
38	+0.45	+0.09
39	+0.47	+0.11
40	+0.48	+0.01
41	+0.45	+0.11
42	+0.44	+0.12
43	+0.41	+0.09
53	+0.51	−0.02

Table 3 Cyclic voltammetric data for compounds **48–52**. (Same conditions as Table 2 with initial oxidative scan.)

Compound	$E_1^{\ddagger}$/V
48	+0.85^a
49	+0.79^a
50	+0.90^a
51	+0.61^b
52	+0.55^b

^{a} Reversible. ^{b} Irreversible.
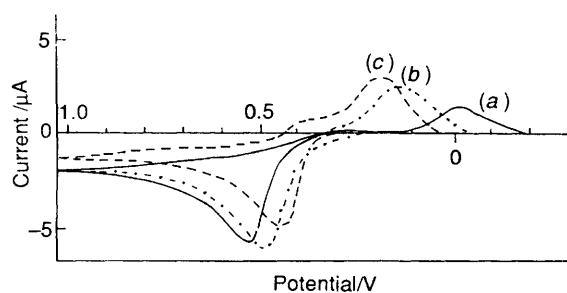
Fig. 1 Cyclic voltammograms: (*a*), donor **53**; (*b*), donor **39**; (*c*), donor **35**

Cyclic Voltammetry of 1,3-*Dithiole and* 1,3-*Selenathiole Systems.*—The electrochemical redox behaviour of the dications **8a, c** and the anthracenediylidene derivatives **35–43** and **53** has been studied by cyclic voltammetry and the results are summarised in Table 2. A striking feature of these data is that these molecules undergo two-electron redox behaviour which is observed as a single wave. Coulometric analysis for donor **36** confirmed this to be a two-electron process. The separate oxidation peaks could not be resolved by reducing the scan rate to 10 mV s^{-1} or by lowering the temperature to −30 °C for donor **36**. Thus, it remains unclear as to whether the oxidation that occurs is truly a single, two-electron process, or two, inseparable, concurrent, one-electron processes. However, the coalescence of the two one-electron processes characteristic of TTF and tetramethyl-TTF (TMTTF) into a single oxidation wave is a clear indication that introduction of the quinonoid fragment into the TTF skeleton has decreased intramolecular Coulombic repulsion in the doubly ionised state. The oxidation potentials for **35–43** and **53** are slightly higher than the first oxidation potentials for TTF ($E_1^{\ddagger}$/V +0.34) and TMTTF ($E_1^{\ddagger}$/V +0.32), indicating that the extended systems **35–43** and **53** are poorer donors when E_1 values are considered. In all cases, the

second electron is donated more readily than for TTF and TMTTF. This observation is consistent with previous work on related systems which has shown that the difference in potential between the first and second redox waves decreases as the conjugation length increases.[6,10,11,27,32]

It is known from previous work that the donor ability of a tetrathiafulvalene derivative is reduced upon incorporation of selenium atoms into the ring system [*cf.* TTF 1: $E_1^{\ddagger}$/V +0.34, $E_2^{\ddagger}$ +0.71 and tetraselenafulvalene: $E_1^{\ddagger}$/V +0.48, $E_2^{\ddagger}$ +0.76, Pt electrode, *versus* Ag/AgCl].[33] This is attributable to selenium forming weaker π-bonds with carbon than does sulphur. Thus, the selenium-containing cations are less stable than their sulphur counterparts, as the former are less able to redistribute charge: this raises the overall energy required for ionisation as selenium is substituted for sulphur. This phenomenon is clearly observed with the extended anthracenediylidene derivatives **35**, **39** and **53** (Table 2 and Fig. 1).

All donors **35–43** and **53** show a single reduction wave at far lower potentials than expected for a reversible process. However, we assign the observed reduction wave as being associated with the process donor^{2+}→donor^0, as there is no detectable change in the voltammograms after 30 min of continuous cycling between 0.00 and +1.00 V. The reduction of the dications **35–43** and **53** to their corresponding neutral donors occurs at low potentials which reflect the high stability of the heteroaromatic bis(1,3-dithiolium) dications, in which the central anthracene ring can gain planarity. The energy required to overcome the loss of this aromaticity in forming the highly distorted quinonoid skeletons of the neutral donors will be high. Single crystal X-ray data for both the neutral and dication stages of redox system **36** support this reasoning. The neutral donor **36** adopts a distorted, butterfly conformation while the dication **8b** in complex **55** adopts a dramatically different conformation, with dihedral angles of 86.0° between the planar anthracene group and the 1,3-dithiole rings.[28]

In contrast to the behaviour of anthracenediylidene donors **35–43** and **53**, the two-electron redox couple of the dications **8a** and **8c** is cleanly reversible. It is notable that the donor ability of molecule **11**, which has a central naphthoquinoid ring, is better by *ca.* 0.35 V than anthracenediylidene analogue **36**. Similar data for benzo-, naphtho- and anthracene-*p*-quinodimethane systems have recently been reported by Yamashita *et al.*[27]

The cyclic voltammetric data for the ketones **48–50** and the thiones **51** and **52** are shown in Table 3. The ketones **48–50** show a single, one-electron redox couple to the radical cation at a high potential, which is consistent with the electron-withdrawing effect of the carbonyl group. Predictably, the oxidation of the 1,3-selenathiole derivative **50** occurs at the highest potential for this series of compounds, while the thiones **51** and **52** are oxidised at significantly lower potentials. The oxidation of the ketones **48–50** is a cleanly reversible process, while in marked contrast to this, the oxidation of the thiones **51** and **52** is completely irreversible, with no observed reduction, reflecting instability of the radical cations of **51** and **52**.

Experimental

General.—M.p.s were recorded on a Kofler hot-stage microscope apparatus and are uncorrected. IR spectra were recorded on Perkin-Elmer 577 and 547 spectrophotometers; samples were either embedded in KBr discs, or Nujol mulls (neat, if liquids) between KBr plates, as indicated. Fourier-transform IR spectra were recorded on a Mattson-Sirius 100 Fourier-transform instrument, with samples embedded in KBr discs. Solution-state UV spectra were recorded on a Kontron Uvikon 930 instrument, with solvents as indicated. UV–visible–near-IR spectra were obtained on a Cary 2300 spectrophotometer; samples were Nujol mulls on CaF$_2$ plates. ^{1}H NMR

and ^{13}C NMR spectra were recorded on a Bruker AC 250 instrument, operating at 250.134 MHz for protons and 62.896 MHz for the carbon nucleus. Chemical shifts, given in ppm, are relative to tetramethylsilane (TMS) as internal standard. All J values are in Hz. Mass spectra were obtained on a VG 7070E instrument, operating at 70 eV, with ionisation modes as indicated. All selenium-containing mass peaks are reported for ^{80}Se. Elemental analyses were performed on either a Carlo-Erba Strumentazione (C, H, N) or a Perkin-Elmer HGA 500 (S). TLC analyses were performed using Merck pre-coated alumina (0.2 mm) or Merck pre-coated silica (0.2 mm) aluminium backed sheets. For column chromatography, Merck alumina (activity II to III, 70–230 mesh) or Merck silica gel (70–230 mesh) were employed as indicated. Neutral alumina refers to alumina pre-soaked in ethyl acetate for 24 h. All solvents were distilled prior to use in chromatography. Solvents were dried from the following agents under a nitrogen atmosphere: THF (sodium metal then $LiAlH_4$); benzene and toluene (sodium metal); chlorocarbons (P_2O_5); acetonitrile (CaH_2); methanol (magnesium methoxide) and ethanol (magnesium ethoxide). All other reagents were reagent grade and used as supplied, unless otherwise stated. Cyclic voltammetry (CV) experiments were performed in a one-compartment cell with platinum working and counter electrodes and a silver–silver chloride reference electrode. Measurements were made with a BAS 100 electrochemical analyser and were iR compensated. The cell contained a solution of donor ($ca.$ 1 × 10^{-5} mol dm^{-3}) with oven-dried (120 °C) tetrabutylammonium perchlorate (TBAP) (0.01 mol dm^{-3}) as supporting electrolyte in dry acetonitrile ($ca.$ 10 ml); all solutions were purged with argon and retained under the inert atmosphere while the CV data were recorded. Conductivity measurements on powdered samples were obtained using the two-probe technique; samples were manually compressed between two steel probes and the sample resistance monitored with a Fluka 8000A Digital Multimeter. Single crystal conductivity measurements were obtained using standard four-probe techniques; four contacts were made using air-drying silver paste and a Keithley 228 voltage/current source was used.

1,3-Dithiolium Tetrafluoroborate **17**.—This compound was prepared following the literature procedure[34] from 1,3-dithiole-2-thione in 88% yield, m.p. 128–130 °C. In our hands this method is preferable to other reported procedures.[35]

4,5-Dimethyl-1,3-dithiolium Tetrafluoroborate **18**.—This was prepared analogously to salt **17** from 4,5-dimethyl-1,3-dithiole-2-thione[36] in 85% yield, m.p. 125–126 °C (lit.,[25b] 123–125 °C).

1,3-Selenathiolium Tetrafluoroborate **19**.—This was prepared in three steps following the literature procedure[37] from 1,3-selenathiole-2-thione in 85% yield, m.p. 70–72 °C; $\delta_H(CF_3-CO_2H)$ 12.41 (1 H, s), 10.15 and 9.53 (each 1 H, AB J 6).

Dipiperidinium Naphthalene-1,4-bis(dithiocarboxylate) **6a**.— A mixture of elemental sulphur (3.8 g, 0.12 mol) and sodium methoxide [from sodium (2.8 g, 0.12 mol)] in dry methanol (250 ml) was refluxed for 2 h under nitrogen with mechanical stirring. 1,4-Bis(bromomethyl)naphthalene **5a**[38] (10 g, 0.03 mol) was added dropwise as a suspension in dry methanol (25 ml) to the refluxing mixture over a period of 2 h. The mixture was then refluxed for a further 15 h, after which it was cooled, and evaporated under reduced pressure. The residue was dissolved in water (100 ml), and the solution filtered and

acidified with dilute hydrochloric acid (2 mol dm^{-3}; 30 ml) to yield the bis(dithiocarboxylic acid) as a pungent deep-red precipitate. Dichloromethane ($ca.$ 120 ml) was added until all the precipitate had dissolved after which the mixture was extracted into dichloromethane (3 × 50 ml). The combined extracts were dried ($MgSO_4$), filtered, and concentrated under reduced pressure to $ca.$ 50 ml. The residue was cooled to -5 °C and piperidine ($ca.$ 9 ml, 0.09 mol) was added dropwise until precipitation was complete. The solid product was collected by filtration, washed with ether (3 × 50 ml) and dried under reduced pressure to afford the *dipiperidinium salt* **6a** (7.8 g, 55%) as an orange powder, m.p. 154–155 °C (decomp.) (Found: C, 58.4; H, 6.4; N, 5.9; S, 28.1. $C_{22}H_{30}N_2S_4$ requires C, 58.6; H, 6.7; N, 6.2; S, 28.5%); $\nu_{max}(Nujol)/cm^{-1}$ 2940, 2830, 1595, 1510, 1460, 1035, 1012, 950 and 865.

Dipiperidinium Anthracene-9,10-bis(dithiocarboxylate) **6b**.— Following the procedure described for the salt **6a**, elemental sulphur (7 g, 0.22 mol), sodium methoxide [from sodium (5 g, 0.22 mol)] and 9,10-bis(chloromethyl)anthracene **5b**[39] (15 g, 0.055 mol) were heated at reflux in dry methanol (400 ml) for 72 h. After work-up, the *dipiperidinium salt* **6b** (21.8 g, 79%) was isolated as an orange solid, m.p. 111–113 °C (decomp.) (Found: C, 62.1; H, 6.0; N, 5.6. $C_{26}H_{32}N_2S_4$ requires C, 62.4; H, 6.4; N, 5.6%]; $\nu_{max}(Nujol)/cm^{-1}$ 2935, 2832, 1590, 1510, 1465, 1040, 1000, 955 and 840.

Dipiperidinium Biphenyl-4,4'-bis(dithiocarboxylate) **6c**.—Following the procedure described for salt **6a**, elemental sulphur (3.8 g, 0.12 mol) sodium methoxide [from sodium (2.8 g, 0.12 mol)] and 4,4'-bis(chloromethyl)biphenyl * **5c** (7.5 g, 0.03 mol) were heated at reflux in dry methanol (150 ml) for 16 h. Work-up afforded the *dipiperidinium salt* **6c** (11.5 g, 80%) as an orange solid, m.p. 161–163 °C (Found: C, 60.2; H, 6.9; N, 5.7. $C_{24}H_{32}N_2S_4$ requires C, 60.5; H, 6.8; N, 5.9%]; $\nu_{max}(Nujol)/cm^{-1}$ 2940, 2860, 2840, 1585, 1510, 1500, 1475, 1465, 1035, 1000, 955 and 840.

Bis(1-methyl-2-oxopropyl)naphthalene-1,4-dithiodicarboxylate **7a**.—A solution of 3-chlorobutan-2-one (2.2 g, 0.02 mol) in dry dichloromethane (20 ml) was added dropwise over 0.5 h to a stirred suspension of salt **6a** (4.5 g, 0.01 mol) in dry dichloromethane (100 ml) under nitrogen at 20 °C. The mixture was stirred for 12 h, and the solvent evaporated under reduced pressure. Column chromatography (silica, 8 × 4 cm) of the residue, eluting with cyclohexane–dichloromethane (1 : 1 v/v), yielded *compound* **7a** (2.7 g, 63%) as a bright red solid, m.p. 150–153 °C (Found: C, 57.3; H, 5.0. $C_{20}H_{20}O_2S_4$ requires C, 57.1; H, 4.8%]; m/z (EI) 420 (M$^+$); (CI) 421; $\nu_{max}(Nujol)/cm^{-1}$ 2940, 1700, 1445, 1372, 1358, 1230br, 1035 and 920; $\delta_H(CDCl_3)$ 7.98 (2 H, s), 8.21 and 7.72 (each 2 H, AA'XX'), 4.91 (2 H, q, J 6), 2.33 (6 H, s) and 1.60 (6 H, d, J 6).

Bis(1-methyl-2-oxopropyl)anthracene-9,10-dithiodicarboxylate **7b**.—Following the procedure described for compound **7a**, a mixture of the salt **6b** (15 g, 0.03 mol) and 3-chlorobutan-2-one (6.5 g, 0.06 mol) was stirred in dry dichloromethane (120 ml) for 14 h to afford *compound* **7b** (10.6 g, 62%) as red crystals, m.p. 172–174 °C (Found: C, 60.9; H, 4.9. $C_{24}H_{22}O_2S_4$ requires C, 61.2; H, 4.7%); m/z (EI) 470 (M$^+$); (CI) 471; $\nu_{max}(Nujol)/cm^{-1}$ 2920, 1705, 1440, 1350, 1238, 1162, 1150, 1090, 1015, 950 and 760; $\delta_H(CDCl_3)$ 7.81 and 7.35 (each 4 H, AA'XX'), 4.89 (2 H, q, J 7), 2.34 (6 H, s) and 1.71 (6 H, d, J 7).

Bis(1-methyl-2-oxopropyl)biphenyl-4,4'-dithiodicarboxylate **7c**.—Following the procedure described for compound **7a**, a mixture of salt **6c** (4.8 g, 0.01 mol) and 3-chlorobutan-2-one (2.2 g, 0.02 mol) in dry dichloromethane (75 ml) was stirred for

---

* 4,4'-Bis(chloromethyl)biphenyl was kindly supplied by Seal Sands Chemical Co. Ltd.

14 h to afford *compound* **7c** (3.4 g, 75%) as a red powder, m.p. 163–167 °C (Found: C, 59.1; H, 4.9. $C_{22}H_{22}O_2S_4$ requires C, 59.2; H, 5.0%); m/z (EI) 446 (M$^+$); (CI) 447; ν_{max}(Nujol)/cm^{-1} 2935, 1710, 1445, 1370, 1345, 1235br, 1145, 1090 and 940; δ_H(CDCl$_3$) 8.04 and 7.65 (each 4 H, AX, J 8), 4.89 (2 H, q, J 7), 2.31 (6 H, s) and 1.57 (6 H, d, J 7).

2,2′-(Naphthalene-1,4-diyl)bis(4,5-dimethyl-1,3-dithiolium) Bis(hydrogensulphate) **8a**.—Compound **7a** (2.5 g, 6 mmol) was added in portions to stirred sulphuric acid (conc., 5 ml) at −10 °C, the reaction temperature being maintained below −5 °C at all times. The solution was stirred for 2.5 h at −10 °C and then allowed to warm slowly to 20 °C over a period of 1 h. Dilution with ethyl acetate (15 ml) precipitated a solid, which was collected by filtration, washed with ice-cold acetone (3 × 10 ml) and dried *in vacuo* to afford the *bis(hydrogensulphate) salt* **8a** (X = HSO$_4$) (3.3 g, 92%) as a brown powder (Found: C, 43.6; H, 2.7. $C_{20}H_{20}O_8S_6$ requires C, 41.4; H, 3.5%); ν_{max}(Nujol)/cm^{-1} 1510, 1370, 1310, 1170, 1020, 860, 775 and 730.

The dication salt **8a** was purified by conversion into its corresponding bis(hexafluorophosphate) salt **8a** (X = PF$_6$) using the following method: hexafluorophosphoric acid (60%, 5 ml) was added dropwise to a stirred solution of the bis-(hydrogensulphate) salt **8a** (2.5 g, 4.5 mmol) in water (5 ml) at 20 °C. The resultant precipitate was collected by filtration, washed with ice-cold acetone (3 × 15 ml), and dried *in vacuo* to yield *salt* **8a** (X = PF$_6$) (2.7 g, 88%) as a golden-yellow powder, m.p. 170 °C (decomp.) (Found: C, 35.6; H, 2.7; S, 19.2. $C_{20}H_{18}F_{12}P_2S_4$ requires C, 35.5; H, 2.7; S, 19.0%]; m/z FAB; (glycerol) 193 (M^{2+}) and 145 (PF$^-_6$); δ_H(CF$_3$CO$_2$H) 8.31 and 7.99 (each 2 H, AA′XX′), 8.13 (2 H, s) and 2.97 (12 H, s).

2,2′-(Anthracene-9,10-diyl)bis(4,5-dimethyl-1,3-dithiolium) Bis(hydrogensulphate) **8b**.—Following the procedure used for salt **8a**, compound **7b** (2.3 g, 5 mmol) in sulphuric acid (conc., 5 ml) for 4 h afforded the *bis(hydrogensulphate) salt* **8b** (X = HSO$_4$) (2.7 g, 86%) as a brown powder, m.p. *ca.* 160 °C (decomp.) (Found: C, 46.0; H, 3.3; S, 29.1. $C_{24}H_{22}O_8S_6$ requires C, 45.7; H, 3.5; S, 30.5%); ν_{max}(Nujol)/cm^{-1} 1515, 1350, 1345, 1335, 1300, 1170, 1005, 860, 830 and 790; δ_H(CF$_3$CO$_2$H) 8.46 and 8.02 (each 4 H, AA′XX′) and 3.01 (12 H, s). Bis(hydrogensulphate) salt **8b** proved to be too insoluble for purification by conversion into any other anion salt.

2,2′-(Biphenyl-4,4′-diyl)bis(4,5-dimethyl-1,3-dithiolium) Bis-(hexafluorophosphate) **8c**.—Compound **7c** (1.3 g, 3 mmol) in sulphuric acid (conc., 5 ml) for 2 h yielded the *salt* **8c** (X = HSO$_4$) (1.6 g, 90%) as a yellow-brown powder (Found: C, 45.1; H, 2.9. $C_{22}H_{22}O_8S_6$ requires C, 43.5; H, 3.7%); ν_{max}(Nujol)/cm^{-1} 1505, 1370, 1340, 1325, 1315, 1150, 1020 and 800. Purification was achieved by conversion into the corresponding bis(hexafluorophosphate) salt **8c** (X = PF$_6$). The salt **8c** (X = HSO$_4$) (1 g, 1.6 mmol) and hexafluoro-phosphoric acid (60%, 3 ml) in water (5 ml) afforded the *dication salt* **8c** (X = PF$_6$) (0.95 g, 85%) as a golden-yellow powder, m.p. *ca.* 220 °C (decomp.) (Found: C, 37.4; H, 3.1; S, 18.6. $C_{22}H_{20}F_{12}P_2S_4$ requires C, 37.6; H, 2.9; S, 18.3%); m/z (FAB; glycerol) 206 (M^{2+}) and 145 (PF$^-_6$); δ_H(CF$_3$CO$_2$H) 8.51 and 8.08 (each 4 H, AX, J 8), and 2.93 (12 H, s).

2,2′-(Naphthalene-1,4-diyl)bis(4,5-dimethyl-1,3-dithiole) **9**.— Sodium borohydride (115 mg, 3 mmol) was added in portions over 0.5 h to a stirred suspension of salt **8a** (X = PF$_6$) (500 mg, 0.7 mmol) in dry ethanol (25 ml) at 20 °C. After a further 2 h at 20 °C, the solvent was evaporated under reduced pressure and the residue dissolved in dichloromethane (25 ml). The solution was filtered and evaporated under reduced pressure. Column

chromatography (silica, 5 × 1 cm) of the residue, eluting with dichloromethane, gave *compound* **9** (165 mg, 58%) as a red-brown solid, m.p. >240 °C (Found: C, 62.0; H, 4.9. $C_{20}H_{20}S_4$ requires C, 61.8; H, 5.2%); m/z (EI) 388 (M$^+$); (CI) 389; ν_{max}(Nujol)/cm^{-1} 1595, 1535, 1515, 1370, 1275, 1100, 965, 940, 760, 745 and 665; δ_H(CDCl$_3$) 8.00 (2 H, s), 7.96 and 7.55 (each 2 H, AA′XX′), 6.48 (2 H, s) and 1.90 (12 H, s).

2-[4-(4,5-Dimethyl-1,3-dithiol-2-yl)-1-naphthyl] Naphthal-*ene(4,5-dimethyl-1,3-dithiolium) Hexachloroantimonate* **10**.—A stirred solution of compound **9** (200 mg, 0.5 mmol) and triphenylcarbenium hexachloroantimonate (580 mg, 1.0 mmol) in dry dichloromethane (30 ml) under nitrogen was refluxed for 3 h. After the solution had cooled, ether (20 ml) was added and the solid collected by filtration, washed with ether (3 × 10 ml) and dried *in vacuo* to afford the *salt* **10** (270 mg, 75%) as a brown powder which could not be obtained analytically pure, m.p. >240 °C (Found: C, 29.7; H, 2.3. $C_{20}H_{19}Cl_6S_4Sb$ requires C, 33.2; H, 2.7%); m/z FAB (glycerol) 387 (M$^+$); δ_H(CF$_3$CO$_2$H) 8.43–7.51 (6 H, m), 5.81 (1 H, s), 2.73 (6 H, s) and 1.91 (6 H, s).

1,4-Bis(4,5-dimethyl-1,3-dithiole-2-ylidene)-1,4-dihydronaph-thalene–2,3-Dichloro-5,6-dicyano-p-benzoquinone (DDQ) Complex (1:1 *Stoicheiometry*) **12**.—A stirred solution of compound **9** (200 mg, 0.5 mmol) and DDQ (230 mg, 1.0 mmol) in dry benzene (10 ml) was refluxed for 2 h under nitrogen. The solution was cooled and the solid collected by filtration, washed with ether (3 × 10 ml) and dried *in vacuo*. The resultant brown powder was identified as *complex* **12** (70 mg, 20%), m.p. 85–90 °C (decomp.) [Found: C, 54.9; H, 2.9; N, 4.7. $C_{28}H_{18}N_2$-$Cl_2O_2S_4$ (*i.e.* a 1:1 complex) requires C, 54.8; H, 3.0; N, 4.6%]; ν_{max}(KBr, FT-IR)/cm^{-1} 3400–3000v br, 2222, 1566, 1500, 1450, 1199, 1064, 1012, 973, 862 and 688; λ_{max}(MeCN)/nm 780, 640, 415, 350, 260 and 210.

1,4-Bis(4,5-dimethyl-1,3-dithiole-2-ylidene)-1,4-dihydronaph-thalene–Iodine Complex (1:2.8 *Stoicheiometry*) **13**.—The dication salt **8a** (X = PF$_6$) (75 mg, 0.1 mmol) was added to a solution of lithium iodide (67 mg, 0.5 mmol) in acetone (15 ml) and the resultant solution heated under reflux for 0.5 h. The solution was cooled and the solid collected by filtration washed with ice-cold acetone (3 × 10 ml) and dried in air to afford *complex* **13** (70 mg, 95%) as a red powder, m.p. 245 °C (decomp.) [Found: C, 32.5; H, 2.4; S, 17.3. $C_{20}H_{18}S_4I_{2.8}$ (*i.e.* a 1:2.8 complex) requires C, 32.4; H, 2.4; S, 17.3%]. The analysis of salt **13** was unchanged after two recrystallisations from acetone.

1,4-Bis(4,5-dimethyl-1,3-dithiole-2-ylidene)-1,4-dihydro-naphthalene–7,7,8,8,-Tetracyano-p-quinodimethane Complex (1:2.4 *Stoicheiometry*) **14**.—The dication salt **8a** (X = PF$_6$) (75 mg, 0.1 mmol) in acetonitrile (5 ml) was added to a solution of Li$^+$TCNQ$^{\cdot-}$ (63 mg, 0.3 mmol) in acetonitrile–acetone (1:1 v/v; 20 ml) and the resultant mixture heated under reflux for 0.5 h. The solution was cooled to 20 °C and the precipitate collected by filtration, washed with acetone (2 × 5 ml) and dried in air to afford *complex* **14** (51 mg, 52%) as a black powder, m.p. 168 °C (decomp.); [Found: C, 66.9; H, 3.2; N, 15.4. $C_{48.8}H_{27.6}N_{9.6}S_4$ (*i.e.* a 1:2.4 complex) requires C, 66.9; H, 3.2; N, 15.3%]; ν_{max}(KBr, FT-IR)/cm^{-1} 3400–3000br, 2197, 2177, 2154, 1559, 1540, 1521, 1506, 1294 and 1090; λ_{max}(MeCN)/nm 845, 745, 395 and 200; λ_{max}(Nujol)/nm 880, 835, 780 and 380; ESR (powder) g 2.0003 (singlet).

Numerous reactions using a variety of cation **8a** (X = PF$_6$):Li$^+$TCNQ$^{\cdot-}$ ratios afforded the same complex, as judged by elemental analysis and spectra; the best yields were obtained from the procedure detailed above.

4,4'-Bis(4,5-dimethyl-1,3-*dithiole*-2-*ylidene)*-4,4'-*dihydrobi-phenyl*-7,7,8,8-*Tetracyano*-p-*quinodimethane Complex* (1:2 *Stoicheiometry*) **15**.—Following the procedure used for complex **14**, dication **8c** (75 mg, 0.1 mmol) and Li$^+$TCNQ^{--} (42 mg, 0.2 mmol) in acetonitrile–acetone (1:1 v/v) gave *complex* **15** (20 mg, 25%) as a black powder, m.p. >250 °C [Found: C, 67.5; H, 3.2; N, 13.1. C$_{46}$H$_{28}$N$_8$S$_4$ (*i.e.* a 1:2 complex) requires C, 67.3; H, 3.4; N, 13.7%]; v_{max}(KBr, FT-IR)/cm^{-1} 3450–3000v br, 2183, 2169, 2151, 1560, 1512, 1331 and 1154; λ_{max}(MeCN)/nm 845, 745, 395 and 200 nm; λ_{max}(Nujol)/nm 895, 835, 780 and 385.

Dimethyl 1,3-*Dithiol*-2-*ylphosphonate* **20**.—Freshly distilled trimethyl phosphite (0.62 ml, 5.3 mmol) and sodium iodide (0.8 g, 5.3 mmol) were added successively to a stirred solution of the cation salt **17** (1.0 g, 5.3 mmol) in dry acetonitrile (50 ml) under a nitrogen atmosphere at 20 °C. A slightly exothermic reaction immediately took place. Stirring was continued for 2 h, whereupon the solvent was evaporated under reduced pressure. Water (25 ml) was added to the residue and the mixture extracted into dichloromethane (3 × 25 ml). The combined extracts were dried (MgSO$_4$), filtered and the solvent evaporated under reduced pressure. The residue was chromatographed (neutral alumina column, 6 × 2 cm), eluting with ethyl acetate, to afford *phosphonate ester* **20** (1.05 g, 95%) as a deep-red hygroscopic oil (Found: C, 28.0; H, 4.5. C$_5$H$_9$O$_3$PS$_2$ requires C, 28.3; H, 4.3%); *m/z* (EI) 212 (M$^+$); v_{max}(neat)/cm^{-1} 3015, 2950, 2920, 2850, 1665, 1570, 1300, 1250br, 1040br, 910 and 890; δ_H(CDCl$_3$) 5.98 (2 H, s), 4.73 (1 H, d, *J* 4.5) and 3.75 (6 H, d, *J* 10.5).

Dimethyl 4,5-*Dimethyl*-1,3-*dithiol*-2-*ylphosphonate* **21**.—Following the procedure detailed for ester **20**, trimethyl phosphite (0.6 ml, 4.8 mmol), sodium iodide (0.72 g, 4.8 mmol) and the cation salt **18** (1.05 g, 4.8 mmol) in acetonitrile (50 ml) afforded the *ester* **21** (1.1 g, 95%) as a deep red hygroscopic oil (Found: C, 35.3; H, 5.4. C$_7$H$_{13}$O$_3$PS$_2$ requires C, 35.0; H, 5.5%); *m/z* (EI) 240 (M$^+$); v_{max}(neat)/cm^{-1} 3005, 2960, 2940, 2860, 1675, 1585, 1305, 1250br, 1170, 1040br, 910, 870, 770 and 680; δ_H(CDCl$_3$) 4.75 (1 H, d, *J* 4.5), 3.80 (6 H, d, *J* 10.4) and 1.86 (6 H, s).

Dimethyl 1,3-*Selenathiol*-2-*ylphosphonate* **22**.—Following the procedure detailed for ester **20**, trimethyl phosphite (0.25 ml, 2 mmol), sodium iodide (300 mg, 2 mmol) and the cation salt **19** (475 mg, 2 mmol) in dry acetonitrile (50 ml) afforded the *ester* **22** (471 mg, 91%) as a deep-red oil that decomposed in air (Found: C, 22.8; H, 3.3. C$_5$H$_9$OSSe requires C, 23.2; H, 3.5%); *m/z* (EI) 260 (M$^+$); (CI) 261; v_{max}(neat)/cm^{-1} 3000, 2940, 2900, 2840, 1670, 1550, 1310, 1240br, 1180, 1030br, 970, 900, 820, 770 and 745; δ_H(CDCl$_3$) 6.67 and 6.43 (each 1 H, AB, *J* 8), 5.26 (1 H, d, *J* 4.5) and 3.81 (6 H, d, *J* 10).

Wittig–Horner Reactions of Dimethyl 1,3-*Dithiol*-2-*ylphosphonate* **20**, *Dimethyl* 4,5-*Dimethyl*-1,3-*dithiol*-2-*ylphosphonate* **21** *and Dimethyl* 1,3-*Selenathiol*-2-*ylphosphonate* **22**.—*General procedure.* Butyllithium (BuLi) (1.6 mol dm^{-3} in hexane; 1.1 mol equiv.) was syringed into a stirred solution of the ester **20**, **21** or **22** (1 mol equiv.) in dry THF at −78 °C under nitrogen; reaction occurred immediately with a concomitant colour change from red to yellow. After 0.5 h at −78 °C, the carbonyl compound, dissolved in dry THF, was syringed into the solution of phosphonate carbanion **23**, **24** or **25**, respectively. The mixture was stirred for 1 h at −78 °C and then allowed to warm to 20 °C overnight. The THF was evaporated under reduced pressure, water (75 ml) added and the residue extracted with dichloromethane (3 × 75 ml). The combined extracts were dried (MgSO$_4$), filtered and the solvent removed under

reduced pressure. Purification of products was achieved by column chromatography on silica, with eluents as indicated. Further purification, if necessary, could be achieved by recrystallisation from ethanol, dichloromethane–hexane (1:1 v/v) or dichloromethane–methanol (1:1 v/v).

2-*Cyclopentylidene*-1,3-*dithiole* **26**. Cyclopentanone (0.095 ml, 1.05 mmol) in dry THF (5 ml) and the carbanion **23** [from ester **20** (220 mg, 1.05 mmol) and BuLi (1.6 mol dm^{-3}, 0.72 ml, 1.15 mmol)] in dry THF (50 ml), followed by column chromatography (silica, 15 × 1 cm), eluting with dichloromethane–hexane (1:1 v/v), afforded *compound* **26** (115 mg, 65%) as a light yellow solid, m.p. 45–47 °C (Found: C, 56.1; H, 6.1; S, 38.0. C$_8$H$_{10}$S$_2$ requires C, 56.4; H, 5.9; S, 37.7%); *m/z* (EI) 170 (M$^+$); (CI) 171; v_{max}(Nujol)/cm^{-1} 1580, 1535, 1270, 1130, 830, 760 and 740; δ_H(CDCl$_3$) 6.21 (2 H, s), 2.57–2.39 (4 H, m) and 1.68–1.51 (4 H, m).

2-(*Diphenylmethylene*)-1,3-*dithiole* **27**. Benzophenone (190 mg, 1.05 mmol) in dry THF (5 ml) and carbanion **23** [from ester **20** (220 mg, 1.05 mmol) and BuLi (1.6 mol dm^{-3}, 0.72 ml, 1.15 mmol)] in dry THF (50 ml) followed by chromatography (silica, 15 × 1 cm), eluting with toluene, afforded *compound* **27** (190 mg, 68%) as a yellow solid, m.p. 85–86 °C (Found: C, 71.7; H, 4.2. C$_{16}$H$_{12}$S$_2$ requires C, 71.6; H, 4.5%); *m/z* (EI) 268 (M$^+$); (CI) 269; v_{max}(Nujol)/cm^{-1} 1595, 1510, 1270, 1135, 1030, 950, 830, 760, 755 and 700; δ_H(CDCl$_3$) 7.37–7.14 (10 H, m) and 6.29 (2 H, s).

2-*Cyclopentylidene*-4,5-*dimethyl*-1,3-*dithiole* **28**. Cyclopentanone (0.1 ml, 1.15 mmol) in dry THF (5 ml) and the carbanion **24** [from the ester **21** (275 mg, 1.15 mmol) and BuLi (1.6 mol dm^{-3}; 0.79 ml, 1.25 mmol)] in dry THF (50 ml) followed by column chromatography (silica, 15 × 1 cm), eluting with dichloromethane–hexane (1:1 v/v), afforded *compound* **28** (164 mg, 72%) as a yellow solid, m.p. 44–45 °C (Found: C, 60.4; H, 6.9. C$_{10}$H$_{14}$S$_2$ requires C, 60.6; H, 7.1%); *m/z* (EI) 198 (M$^+$); (CI) 199; v_{max}(Nujol)/cm^{-1} 1590, 1530, 1270, 1235, 1220, 820 and 750; δ_H(CDCl$_3$) 2.51–2.36 (4 H, m), 1.90 (6 H, s) and 1.61–1.49 (4 H, m).

2-(*Diphenylmethylene*)-4,5-*dimethyl*-1,3-*dithiole* **29**. Benzophenone (210 mg, 1.15 mmol) in dry THF (5 ml) and the carbanion **24** [from the ester **21** (275 mg, 1.15 mmol) and BuLi (1.6 mol dm^{-3}, 0.72 ml, 1.25 mmol)] in dry THF (50 ml) followed by chromatography (silica, 15 × 1 cm), eluting with toluene, afforded *compound* **29** (210 mg, 62%) as a yellow solid, m.p. 88–90 °C (Found: C, 72.8; H, 5.5. C$_{18}$H$_{16}$S$_2$ requires C, 73.0; H, 5.4%); *m/z* (EI) 296 (M$^+$); (CI) 297; v_{max}(Nujol)/cm^{-1} 1580, 1500, 1200, 980, 820, 770 and 690; δ_H(CDCl$_3$) 7.31–7.09 (10 H, m) and 1.87 (6 H, s).

2-*Cyclopentylidene*-1,3-*selenathiole* **30**. Cyclopentanone (0.05 ml, 0.6 mmol) in dry THF (5 ml) and the carbanion **25** [from the ester **22** (155 mg, 0.6 mmol) and BuLi (1.6 mol dm^{-3}; 0.4 ml, 0.65 mmol)] in dry THF (50 ml) followed by chromatography (silica, 20 × 2 cm), eluting with hexane–toluene (1:1 v/v) afforded *compound* **30** (95 mg, 71%) as a yellow semi-solid (Found: C, 44.7; H, 4.8. C$_8$H$_{10}$SSe requires C, 44.2; H, 4.6%); *m/z* (EI) 218 (M$^+$); (CI) 219; v_{max}(neat)/cm^{-1} 3025, 1580, 1535, 1130, 980, 870, 810, 790 and 650; δ_H(CDCl$_3$) 6.52 and 6.37 (each 1 H, AB, *J* 8), 2.32–2.19 (4 H, m) and 1.71–1.66 (4 H, m); δ_C(CDCl$_3$) 147.8, 126.7, 119.4, 110.8, 34.2, 30.8, 26.8 and 28.3.

2-*Cyclohexylidene*-1,3-*selenathiole* **31**. Cyclohexanone (0.072 ml, 0.7 mmol) in dry THF (5 ml) and the carbanion **25** [from the ester **22** (180 mg, 0.7 mmol) and BuLi (1.6 mol dm^{-3}; 0.47 ml, 0.75 mmol)] followed by chromatography (silica, 20 × 2 cm) eluting with hexane–toluene (1:1 v/v) afforded *compound* **31** (115 mg, 71%) as a yellow semi-solid (Found: C, 46.5; H, 4.9. C$_9$H$_{12}$SSe requires C, 46.8; H, 5.2%]; *m/z* (EI) 232 (M$^+$); (CI) 233; v_{max}(neat)/cm^{-1} 3025, 1590, 1520, 1270, 1090, 870 and 650; δ_H(CDCl$_3$) 6.51 and 6.43 (each 1 H, AB, *J* 8), 2.74 (2

H, t, J 7.5), 1.71–1.67 (4 H, m) and 1.49–1.40 (4 H, m); $\delta_C(CDCl_3)$ 143.7, 127.3, 118.0, 112.6, 36.2, 32.8, 30.3, 26.9 and 22.6.

2-(*Diphenylmethylene*)-1,3-*selenathiole* **32**. Benzophenone (73 mg, 0.4 mmol) in dry THF (5 ml) and the carbanion **25** [from the ester **22** (105 mg, 0.4 mmol) and BuLi (1.6 mol dm^{-3}; 0.28 ml, 0.45 mmol)] in dry THF (50 ml) at −78 °C followed by chromatography (silica, 15 × 2 cm), eluting with toluene, afforded *compound* **32** (77 mg, 61%) as a light orange solid, m.p. 61–63 °C (Found: C, 61.0; H, 3.7. $C_{16}H_{12}SSe$ requires C, 60.9; H, 3.8%); m/z (EI) 316 (M$^+$); (CI) 317; $v_{max}(Nujol)/cm^{-1}$ 3020, 1585, 1510, 1270, 1250, 1130, 1020, 790, 710 and 650; $\delta_H(CDCl_3)$ 7.30–7.13 (10 H, m), 6.56 and 6.44 (each 1 H, AB, J 6); $\delta_C(CDCl_3)$ 141.4, 139.9, 129.6, 128.2, 127.7, 127.0, 125.5, 123.0 and 122.3.

2-*Benzylidene*-1,3-*selenathiole* **33**. Benzaldehyde (42 mg, 0.4 mmol) in dry THF (5 ml) and the carbanion **25** [from the ester **22** (105 mg, 0.4 mmol) and BuLi (1.6 mol dm^{-3}; 0.28 ml, 0.45 mmol)] in dry THF (50 ml) at −78 °C followed by chromatography (silica, 25 × 2 cm), eluting with carbon tetrachloride afforded *compound* **33** (55 mg, 58%) as a yellow solid, m.p. 52–55 °C (Found: C, 50.3; H, 3.3. $C_{10}H_8SSe$ requires C, 50.2; H, 3.4%); m/z (EI) 240 (M$^+$); (CI) 241; $v_{max}(Nujol)/cm^{-1}$ 1590, 1525, 1500, 1305, 1275, 1160, 1150, 1035, 850, 800 and 640; $\delta_H(CDCl_3)$ 7.63–7.40 (5 H, m), 6.61 (1 H, s), 6.49 and 6.37 (2 H, AB, J 6).

9-(4,5-*Dimethyl*-1,3-*dithiol*-2-*ylidene*)*thioxanthene* **34**. Thioxanthen-9-one (243 mg, 1.15 mmol) in dry THF (5 ml) and carbanion **24** [from the ester **21** (275 mg, 1.15 mmol) and BuLi (1.6 mol dm^{-3}; 0.72 ml, 1.25 mmol)] in dry THF (50 ml) followed by chromatography (silica, 15 × 2 cm) eluting with hexane–dichloromethane (1 : 1 v/v) yielded *compound* **34** (262 mg, 70%) as yellow crystals, m.p. 210–212 °C (Found: C, 66.0; H, 4.3. $C_{18}H_{14}S_3$ requires C, 66.2; H, 4.3%); m/z (EI) 326 (M$^+$); (CI) 327; $v_{max}(KBr)/cm^{-1}$ 1590, 1520, 1460, 1435, 1270, 1135, 1065, 1030, 950, 940, 865, 830, 760, 740, 695, 650 and 625; $\delta_H(CDCl_3)$ 7.59, 7.37, 7.24 and 7.14 (each 2 H, first order AMRX, all *ortho* J_{HH} 7.7) and 1.84 (6 H, s).

9,10-*Bis*(1,3-*dithiole*-2-*ylidene*)-9,10-*dihydroanthracene* **35**. A suspension of anthraquinone (310 mg, 1.5 mmol) in dry THF (15 ml) was added to a solution of the carbanion **23** [from the ester **30** (635 mg, 3 mmol) and BuLi (1.6 mol dm^{-3}; 2.05 ml, 3.3 mmol)] in dry THF (100 ml). Column chromatography (silica, 30 × 2 cm), eluting with cyclohexane–toluene (3 : 1 v/v), afforded *compound* **35** (350 mg, 62%) as an orange solid, m.p. >240 °C (Found: C, 63.2; H, 3.0; S, 34.0. $C_{20}H_{12}S_4$ requires C, 63.1; H, 3.2; S, 33.7%); m/z (EI) 380 (M$^+$); (CI) 381; $v_{max}(Nujol)/cm^{-1}$ 3030, 1595, 1535, 1515, 1370, 1280, 1090, 970, 940, 775, 755, 740 and 670; $\lambda_{max}(MeCN)/nm$ 415, 323, 273, 253 and 206; $\delta_H(CDCl_3)$ 7.69 and 7.28 (each 2 H, first order AA′XX′) and 6.30 (4 H, s).

Continued elution of the column with dichloromethane yielded unchanged anthraquinone (60 mg, 20%), followed by a second product, further purification of which, by preparative TLC (silica plate, 25 × 25 cm), eluting with dichloromethane–hexane (1 : 1 v/v), followed by recrystallisation from dichloromethane, afforded 10-(1,3-*dithiol*-2-*ylidene*)*anthracene*-9(10H)-*one* **48** (45 mg, 10%), as a bright orange solid, m.p. 219–221 °C; (Found: C, 69.0; H, 3.6; S, 22.2. $C_{17}H_{10}OS_2$ requires C, 69.3; H, 3.4; S, 21.8%); m/z (EI) 294 (M$^+$); (CI) 295; $v_{max}(Nujol)/cm^{-1}$ 2940, 2680, 1635, 1590, 1330, 1305, 1290, 1265, 1165, 935, 760, 720 and 680; $\lambda_{max}(MeCN)/nm$ 467, 360, 246 and 192; $\delta_H(CDCl_3)$ 8.27, 7.95, 7.66 and 7.45 (each 2 H, first order AMRX, all *ortho* J_{HH} 8) and 6.48 (2 H, s).

9,10-*Bis*(4,5-*dimethyl*-1,3-*dithiol*-2-*ylidene*)-9,10-*dihydroanthracene* **36**. Anthraquinone (520 mg, 2.5 mmol) in dry THF (20 ml) and the carbanion **24** [from the ester **21** (1.2 g, 5 mmol) and BuLi (1.6 mol dm^{-3}; 3.4 ml, 5.5 mmol)] in dry

THF (100 ml) at −78 °C followed by chromatography (silica, 30 × 2 cm), eluting with cyclohexane–toluene (4:1 v/v), afforded *compound* **36** (742 mg, 68%) as an orange solid, m.p. >240 °C (Found: C, 65.9; H, 4.6; S, 29.5. $C_{24}H_{20}S_4$ requires C, 66.0; H, 4.6; S, 29.4%); m/z (EI) 436 (M$^+$); (CI) 437; $v_{max}(Nujol)/cm^{-1}$ 1590, 1575, 1540, 1520, 1275, 1150, 1085, 960, 860, 775, 745 and 660; $\lambda_{max}(MeCN)/nm$ 433, 369, 235 and 206; $\delta_H(CDCl_3)$ 7.62 and 7.25 (each 4 H, first order AA′XX′) and 1.91 (12 H, s).

Continued elution with dichloromethane yielded unchanged anthraquinone (80 mg, 15%), followed by a second product, which was purified by preparative TLC (silica plate, 25 × 25 cm), eluting with cyclohexane–dichloromethane (2:1 v/v), followed by recrystallisation from dichloromethane, to yield 10-(4,5-*dimethyl*-1,3-*dithiol*-2-*ylidene*)*anthracene*-9(10H)-*one* **49** (96 mg, 12%) as an orange solid, m.p. 217–218 °C (Found: C, 71.0; H, 4.5; S, 20.1. $C_{19}H_{14}OS_2$ requires C, 70.8; H, 4.4; S, 19.9%); m/z (EI) 322 (M$^+$); (CI) 323; $v_{max}(Nujol)/cm^{-1}$ 2940, 2860, 1645, 1595, 1335, 1310, 1300, 1170, 765 and 685; $\lambda_{max}(MeCN)/nm$ 481, 370, 272, 247 and 194; $\delta_H(CDCl_3)$ 8.26, 7.89, 7.62 and 7.39 (each 2 H, first order AMRX, all *ortho* J_{HH} 8) and 1.98 (6 H, s).

10,10′-*Bis*(1,3-*dithol*-2-*ylidene*)-9,9′-*bi*(9,10-*dihydroanthracene*) **40**. Bianthrone (96 mg, 0.25 mmol) in dry THF (10 ml) and the carbanion **23** [from the ester **20** (105 mg, 0.5 mmol) and BuLi (1.6 mol dm^{-3}, 0.35 ml, 0.55 mmol)] in dry THF (50 ml) followed by chromatography (silica, 25 × 2 cm), eluting with cyclohexane–toluene (1:1 v/v), afforded *compound* **40** (57 mg, 41%) as an orange–red solid, m.p. >240 °C (Found: C, 72.8; H, 3.9; S, 22.7. $C_{34}H_{20}S_4$ requires: C, 73.3; H, 3.6; S, 23.1%); m/z (DEI) 556 (M$^+$); (DCI) absent; $v_{max}(Nujol)/cm^{-1}$ 3025, 1575, 1530, 1525, 1270, 1255, 970, 760, 755 and 670; $\lambda_{max}(MeCN)/nm$ 438, 378, 235 and 200.

10,10′-*Bis*(4,5-*dimethyl*-1,3-*dithiol*-2-*ylidene*)-9,9′-*bi*(9,10-*dihydroanthracene*) **41**. Bianthrone (96 mg, 0.25 mmol) in dry THF (10 ml) and the carbanion **24** [from the ester **21** (120 mg, 0.5 mmol) and BuLi (1.6 mol dm^{-3}; 0.35 ml, 0.55 mmol)] in dry THF (50 ml) followed by chromatography (silica, 20 × 2 cm), eluting with toluene–cyclohexane (1:1 v/v), afforded *compound* **41** (58 mg, 38%) as an orange–red solid, m.p. >240 °C (Found: C, 74.9; H, 4.3; S, 21.3. $C_{38}H_{28}S_4$ requires: C, 74.5; H, 4.6; S, 20.9%); m/z (DEI) 612 (M$^+$); (DCI) absent; $v_{max}(Nujol)/cm^{-1}$ 1580, 1525, 1255, 970, 790 and 690; $\lambda_{max}(MeCN)/nm$ 447, 381, 240 and 200.

5,12-*Bis*(1,3-*dithiole*-2-*ylidene*)-5,12-*dihydronaphthacene* **42**. Naphthacene-5,12-quinone (105 mg, 0.4 mmol) in dry THF (10 ml) and the carbanion **23** [from the ester **20** (170 mg, 0.8 mmol) and BuLi (1.6 mol dm^{-3}; 0.56 ml, 0.9 mmol)] in dry THF (75 ml) followed by chromatography (silica, 30 × 2 cm), eluting with cyclohexane–toluene (4:1 v/v), afforded *compound* **42** (93 mg, 59%) as an orange solid, m.p. >240 °C (Found: C, 66.6; H, 3.4; S, 30.3. $C_{24}H_{14}S_4$ requires: C, 66.9; H, 3.3; S, 29.8%); m/z (DEI) 430 (M$^+$); (DCI) 431; $v_{max}(Nujol)/cm^{-1}$ 3025, 1590, 1550, 1265, 1100, 870, 755, 740 and 650; $\lambda_{max}(MeCN)/nm$ 417, 385, 235 and 200; $\delta_H(CDCl_3)$ 7.98 (2 H, s), 7.85 and 7.49 (each 2 H, first order AA′XX′), 7.68 and 7.31 (each 2 H, first order AA′XX′) and 6.30 (4 H, s).

5,12-*Bis*(4,5-*dimethyl*-1,3-*dithiol*-2-*ylidene*)-5,12-*dihydronaphthacene* **43**. Naphthacene-5,12-quinone (105 mg, 0.4 mmol) in dry THF (10 ml) and carbanion **24** [from ester **21** (190 mg, 0.8 mmol) and BuLi (1.6 mol dm^{-3}; 0.56 ml, 0.9 mmol)] in dry THF (75 ml) followed by chromatography (silica, 30 × 2 cm), eluting with cyclohexane–toluene (4:1 v/v) afforded *compound* **43** (107 mg, 55%) as an orange solid, m.p. >240 °C (Found: C, 68.7; H, 4.7; S, 25.9. $C_{28}H_{22}S_4$ requires: C, 69.1; H, 4.6; S, 26.3%); m/z (DEI) 486 (M$^+$); (DCI) 487; $v_{max}(Nujol)/cm^{-1}$ 1595, 1535, 1500, 1270, 1095, 870, 765, 760, 745 and 690; $\lambda_{max}(MeCN)/nm$ 428, 327, 230 and 205; $\delta_H(CDCl_3)$ 7.93 (2 H,

s), 7.82 and 7.44 (each 2 H, first order AA'XX'), 7.65 and 7.28 (each 2 H, first order AA'XX') and 1.92 (12 H, s).

Alternative, More Efficient, Synthesis of the Ketones **48** *and* **49**.—*Ketone* **48**. A stirred mixture of anthrone **44** (5.0 g, 0.025 mol) and the methiodide salt **45** (8.3 g, 0.03 mol) in pyridine–acetic acid (3:1 v/v; 70 ml) was heated at reflux for 4 h. It was then cooled, evaporated under reduced pressure, diluted with water (75 ml) and extracted with dichloromethane (3 × 75 ml). The combined extracts were washed sequentially with 5% aqueous sodium carbonate (2 × 25 ml) and water (2 × 25 ml), dried (MgSO₄), filtered and evaporated under reduced pressure. Column chromatography (silica, 25 × 4 cm) of the residue, eluting with dichloromethane–hexane (2:1 v/v), afforded the *ketone* **48** (6.25 g, 85%). Spectroscopic data were identical with those for the material described above.

Ketone **49**. This compound (11.8 g, 88%) was prepared analogously to compound **48** from anthrone **44** (8.0 g, 0.041 mol) and the methiodide salt **46** (15.2 g, 0.05 mol) in pyridine–acetic acid (100 ml, 3:1 v/v).

10-(1,3-*Selenathiole-2-ylidene*)*anthracen*-9(10H)-*one* **50**. Following the procedure described above for the ketone **48**, anthrone (5 g, 0.026 mol) and the methiodide salt **47** (9.4 g, 0.03 mol) in pyridine–acetic acid (3:1 v/v; 50 ml) were heated at reflux for 8 h to afford the *ketone* **50** (7.6 g, 86%), a red solid after chromatography and recrystallisation from dichloromethane, m.p. 189–192 °C (Found: C, 59.6; H, 3.2. $C_{17}H_{10}OSSe$ requires C, 59.8; H, 3.0%); m/z (EI) 342 (M⁺); (CI) 343; v_{max}(Nujol)/cm⁻¹ 2840, 1640, 1590, 1325, 1300, 1295, 1265, 1165, 1090, 930, 760, 720, 685 and 630; $λ_{max}$(MeCN)/nm 465, 362, 246 and 200; $δ_H$(CDCl₃) 7.97, 7.83, 7.67 and 7.48 (each 2 H, first order AMRX), 6.83 and 6.57 (each 1 H, AB J 7).

10-(1,3-*Dithiol-2-ylidene*)*anthracene*-9(10H)-*thione* **51**.—A stirred mixture of the ketone **48** (440 mg, 1.5 mmol) and phosphorus pentasulphide (450 mg, 1 mmol) in pyridine (15 ml) was heated at reflux for 2 h. It was then cooled, filtered, evaporated under reduced pressure, diluted with water (25 ml), and extracted with dichloromethane (3 × 30 ml). The combined extracts were washed sequentially with 20% aqueous sodium hydroxide (2 × 25 ml), 10% brine (30 ml) and water (25 ml), and then dried (MgSO₄), filtered and evaporated under reduced pressure. Column chromatography (silica, 15 × 2 cm) of the residue, eluting with cyclohexane–toluene (5:1 v/v), afforded *compound* **51** (350 mg, 75%) as a dark-blue solid, m.p. 215–217 °C (Found: C, 65.4; H, 2.9; S, 3.07. $C_{17}H_{10}S_3$ requires: C, 65.8; H, 3.2; S, 3.10%); m/z (EI) 310 (M⁺); (CI) 311; v_{max}(Nujol)/cm⁻¹ 1590, 1255, 1195, 1090, 1085, 1015, 800, 795, 780, 705, 670 and 645; $λ_{max}$(MeCN)/nm 579, 366 and 230; $δ_H$(CDCl₃) 8.24, 7.93, 7.65 and 7.43 (each 2 H, first order AMRX, all *ortho* J_{HH} 8) and 6.40 (2 H, s).

10-(4,5-*Dimethyl*-1,3-*dithiol-2-ylidene*)-9(10H)-*thione* **52**.— Following the procedure detailed above for the thioketone **51**, the ketone **49** (650 mg, 2 mmol) and phosphorus pentasulphide (450 mg, 1 mmol) in pyridine (50 ml) gave *compound* **52** (460 mg, 68%) as a deep-blue solid, m.p. 214–216 °C (Found: C, 67.6; H, 4.2; S, 28.0. $C_{19}H_{14}S_3$ requires C, 67.4; H, 4.2; S, 28.4%); m/z (EI) 338 (M⁺); (CI) 339; v_{max}(Nujol)/cm⁻¹ 1585, 1295, 1265, 1200, 1195, 1150, 1080, 1010, 810, 780, 750, 720 and 645; $λ_{max}$(MeCN)/nm 598, 332, 230 and 192; $δ_H$(CDCl₃) 8.23, 7.84, 7.58 and 7.36 (each 2 H, first order AMRX, all *ortho* J_{HH} 8) and 1.96 (6 H, s).

9-(1,3-*Dithiol-2-ylidene*)-10-(4,5-*dimethyl*-1,3-*dithiol-2-ylid-ene*)-9,10-*dihydroanthracene* **37**.—A solution of the ketone **48** (90 mg, 0.3 mmol) in dry THF (5 ml) was added to a solution of the carbanion **24** [from the ester **21** (70 mg, 0.3 mmol) and BuLi

(1.6 mol dm⁻³; 0.2 ml, 0.33 mmol)] in dry THF (50 ml) at −78 °C. Column chromatography (silica, 30 × 2 cm), eluting with cyclohexane–toluene (1:1 v/v), afforded *compound* **37** (90 mg, 74%) as an orange solid, m.p. >240 °C (Found: C, 64.8; H, 3.9; S, 31.6. $C_{22}H_{16}S_4$ requires C, 64.7; H, 3.9; S, 31.4%); m/z (EI) 408 (M⁺); (CI) 409; v_{max}(Nujol)/cm⁻¹ 3030, 1585, 1545, 1535, 1510, 1275, 1095, 960, 865, 755, 740 and 630; $λ_{max}$(MeCN)/nm 430, 360, 235 and 200; $δ_H$(CDCl₃) 7.69–7.62 (4 H, m), 7.28–7.25 (4 H, m), 6.27 (2 H, s) and 1.92 (6 H, s).

Alternatively, reaction of the ketone **49** (95 mg, 0.3 mmol) with the carbanion **23** [from the ester **20** (60 mg, 0.3 mmol) and BuLi (1.6 mol dm⁻³; 0.2 ml, 0.33 mmol)] in dry THF (50 ml) at −78 °C afforded *compound* **37** (83 mg, 68%), spectroscopically identical with the sample described above.

9-(4,5-*Dimethyl*-1,3-*dithiol-2-ylidene*)-10-(1,3-*selenathiol-2-ylidene*)-9,10-*dihydroanthracene* **38**.—The ketone **49** (248 mg, 0.8 mmol) in dry THF (10 ml) and carbanion **25** [from ester **22** (210 mg, 0.8 mmol) and BuLi (1.6 mol dm⁻³; 0.56 ml, 0.9 mmol)] in dry THF (50 ml) at −78 °C followed by chromatography (silica, 25 × 2 cm), eluting with cyclohexane–toluene (3:1 v/v), afforded *compound* **38** (248 mg, 68%) as an orange solid, m.p. >240 °C (Found: C, 58.2; H, 3.7; S, 20.7. $C_{22}H_{16}S_3Se$ requires C, 58.0; H, 3.5; S, 21.2%); m/z (DEI) 456 (M⁺); (DCI) 457; v_{max}(Nujol)/cm⁻¹ 1590, 1540, 1250, 1130, 1090, 1005, 970, 890, 775 and 750; $λ_{max}$(MeCN)/nm 427, 363 and 242; $δ_H$(CDCl₃) 7.72–7.59 (4 H, m), 7.31–7.26 (4 H, m), 6.78 and 6.54 (each 1 H, AB, J 7) and 1.94 (6 H, s).

9-(1,3-*Dithiol-2-ylidene*)-10-(1,3-*selenathiol-2-ylidene*)-9,10-*dihydroanthracene* **39**.—The ketone **48** (235 mg, 0.8 mmol) in dry THF (10 ml) and the carbanion **25** [from the ester **22** (210 mg, 0.8 mmol) and BuLi (1.6 mol dm⁻³; 0.56 ml, 0.9 mmol)] in dry THF (50 ml) at −78 °C followed by chromatography (silica, 25 × 2 cm), eluting with cyclohexane–toluene (3:1 v/v), afforded *compound* **39** (198 mg, 58%) as an orange solid, m.p. >240 °C (Found: C, 56.0; H, 2.7; S, 22.9. $C_{20}H_{12}S_3Se$ requires C, 56.2; H, 2.8; S, 22.5%); m/z (DEI) 428 (M⁺); (DCI) 429; v_{max}(Nujol)/cm⁻¹ 1585, 1520, 1270, 1150, 1120, 1090, 1010, 960 and 850; $λ_{max}$(MeCN)/nm 419, 365 and 240; $δ_H$(CDCl₃) 7.73–7.60 (4 H, m), 7.34–7.20 (4 H, m), 6.79 and 6.55 (each 1 H, AB, J 7) and 6.30 (2 H, s).

cis *and* trans-9,10-*Bis*(1,3-*selenathiol-2-ylidene*)-9,10-*dihydro-anthracene* **53a** *and* **53b**.—Following the procedure detailed above for compound **35**, anthraquinone (155 mg, 0.75 mmol) in dry THF (15 ml) and the carbanion **25** [from the ester **22** (390 mg, 1.5 mmol) and BuLi (1.6 mol dm⁻³; 1.0 ml, 1.6 mmol)] in dry THF (100 ml) at −78 °C followed by chromatography (silica, 30 × 2 cm), eluting with cyclohexane–toluene (3:1 v/v), afforded an inseparable mixture of *compound* **53a** and **53b** (225 mg, 63%) as a dark orange solid, m.p. >240 °C (Found: C, 50.4; H, 2.5; S, 13.0. $C_{20}H_{12}S_2Se_2$ requires C, 50.6; H, 2.6; S, 13.5%); m/z (DEI) 476 (M⁺); (DCI) 477; v_{max}(Nujol)/cm⁻¹ 3030, 1595, 1520, 1495, 1310, 1280, 1260, 850, 765, 735, 670 and 640; $λ_{max}$(MeCN)/nm 409, 377, 265 and 236 nm; $δ_H$(CDCl₃) 7.67–7.19 (16 H, m), 6.79 and 6.60 (each 2 H, AB, J 7.1), 6.71 and 6.50 (each 2 H, AB, J 6.7).

Continued elution with dichloromethane yielded unchanged anthraquinone (20 mg, 13%) followed by the ketone **50** (25 mg, 10%) spectroscopically identical with the sample described above.

9,10-*Bis*(1,3-*dithiol-2-ylidene*)-9,10-*dihydroanthracene*–7,7,8,8-*Tetracyano*-p-*quinodimethane Complex* (1:4 *Stoicheio-metry*): *Complex* **54**.—A boiling solution of the donor **35** (38 mg, 0.1 mmol) in dry acetonitrile (20 ml) was added to a solution of TCNQ (81 mg, 0.4 mmol) in dry acetonitrile (10 ml) and the resultant dark-green solution refluxed for 0.5 h under nitrogen.

The mixture was slowly cooled to 0 °C and the solid was collected by filtration, washed with ice-cold acetonitrile (3 × 5 ml) and dried *in vacuo* to afford *complex* **54** (49 mg, 41%) as a black powder, m.p. >260 °C [Found: C, 68.2; H, 2.5; N, 18.5; S, 10.8. $C_{68}H_{28}N_{16}S_4$ (*i.e.* a 1:4 complex) requires C, 68.2; H, 2.4; N, 18.7; S, 10.7%]; v_{max}(KBr, FT-IR)/cm^{-1} 3450–3000v br, 2185, 2155, 1559, 1508, 1294, 1090 and 610; λ_{max}(MeCN)/nm 842, 746, 395 and 200.

9,10-*Bis*(4,5-*dimethyl*-1,3-*dithiol*-2-*ylidene*)-9,10-*dihydro-anthracene*–7,7,8,8-*Tetracyano*-p-*quinodimethane Complex* (1:4 *Stoicheiometry*): *Complex* **55**.—This complex was prepared in exactly the same manner as complex **54**. Donor **36** (44 mg, 0.1 mmol) and TCNQ (81 mg, 0.4 mmol) in dry acetonitrile (30 ml) yielded *complex* **55** (60 mg, 48%) as a black powder, m.p. >260 °C [Found: C, 68.8; H, 3.1; N, 18.2; S, 9.9. $C_{72}H_{36}N_{16}S_4$ (*i.e.* a 1:4 complex) requires C, 69.0; H, 2.9; N, 17.9; S, 10.2%]; v_{max}(KBr, FT-IR)/cm^{-1} 3450–3000v br, 2209, 2187, 2158, 1560, 1327, 1154 and 1077; λ_{max}(MeCN)/nm 843, 744, 394 and 200. Recrystallisation from acetonitrile gave the complex as long, shiny black needles.

9,10-*Bis*(4,5-*dimethyl*-1,3-*dithiole*-2-*ylidene*)-9,10-*dihydro-anthracene*–2,5-*Dibromo*-7,7,8,8-*tetracyano*-p-*quinodimethane Complex* (1:2 *Stoicheiometry*): **36**–(TCNQBr$_2$)$_2$—This complex was prepared in exactly the same manner as complex **54**. Donor **36** (44 mg, 0.1 mmol) and 2,5-dibromo TCNQ^{40} (72 mg, 0.2 mmol) in dry acetonitrile (30 ml) yielded the *complex* (44 mg, 38%) as a black powder, m.p. >250 °C (Found: C, 50.0; H, 1.9; N, 10.1. $C_{48}H_{24}N_8S_4Br_4$ (*i.e.* a 1:2 complex) requires C, 49.7; H, 2.1; N, 9.7%); v_{max}(KBr)/cm^{-1} 2190, 1550, 1485, 1440, 1360, 1315, 1275, 1155, 1070, 990, 870, 790 and 755.

9-(1,3-*Dithiol*-2-*ylidene*)-10-(4,5-*dimethyl*-1,3-*dithiol*-2-*ylid-ene*)-9,10-*dihydroanthracene*–7,7,8,8-*Tetracyano*-p-*quinodi-methane Complex* (1:4 *Stoicheiometry*): *Complex* **56**.—This complex was prepared in exactly the same manner as complex **54**. Donor **37** (41 mg, 0.1 mmol) and TCNQ (81 mg, 0.4 mmol) in dry acetonitrile (30 ml) yielded the *complex* **56** (39 mg, 32%) as a black powder, m.p. *ca.* 250 °C (decomp.) [Found: C, 68.8; H, 2.7; N, 18.5; S, 10.0. $C_{70}H_{32}N_{16}S_4$ (*i.e.* a 1:4 complex) requires C, 68.6; H, 2.6; N, 18.3; S, 10.5%]; v_{max}(KBr, FT-IR)/cm^{-1} 3450–3000v br, 2180, 2158, 1563, 1497 and 1081; λ_{max}(MeCN)/nm 847, 740, 380 and 195.

Acknowledgements

References

1 (*a*) J. Ferraris, D. O. Cowan, V. V. Walatka and J. H. Perlstein, *J. Am. Chem. Soc.*, 1973, **95**, 948; (*b*) L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito and A. J. Heeger, *Solid State Comm.*, 1973, **12**, 1125.

2 (*a*) J. B. Torrance, *Acc. Chem. Res.*, 1979, **12**, 79; (*b*) M. R. Bryce and L. C. Murphy, *Nature (London)*, 1984, **309**, 119; (*c*) F. Wudl, *Acc. Chem. Res.*, 1984, **17**, 227; (*d*) M. R. Bryce, *Annual Reports on the Progress of Chemistry B*, Royal Society of Chemistry, London, 1985, **82**, 377; (*e*) D. O. Cowan and F. M. Wiygul, *Chem. Eng. News*, 1986, **64**(19), 28.

3 (*a*) J. R. Ferraro and J. M. Williams, *Introduction to Synthetic Electrical Conductors*, Academic Press, London, 1987; (*b*) *Semiconductors and Semimetals*, ed. E. Conwell, vol. 27, Academic Press, London, 1988.

4 (*a*) Proceedings of the International Conference on Synthetic Metals, Kyoto (ICSM 86), published in *Synth. Metals*, 1987, **17–19**; (*b*) Proceedings of the International Conference on Synthetic Metals, Santa Fe (ICSM 88), published in *Synth. Metals*, 1988 and 1989, **27–29**.

5 (*a*) M. Sato, M. V. Lakshmikantham, M. P. Cava and A. F. Garito, *J. Org. Chem.*, 1978, **43**, 2084; (*b*) Z. Yoshida, T. Kawase, H. Awaji, I. Sugimoto, T. Sugimoto and S. Yoneda, *Tetrahedron Lett.*, 1983, **24**, 3469; (*c*) M. R. Bryce, *J. Chem. Soc., Perkin Trans. 1*, 1985, 1675 and references therein.

6 (*a*) K. Deuchert and S. Hünig, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 875; (*b*) S. Hünig and H. Berneth, *Top. Curr. Chem.*, 1980, **92**, 1.

7 (*a*) K. Hirai, H. Sugimoto and T. Isheba, *Sulfur Reports*, 1983, **3**, 1; (*b*) N. Lozac'h and M. Stavaux, *Adv. Heterocycl. Chem.*, 1980, **27**, 151.

8 Preliminary communication: M. R. Bryce and A. J. Moore, *Tetrahedron Lett.*, 1988, **29**, 1075.

9 K. Takahashi and T. Nihira, *Tetrahedron Lett.*, 1989, **30**, 5903.

10 T. Sugimoto, H. Awaji, I. Sugimoto, Y. Misaki and Z. Yoshida, *Synth. Metals*, 1987, **19**, 569.

11 W. Frank and R. Gompper, *Tetrahedron Lett.*, 1987, **28**, 3083.

12 H. Awaji, T. Sugimoto and Z. Yoshida, *J. Phys. Org. Chem.*, 1988, **1**, 47.

13 (*a*) M. Narita and C. U. Pittman, *Synthesis*, 1976, 489; (*b*) M. R. Bryce, *Aldrichimica Acta*, 1985, **18**, 73; (*c*) A. Krief, *Tetrahedron*, 1986, **42**, 1209; (*d*) D. O. Cowan and A. Kini, in *The Chemistry of Organic Selenium and Tellurium Compounds*, ed. S. Patai, Wiley, 1987, vol. 2, ch. 12.

14 D. Leaver, W. A. H. Robertson and D. M. McKinnon, *J. Chem. Soc.*, 1962, 5104.

15 Y. Ueno, A. Nakayama and M. Okawara, *Synthesis*, 1975, 277.

16 F. Becke and H. Hagen, *Ger. Pat.* 1968, 1274121 (*Chem. Abstr.*, 1969, **70**, 3573).

17 For a monograph on the chemistry of dithiocarboxylic acids see S. Scheithauer and R. Mayer, *Topics in Sulphur Chem.*, 1979, **4**, 1.

18 (*a*) Y. Ueno, A. Nakayama and M. Okawara, *J. Chem. Soc., Chem. Commun.*, 1978, 74; (*b*) K. Takahashi, T. Nihira, K. Takase and K. Shibata, *Tetrahedron Lett.*, 1989, **30**, 2091.

19 K. Nakasuji, H. Kubota, T. Kotani, I. Murata, G. Saito, T. Enoki, K. Imaeda, H. Inokuchi, M. Honda, C. Katayama and J. Tanaka, *J. Am. Chem. Soc.*, 1986, **108**, 3460.

20 Y. Ueno, M. Bahry and M. Okawara, *Tetrahedron Lett.*, 1977, 4607.

21 J. S. Chappell, A. N. Bloch, W. A. Bryden, M. Maxfield, T. O. Poehler and D. O. Cowan, *J. Am. Chem. Soc.*, 1981, **103**, 2442.

22 K. Yakushi, M. Iguchi, G. Katagiri, T. Kusada, T. Ohta and H. Kuroda, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 348.

23 Preliminary communications: (*a*) M. R. Bryce and A. J. Moore, *Synth. Metals*, 1988, **25**, 203; (*b*) M. R. Bryce, A. J. Moore, D. Lorcy, A. S. Dhindsa and A. Robert, *J. Chem. Soc., Chem. Commun.*, 1990, 470.

24 (*a*) M. Sato, N. C. Gonnella and M. P. Cava, *J. Org. Chem.*, 1979, **44**, 930; (*b*) J-M. Fabre, A. K. Gouasmia, L. Giral and D. Chasseau, *Tetrahedron Lett.*, 1988, **29**, 2185.

25 (*a*) K. Ishikawa, K. Akiba and N. Inamoto, *Tetrahedron Lett.*, 1976, **41**, 3695; (*b*) K. Akiba, K. Ishikawa and N. Inamoto, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2674.

26 K. Lerstrup, I. Johannsen and M. Jorgensen, *Synth. Metals*, 1988, **27**, B9.

27 Y. Yamashita, Y. Kobayashi and T. Miyashi, *Angew. Chem., Int. Edn. Engl.*, 1989, **28**, 1052.

28 M. R. Bryce, A. J. Moore, M. Hasan, G. J. Ashwell, A. T. Fraser, W. Clegg, M. B. Hursthouse and A. I. Karaulov, *Angew. Chem.*, 1990, in the press.

29 R. Gompper and E. Kutter, *Chem. Ber.*, 1965, **98**, 2825.

30 (*a*) K. Kikuchi, T. Namiki, I. Ikemoto and K. Kobayashi, *J. Chém. Soc., Chem. Commun.*, 1986, 1472; (*b*) A. M. Kini, S. F. Tytko, J. E. Hunt and J. M. Williams, *Tetrahedron Lett.*, 1987, **28**, 4153; (*c*) Y. Gimbert, A. Moradpour and S. Bittner, *Tetrahedron Lett.*, 1990, **31**, 1007.

31 E. M. Engler and V. V. Patel, *J. Chem. Soc., Chem. Commun.*, 1975, 671.

32 (*a*) M. Horner, S. Hünig and H. Pütter, *Electrochimica Acta*, 1982, **27**, 205; (*b*) C. H. Chen, J. J. Doney, G. A. Reynolds and F. D. Saeva, *J. Org. Chem.*, 1983, **48**, 2757; (*c*) K. Hesse and S. Hünig, *Liebigs Ann. Chem.*, 1985, 708.

33 E. M. Engler, F. B. Kaufman, D. C. Green, C. E. Klots and R. N. Compton, *J. Am. Chem. Soc.*, 1975, **97**, 2921.

34 F. Wudl, M. L. Kaplan, E. J. Hufnagel and E. W. Southwick, *J. Org. Chem.*, 1974, **39**, 3608.

35 (*a*) H. K. Spencer and M. P. Cava, *J. Org. Chem.*, 1976, **41**, 730; (*b*) E. M. Engler, V. V. Patel, J. R. Andersen, R. R. Schumaker and A. A. Fukushima, *J. Am. Chem. Soc.*, 1978, **100**, 3769.

36 J. P. Ferraris, T. O. Poehler, A. N. Bloch and D. O. Cowan, *Tetrahedron Lett.*, 1973, **27**, 2553.
37 M. V. Lakshmikantham and M. P. Cava, *J. Org. Chem.*, 1980, **45**, 2632.
38 W. Reid and H. Bodem, *Chem. Ber.*, 1958, **91**, 1981.
39 M. W. Miller, R. W. Amidon and P. O. Tawney, *J. Am. Chem. Soc.*, 1955, **77**, 2845.

40 M. R. Bryce, M. Hasan and G. J. Ashwell, *J. Chem. Soc., Chem. Commun.*, 1989, 529.