Functionalised tetrathiafulvalenes in supramolecular chemistry

Peter John Skabara

This thesis is dedicated to the memory of my brother, Wolodymyr Skabara, without whom I would never have discovered my fascination with chemistry. I am sure that if he was around today he would have been proud of what he has helped to achieve.

DECLARATION

The work described in this thesis was carried out by the author, in the Department of Chemistry, University of Durham, between October 1991 and August 1994. It has not been submitted previously for a degree at this, or any other, University.

MEMORANDUM

FUNCTIONALISED TETRATHIAFULVALENES IN SUPRAMOLECULAR CHEMISTRY

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ABSTRACT

Functionalised Tetrathiafulvalenes in Supramolecular Chemistry

by
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A thesis submitted for the degree of Doctor of Philosophy
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Using a range of functionalised tetrathiafulvalene (TTF) derivatives, developed at Durham, the first examples of covalently linked TTF-ferrocene systems have been prepared. The redox properties of these molecules, as studied by cyclic voltammetry, provide evidence that these species are efficient π-electron donors.

Highly reactive 1,3-dithiole Wittig and Wittig-Horner reagents have been used in the synthesis of complex mixed redox-active systems containing ferrocenyl units. A series of [3]- and [4]-dendralenes has also been developed from this synthetic methodology. Cyclic voltammetry shows that tri- and tetracationic states can be achieved with these systems at relatively low potentials.

The potential for vinyl-TTF compounds to undergo [4+2] cycloaddition has been investigated for the first time. The peripheral C=C unit of TTF, together with the adjacent vinylic substituent, is able to act as the diene functionality in Diels-Alder reactions. Remarkably, the π-delocalisation within the TTF moieties is readily disrupted by the addition of strong dienophiles.

The reactivity of lithiated TTF towards aldehydes and ketones has established an array of hydroxy-functionalised TTF, bis-TTF and TTF-ferrocene derivatives. The conducting and magnetic properties of the chloranil charge transfer salt of one of these species is also reported.

CONTENTS

CHAPTER 1

INTRODUCTION

1.1 ORGANIC METALS

1.1.1 INTRODUCTION

The possibility for organic materials to exhibit conductivity was first suggested towards the beginning of this century.[1,2] Supported by the ability to produce an infinite number of suitable candidates, organic metals are arguably more versatile than their inorganic counterparts. Due to the nature of organic chemistry, such compounds can be modified via molecular fine tuning to yield materials with a range of conductivity values; there is also the possibility of incorporating other components into the molecule to provide, for example, optical or magnetic properties. However, the majority of organic compounds are insulators, and inorganic species massively dominate the field of higher temperature superconducting materials.

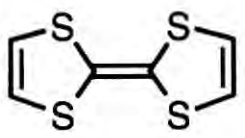
Much of the recent work has revolved around different groups of organic conductors: those based upon charge-transfer complexes, conjugated polymers, graphite and its related compounds, as well as organometallic species. This thesis is concerned with the synthesis of new electron donors for the purpose of forming charge-transfer salts (CT salts).

1.1.2 HISTORICAL BACKGROUND

The first organic conducting material ($\sigma_{rt} = ca.1 Scm^{-1}$), an unstable perylene-bromine salt, was reported in 1954 by Japanese workers.[3] Previously, in 1911, superconductivity was first recognised in the metal mercury;[4] in the same year it was predicted that metallic behaviour in a material composed of non-metallic elements could be a possibility.[1] It was thus 62 years later that the prospect of a 'synthetic metal' became reality, when Ferraris and co-workers[6] reported that the CT salt of tetrathiafulvalene (TTF) **1** and tetracyano-*p*-quinodimethane (TCNQ) **2** - $TTF^{+\cdot}$-$TCNQ^{-\cdot}$ showed a room temperature conductivity value of 500 Scm^{-1}.

1.1.3 TTF-TCNQ

During the 1960s a number of CT salts were prepared using TCNQ as the electron acceptor:[6] at best these materials were organic semi-conductors. This changed, however, soon after the first published synthesis of TTF **1** by Wudl *et al.* in 1970.[7]



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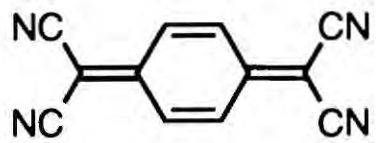

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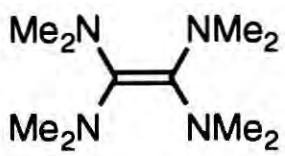

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The preparation of TTF **1** was developed by Wudl for the purpose of producing a better reducing agent than tetrakis(dimethylamino)ethylene **3**. Although TTF is a poorer donor than molecule **3** (probably due to the stronger electron-withdrawing effect of the sulfur atoms over the nitrogen atoms, with respect to the central double bond), the former affords radical cations that are much more stable than those derived from structure **3**.

The electrochemistry of TTF shows two reversible oxidations (Figure 1.1), the first at $E^{1/2}$ = +0.34V followed by a second at $E^{1/2}$ = +0.71V, due to sequential formation of cation radical and dication species (Figure 1.2).

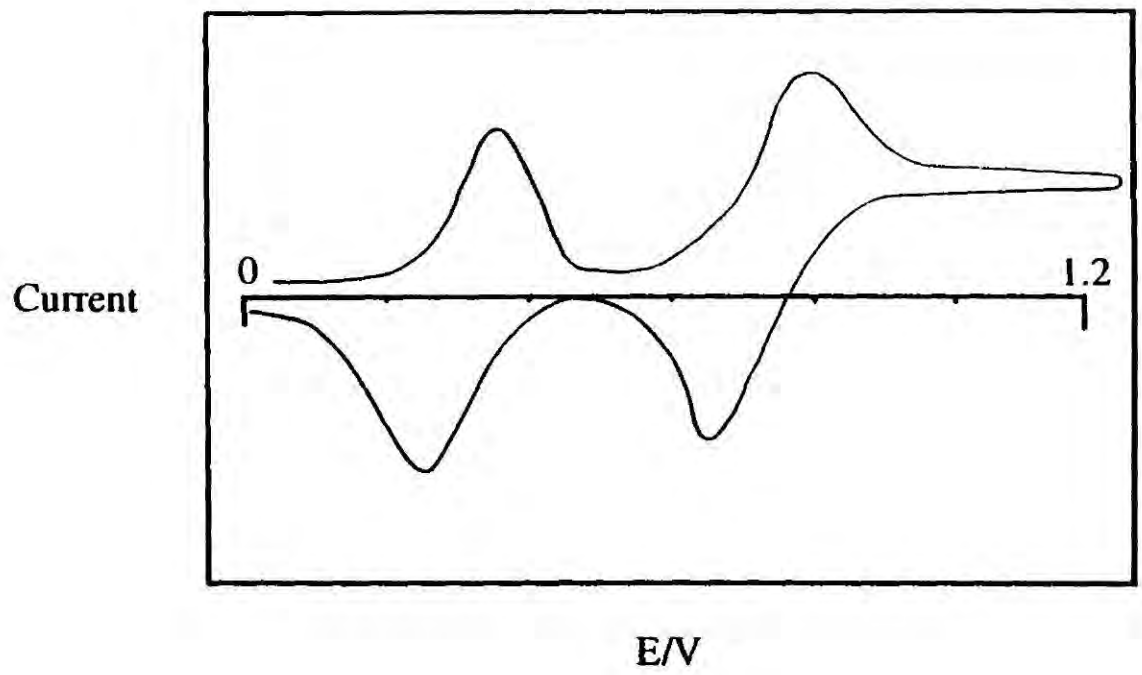


Figure 1.1: Cyclic Voltammogram of Tetrathiafulvalene. Pt working electrode, Pt gauze counter electrode, Ag/AgCl reference electrode, 0.2 mol dm^{-3} $Bu^t_4N^+PF_6^-$, 10^{-4} mol dm^{-3} TTF **1** in dry acetonitrile, under argon at 20°C, with iR compensation.

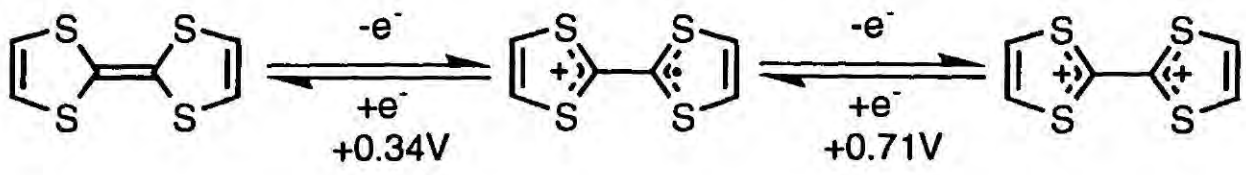


Figure 1.2: Redox Behaviour of TTF

Despite the emergence of this interesting new electron donor, TTF was not reported to be complexed with TCNQ until 1973. The crystal structure of TTF-TCNQ[8,9] (Figure 1.3) shows 1:1 stoichiometry, with TTF radical cations and TCNQ radical anions aligned in interlocking, segregated stacks. Within the acceptor and donor columns the molecules are laterally displaced, with the exocyclic carbon-carbon double bond lying over the ring of the molecule adjacent to it in the stack.

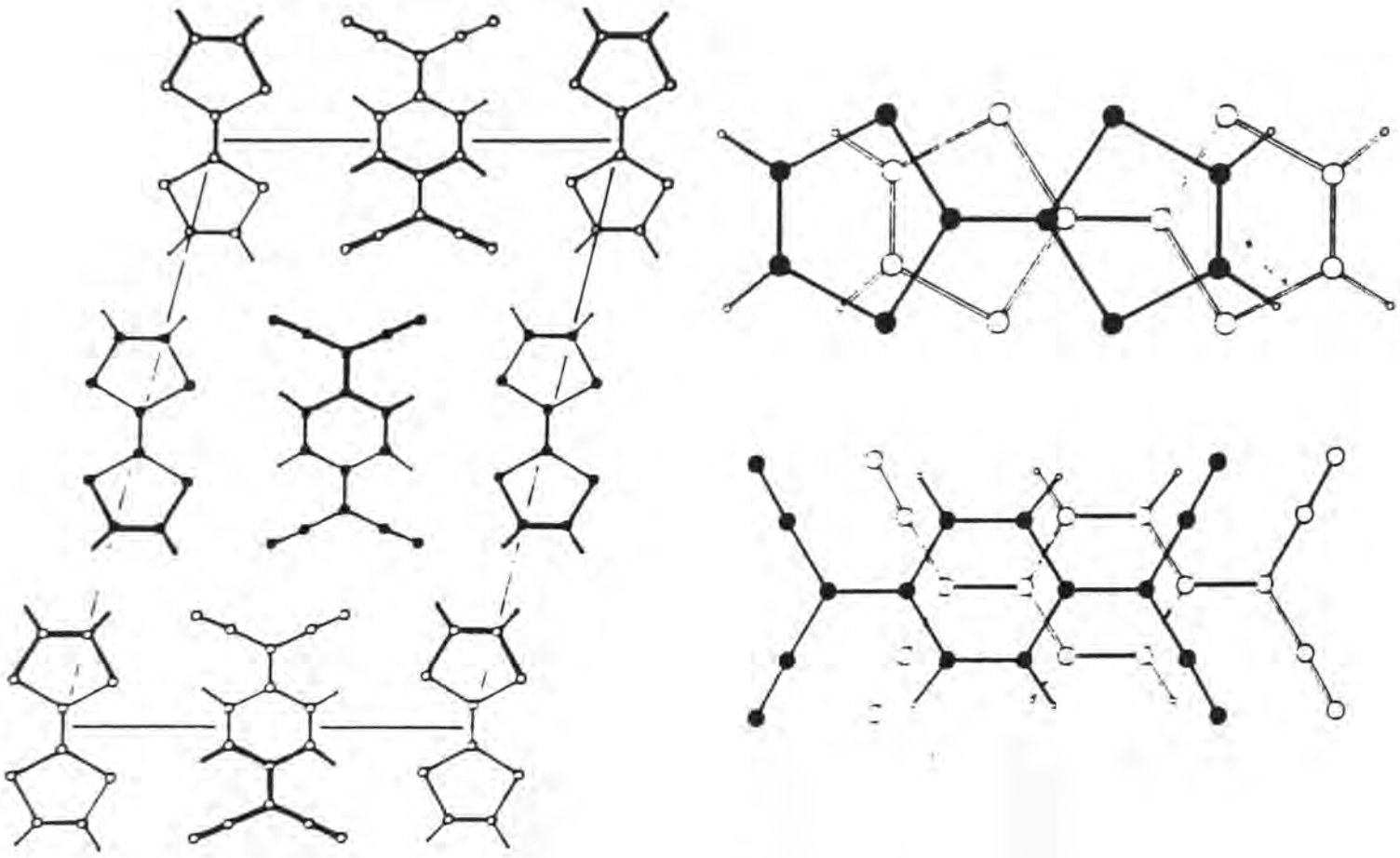


Figure 1.3: X-Ray Crystal Structure of TTF-TCNQ

Charge transfer within the complex is incomplete, based upon infra-red[10] and diffuse X-ray scattering techniques[11]. Statistically, only 0.59 electrons are transferred from each TTF molecule to a corresponding TCNQ unit. Subsequently, the formation of partially filled electron bands gives rise to metallic conductivity within both stacks. Other factors are also thought to favour high conductivity of the TTF-TCNQ salt: both the TTF and TCNQ molecules are of a similar size, possess a high degree of symmetry (D_2h), and are planar, exhibiting good π-delocalisation. Furthermore, the regular 'ring over bond' overlap results in extensive π-interaction along the columns.

1.1.4 PHYSICAL REQUIREMENTS FOR CONDUCTIVITY

Conduction in materials arises from the movement of ions or electrons, with the latter dominating in most cases. It is the valence electrons which are responsible for electron conduction, and not those from the inner core shells. The valence electrons arise from the highest occupied molecular orbital (HOMO), and it is the mobility of these electrons through the solid that determines how effective the conduction is.

If we consider sodium as an example for metallic conductivity, the valence band arising from the 3s orbitals is only half full, because there is only one electron available per atom. With this resulting partially filled band (Figure 1.4a), on excitation the electrons close to the Fermi energy level (E_f - the energy state corresponding to the highest occupied level) can easily jump into the conductance band, the lowest unoccupied molecular orbital (LUMO), thus causing conduction.

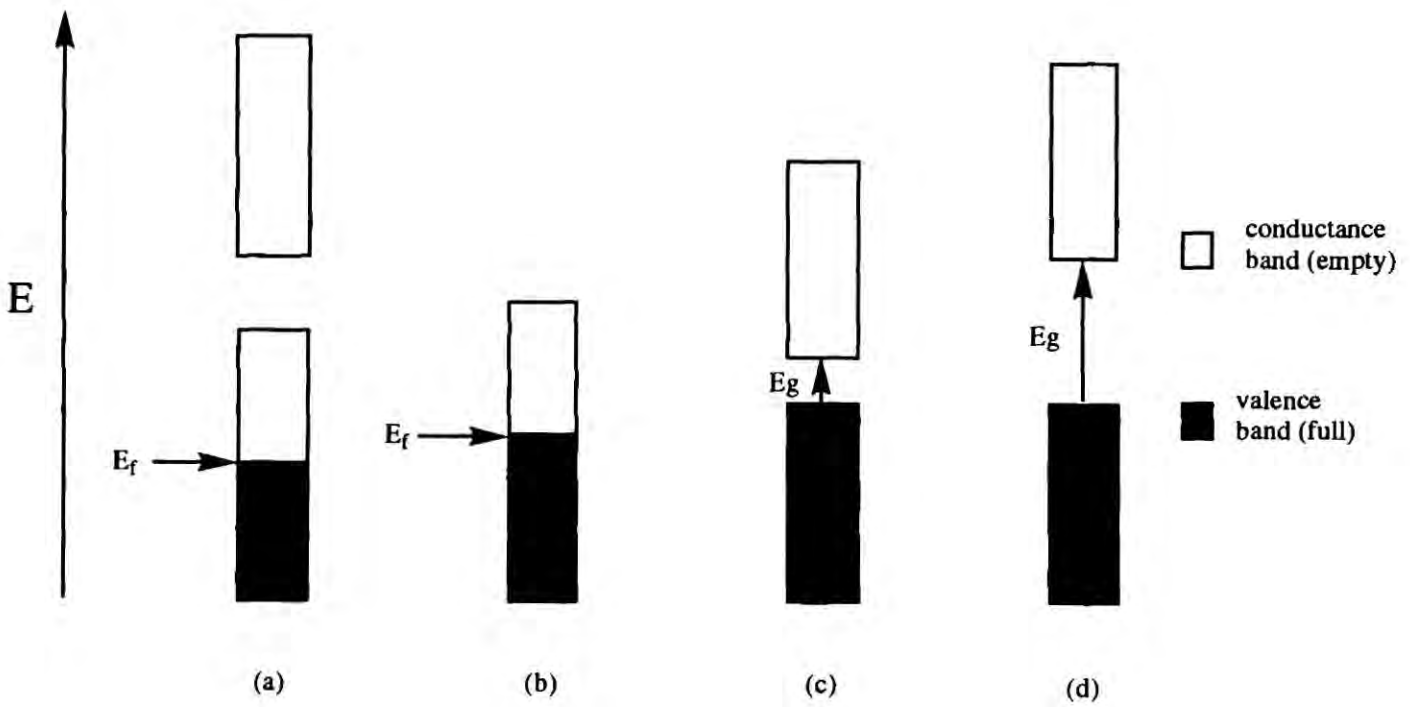


Figure 1.4: Band structures of (a) a metal, (b) a semi-metal, (c) a semiconductor, and (d) an insulator.

With the alkaline earth metals the s band is full (a closed shell state), but there is an overall sp band overlap allowing good conduction (Figure 1.4b). This conductance, however, is reduced compared to Figure 1.4a, since there is a low population of electrons at the Fermi level.

In some cases sp band overlap will not arise, but if the energy gap (Eg) between the bands is sufficiently small then some electrons will be able to jump into the empty

conductance band (Figure 1.4c). This process occurs with semi-conducting materials (*e.g.* Si, Eg=1.1eV).

With other species, Eg is too large for the efficient movement of electrons, and this gives rise to insulators (*e.g.* diamond, NaCl, Eg>4eV) (Figure 1.4d).

The effect of temperature is an important factor for these materials. In the case of metals, as temperature decreases, crystallinity increases with a reduction in lattice vibrations. This results in more efficient intermolecular overlap, and conductivity will increase.

With semi-conductors and insulators, increasing the temperature induces a Boltzmann-type factor:

$$n \alpha e^{-Eg/kT}$$

where n is the number of charge carriers, and these will increase if Eg is not greater than kT. Subsequently, in this case conductivity increases with temperature due to thermal excitation.

1.1.5 CONDUCTION IN MOLECULAR SOLIDS AND THE BASIS OF SUPERCONDUCTIVITY

If a large number of atoms or molecules congregate to form a polymeric chain or crystalline solid, whose atomic or molecular orbitals provide sufficient interaction or mixing, then an energy gap may form.

For a simple electron rich neutral species, *e.g.* ethylene, the resulting band gap between HOMO and LUMO will decrease as more molecules interact (Figure 1.5).

In an ideal situation where an infinite number of molecules actively participate in molecular orbital overlap, the resulting band gap may be small enough to give rise to a semi-conducting or semi-metallic state.

Conducting CT complexes can be either single-chain conductors (where the anion is a closed-shell species, *e.g.* Cl^-, PF_6^-), or two-chain conductors (*e.g.* $TTF^{+\cdot}$-$TCNQ^{-\cdot}$). In each case, however, the complex contains stacks of open-shell radical moieties, which form partially filled bands capable of one-dimensional (anisotropic) conductivity. Up to this point band theory can be used to explain adequately the behaviour of conducting materials. The question remains, however, as to how a 'metallic' species can transgress to a superconducting state.

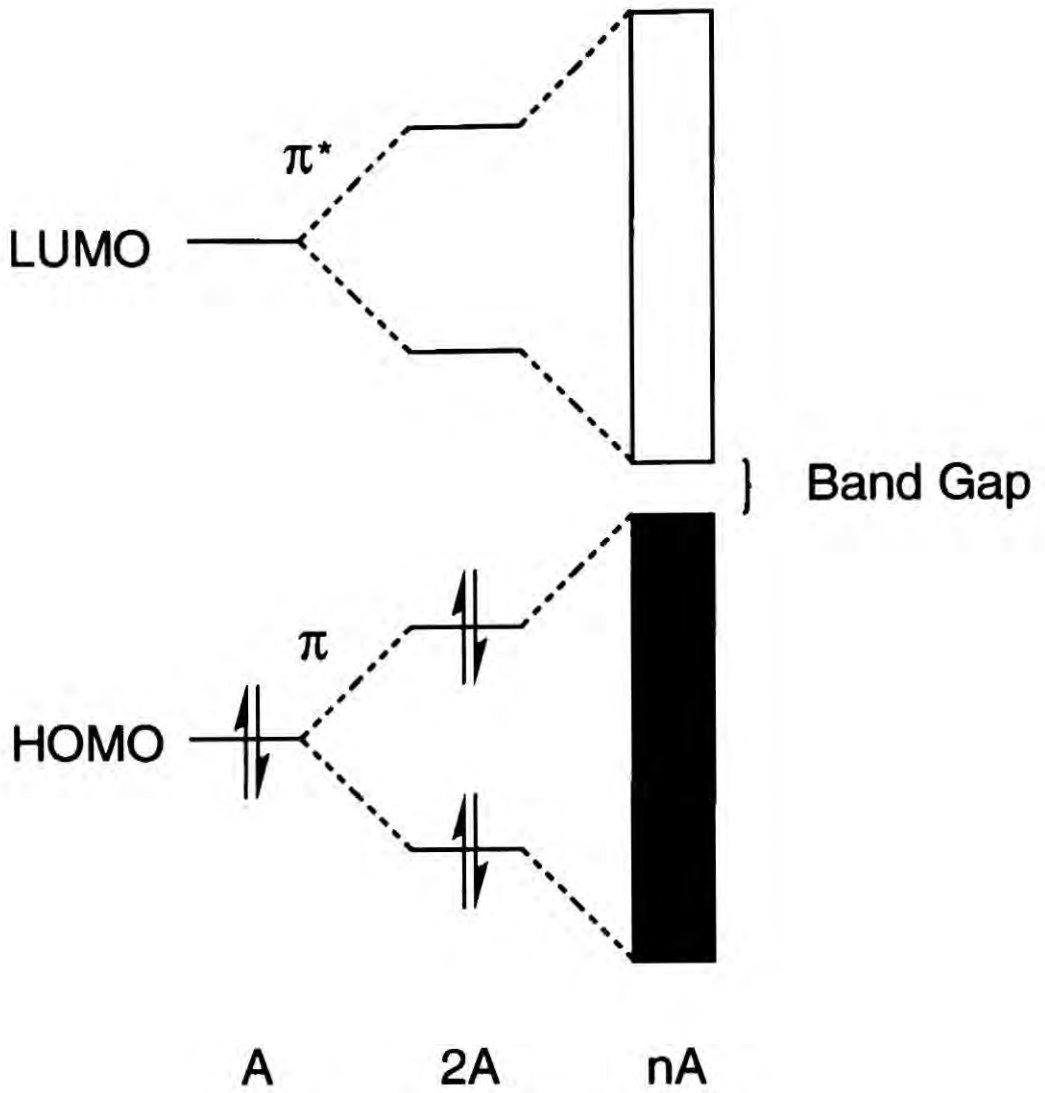


Figure 1.5: MO diagram showing the formation of electronic bands arising from a chain of molecules.

The theory of superconductivity (electrical current flowing with zero resistance), was first postulated in 1957 by Bardeen, Cooper, and Schrieffer,[12] and is thought to be governed by the highly coordinated motion of electron pairs (Cooper pairs). Both electrons of a Cooper pair move at the same speed in opposite directions, and their properties are sufficiently different from normal electrons to be classed as an entirely different type of particle.

As mobile valence electrons travel through the lattice of a material, an attraction with the positive ions in the structure may lead to a ripple or distortion in the lattice. Thus, as an electron passes through a region, a cluster of positive ions will form at the point of nearest contact. Because the electron moves faster than the rate of vibrational motion will allow the positive species to relax to their normal state, a temporary zone of net positive charge is generated. Subsequently, a second electron can be attracted into the system, and a Cooper pair is formed.

Electrical resistance, produced by the scattering of mobile electrons, is a result of imperfections and thermal vibrations within the atomic lattice. Resistivity, therefore, would be zero at 0K for a perfect regular metallic lattice, since there is no vibrational energy present in the lattice for the scattering of electrons. Once the temperature rises above absolute zero, a small amount of energy is sufficient to cause scattering and subsequent resistivity.

In superconducting materials, however, once the formation of Cooper pairs is achieved, the highly coordinated electrons acquire a unique net momentum. For this net momentum to be broken down, and hence produce scattering, much more energy is required than the binding energy of the Cooper electrons. In addition, due to the synchronisation of the Cooper pairs, a change of state in the momentum of one pair would require a similar change in the states of all other pairs as well. For this reason, superconductivity can remain at elevated temperatures since the energy needed to alter the momentum of Cooper pairs far exceeds the vibrational energy present in the lattice at low temperatures.

1.1.6 PEIERLS DISTORTION IN ORGANIC METALS

The behaviour of anisotropic organic metals was considered by Fröhlich[13] and Peierls,[14] who predicted that at low temperature a quasi-one-dimensional metal could not support long-range order, and would be unstable to lattice distortions.

As stated in Section 1.1.5, a stack of open-shell radicals can form a half-filled band, which in turn gives rise to conduction. In the presence of radicals, however, there is always some electronic driving force for dimerisation, and at a critical temperature spin pairing may occur. In consequence, a band gap (known as the Peierls gap) will emerge, separating the bonding and anti-bonding energy levels. Metallic conduction, therefore, will be reduced to a semi-conducting or insulating state.

Parallel to this scenario is the formation of a charge density wave (CDW). As dimerisation takes place, the conducting chain becomes contracted at the points where two radical entities come together, and stretched in the regions they have vacated. This results in alternating zones of high and low charge density, forming a charge density wave. In conjunction with the creation of a band gap this phenomenon is known as the Peierls distortion and is restricted to one-dimensional conducting systems - in a two or three-dimensional system lattice rearrangement of this order would be very difficult to simulate.

Over the past 20 years variable temperature experiments have proved this theory to be correct; as an example TTF-TCNQ exhibits Peierls distortion below 40K,[15] where the complex is reduced to an insulating state.

1.1.7 TOWARDS THE IDEAL ORGANIC METAL

The key features of highly conducting organic CT materials have been briefly discussed. A more detailed account of the design constraints for organic metals and superconductors has been provided by Cowan[16]. In summary, the guidelines for obtaining successful conducting CT salts are as follows:

1. Stable open-shell free radical components which form partially filled bands. Alternatively, orbital overlap between neutral molecular species should be sufficient to give increased bandwidths with a substantially reduced HOMO-LUMO energy gap.

2. Planar molecules with delocalised π-molecular orbitals to aid effective overlap, and hence band formation.

3. Inhomogeneous charge and spin distribution to compensate for the repulsion of like charged species in any one stack.

4. Segregated stacks of radical species, since alternating donor-acceptor stacks will contain filled HOMO and empty LUMO bands with large energy gaps.

5. An aversion to Peierls distortion.

6. Little or no disorder in the structure which would otherwise lead to localised wave functions.

7. Donor and acceptor molecules of the same size. It is postulated that this, as well as other factors, contribute to the successful growth of well ordered single crystals of the complex. (N.B. There are several exceptions to this guideline).

8. Fractional charge transfer which can minimise Coulombic repulsion.

9. Strong interchain coupling to suppress the formation of a CDW.

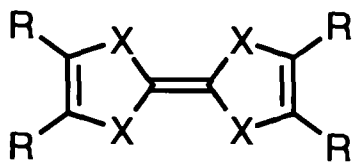
10. A divalent cation and/or anion giving highly polarizable components, also helps to reduce Coulombic repulsion.

1.1.8 CONDUCTING CT MATERIALS BASED UPON CHALCOGENATED FULVALENES AS Π–DONORS

Since its first synthesis in 1970, TTF has initiated the birth of many analogous π-donor molecules. Although not in chronological order, a brief overview of these systems is presented, with respect to increasing complexity of the structures.

1.1.8.1 ANALOGOUS 'CORE-TTF' DONORS

The substitution of sulfur by other chalcogens has been successfully achieved. Although the syntheses of both tetraselenafulvalene (TSF, **4**)[17] and tetratellurafulvalene (TTeF, **5**)[18] are more chemically demanding than for TTF, the resulting fulvalenes exhibit higher conductivity values on complexation with TCNQ. Indeed, room temperature conductivity values for the TCNQ complexes are 700-800 Scm^{-1} for TSF, and 2200 Scm^{-1} for TTeF (*c.f.* σ_{rt} = 500 Scm^{-1} for TTF-TCNQ). The gain in conductivity has been attributed to an enhancement in intrastack π-interactions within the donor regions. This in turn is facilitated by the increasingly diffuse p and d orbitals of the selenium and tellurium atoms, leading to improved π-delocalisation throughout the molecule.



4 TSF, X = Se, R = H
5 TTeF, X = Te, R = H
6 TMTTF, X = S, R = Me
7 TMTSF, X = Se, R = Me

Extending the σ–bond framework of these donors with methyl groups has provided the compounds tetramethyl-TTF (TMTTF, **6**),[19] and tetramethyl-TSF (TMTSF, **7**).[20] Tetramethyl-TTeF is still unknown.

Although molecule **6** gave the first example of metallic behaviour with acceptors[21] (tetrahalo-*p*-benzoquinones) other than TCNQ, the salts of donor **7** aroused more interest in the field of organic conducting materials. By varying the anion, salts of the general formula $(TMTSF)_2X$ were formed (*e.g.* where X = PF_6^-, AsF_6^-, FSO_3^-, ReO_4^-, and ClO_4^-), known as the Bechgaard salts.

These salts display metal-insulator transitions between 10 and 200K. Under hydrostatic pressure, however, $(TMTSF)_2^{+\cdot}PF_6^-$ became the first organic superconductor at 0.9K, 12kbar.[22a] Under similar conditions, superconductivity was recorded with the remaining Bechgaard salts. One notable exception was the ClO_4^- salt, which proved to be a superconductor under ambient pressure at 1.4K.[22b]

The X-ray crystal structure of $(TMTSF)_2^{+\cdot}BrO_4^-$ can be seen in Figure 1.6.[23] The donor molecules are essentially planar and are stacked in a ring-over-bond fashion. The most striking aspect of the donor columns is that both interstack and intrastack Se---Se distances are very similar. This gives rise to two-dimensionality, rather than the one-dimensionality of TTF-TCNQ, with the advantage that Peierls distortion is more likely to be suppressed. The formation of a three-dimensional array is foiled by the presence of the BrO_4^- anions.

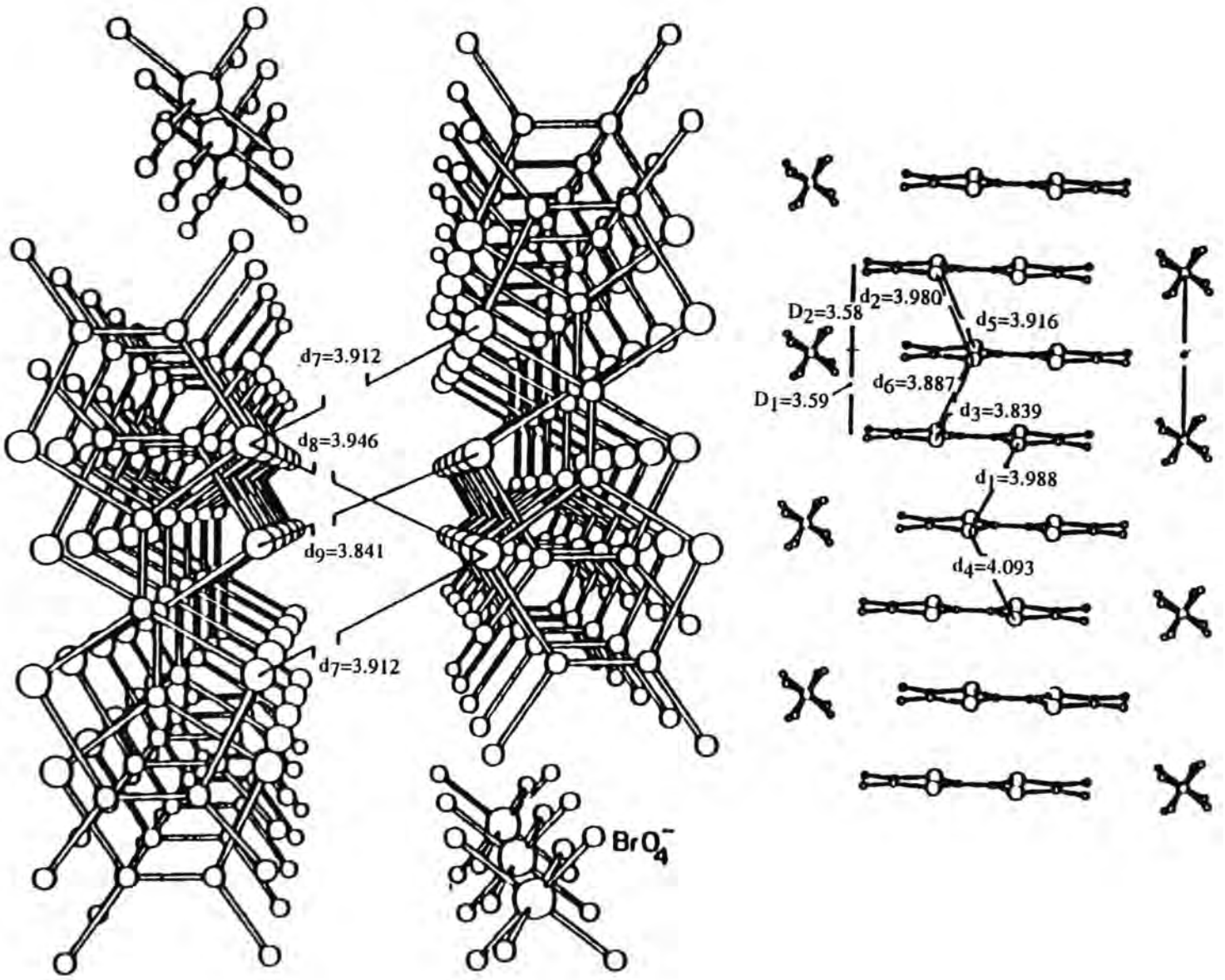
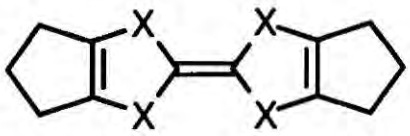


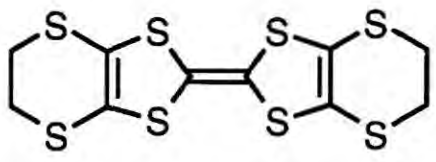
Figure 1.6: X-ray structure of $(TMTSF)_2^{+\cdot}BrO_4^-$. Interstack Se---Se distances are shown on the left, whilst the intrastack distances are on the right.

The hexamethylene derivatives **8** (HMTTF),[24] **9** (HMTSF),[25] and **10** (HMTTeF)[26] have also been prepared. The conducting behaviour of the CT salts derived from these donors is inferior, compared to the related tetramethyl derivatives. HMTSF-TCNQ, however, retains its metallic character down to <1K.[27] This is probably due to increased dimensionality resulting from close interstack Se---N contacts.



8 HMTTF, X = S
9 HMTSF, X = Se
10 HMTTeF, X = Te

Another possible reason for the failure of the hexamethylene derivatives **8-10** to match up to the tetramethyl donors **6** and **7**, is the loss in planarity of the former, due to the incorporation of the methylene bridges, although consideration of salts derived from the donor bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) **11**, suggests that this is not the only reason.



11 BEDT-TTF

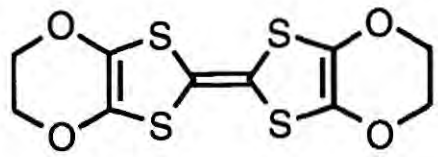
After the first synthesis of BEDT-TTF in 1977,[28] many salts were prepared from this new exciting donor with impressive results. Indeed, the majority of known ambient pressure superconductors are salts of BEDT-TTF;[29] together with the Bechgaard salts they are the most commonly studied chalcogen-based π-donor materials. A selection of complexes has been tabulated, and are shown in Table 1.1.

CT COMPLEX	CONDUCTIVITY	PRESSURE	REFERENCE
$(BEDT\text{-}TTF)_2ClO_4$ $(1,1,2\text{-trichloroethane})_{0.5}$	Metallic conductivity 298-1.4K	------	30
$\beta\text{-}(BEDT\text{-}TTF)_2I_3$	T_c 1.4K T_c 8K	Ambient Anisotropic	31 32
$(BEDT\text{-}TTF)_2ReO_4$	T_c 1.4K	4kbar	33
$(BEDT\text{-}TTF)_2IBr_2$	T_c 2.6K	Ambient	34
$\kappa\text{-}(BEDT\text{-}TTF)_2Cu(SCN)_2$	T_c 10.4K	Ambient	35
$\kappa\text{-}(BEDT\text{-}TTF)_2\text{-}Cu[N(CN)_2]Br$	T_c 11.6K	Ambient	36
$\kappa\text{-}(BEDT\text{-}TTF)_2\text{-}Cu[N(CN)_2]Cl$	T_c 12.5K	0.3kbar	37
$(BEDO\text{-}TTF)_{2.4}I_3$	Organic Metal $\sigma_{rt} = 100\text{-}280 Scm^{-1}$	Ambient	38
$(BEDO\text{-}TTF)_3Cu_2(NCS)_3$	T_c 12.5K	Ambient	39

Table 1.1: Conductivity values of sample BEDT-TTF - type complexes, where T_c is the critical temperature at which the material undergoes the transition into a superconducting state.

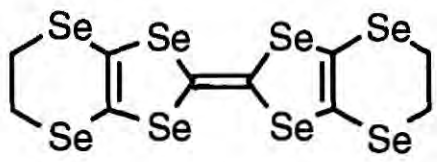
In the case of $(BEDT\text{-}TTF)_2ClO_4(1,1,2\text{-trichloroethane})_{0.5}$ metallic conductivity is retained over a large temperature range; by tailoring the anion of the CT salts, the onset of superconductivity is observed over the range 1.4-12.5K, both at elevated and ambient pressures.

Substitution of two of the peripheral sulphur atoms with oxygen afforded the new donor BEDO-TTF **12**. The subsequent CT complex $(BEDO\text{-}TTF)_3Cu_2(NCS)_3$, although inferior to the BEDT-TTF salts, became the first superconductor in this class to contain oxygen.

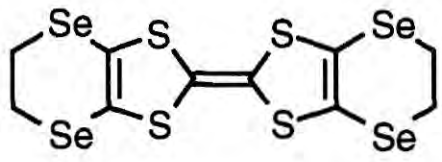


12 BEDO-TTF

With the Bechgaard salts in mind, it is surprising that no complexes of donors BEDS-TSF[40,41] **13** and BEDS-TTF[42] **14** exhibit superconducting properties. In particular, the salts $(BEDS\text{-}TTF)_2I_3$ and $(BEDT\text{-}TTF)_2I_3$ are isostructural, with only the latter showing superconductivity, both at ambient and applied pressures.



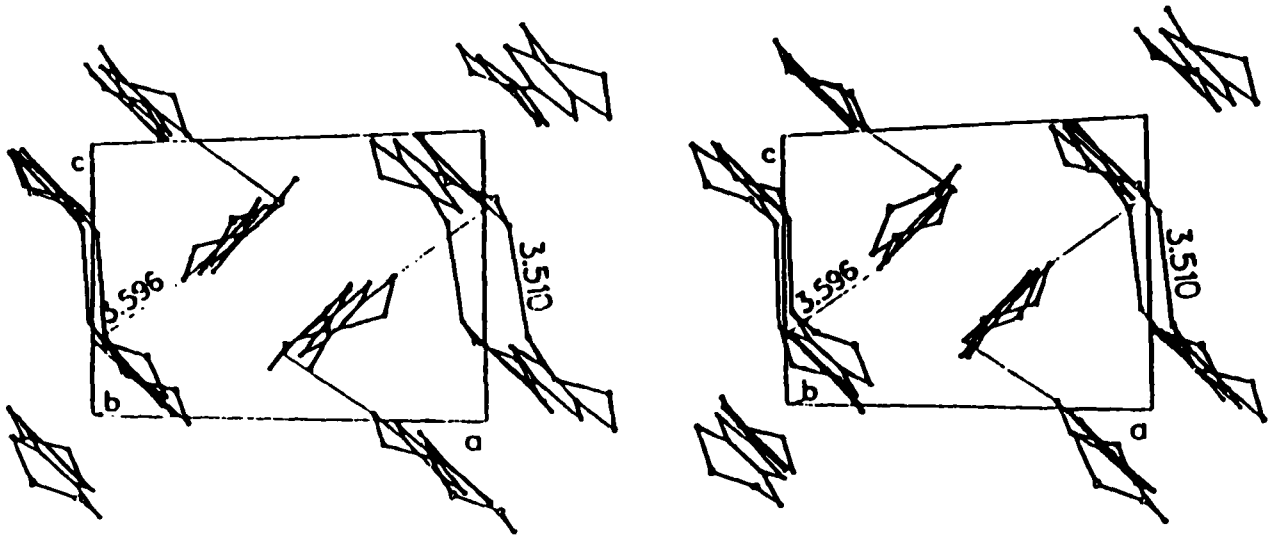
13 BEDS-TSF



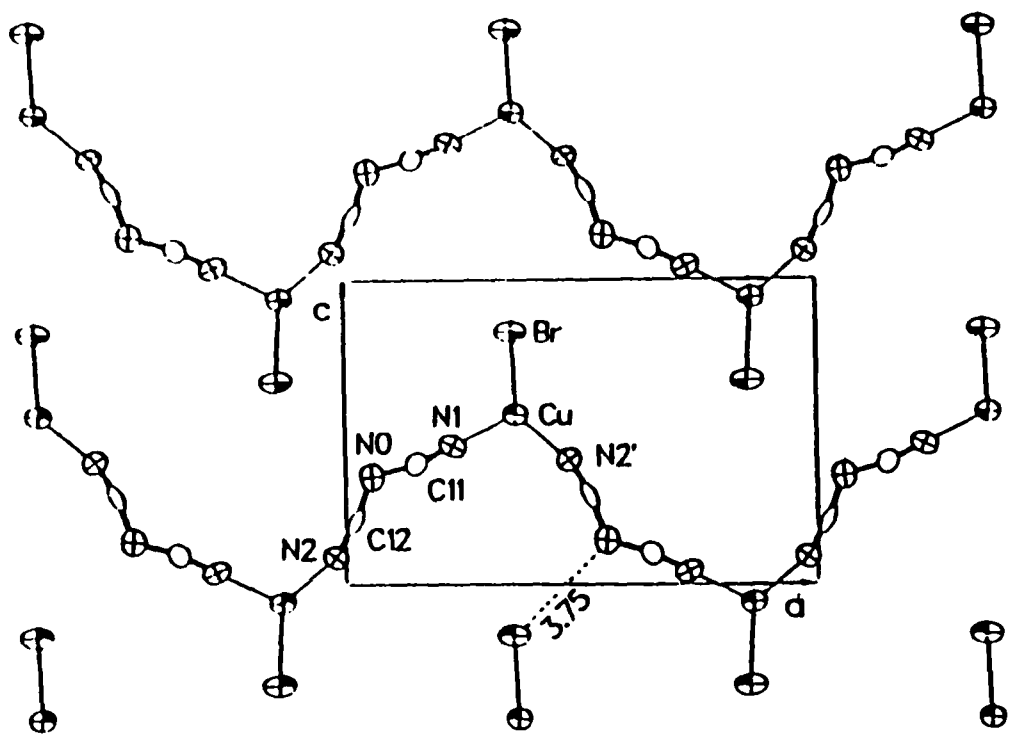
14 BEDS-TTF

Clearly there is a subtle difference between the structures of the Bechgaard salts and those of the BEDT-family, notably a deviation in the latter series from one of the guidelines previously outlined by Cowan[16] (Section 1.1.7). The non-planarity of the donor molecule BEDT-TTF, together with the large thermal vibration of the peripheral ethylene bridges, hinders the formation of good π-overlap within face-to-face columnar donor stacks. As indicated from the values given in Table 1.1, however, superconductivity is still observed in these complexes despite this situation.

The best example of this new type of assembly is seen in the X-ray crystallographic structure of the salt $\kappa\text{-}(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$, Figure 1.7.[42]



(a)



(b)

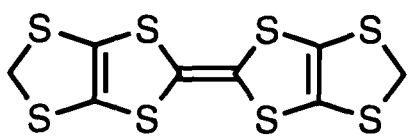
Figure 1.7: X-ray crystal structure of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br

Figure 1.7(a) shows the formation of orthogonal BEDT-TTF dimers (κ-packing), with close intermolecular S---S contacts shorter than 3.60Å. Forming a highly ordered conducting three-dimensional S---S network, the material is able to support superconductivity at higher temperatures than seen previously. Indeed, the salt (BEDT-TTF)$_2$I$_3$ forms four different types of stoicheiometric phases - termed α, β, θ, and κ - of which the latter three are superconductors.[31,43] The anions of these salts

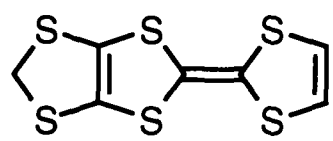
also play an important role. As seen in Figure 1.7(b), insulating linear V-shaped polymeric chains result with the anion; it has been suggested that increasing anion length is responsible for the increase in T_c of the BEDT-TTF salts.[44] This can clearly be seen on inspection of Table 1.1.

In summary, organic-based superconductors can now be synthesised without relying upon the formation of segregated donor/acceptor stacks. More recently, it has become a major challenge to produce further β, θ, or κ–type CT salts.

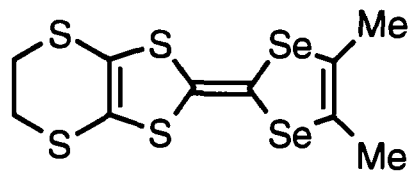
Other κ–type dimer structures include $(BMDT\text{-}TTF)_2Au(CN)_2$,[45] $(MDT\text{-}TTF)_2AuI_2$,[46,47] and $(DMET)_2AuBr_2$,[48] derived from the donors **15**, **16**, and **17**, respectively. The above species provide evidence that a symmetrical donor is not necessary for superconductivity. Indeed, both MDT-TTF and DMET provide superconducting salts, whilst the parent symmetrical donors of the former (TTF and BMDT-TTF) yield, at best, only metallic CT materials.



15 BMDT-TTF

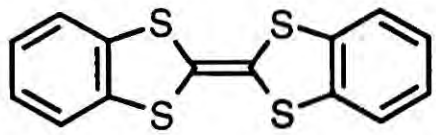


16 MDT-TTF



17 DMET

It is worth noting that extending the π-orbital system, by fusing benzo-rings to the fulvalene framework, does not afford particularly interesting donors. Dibenzotetrathiafulvalene[49] (DBTTF, **18**) forms highly conducting CT materials [*e.g.* $(DBTTF)_8(SnCl_6)_3$],[50,51] but on the whole is a poor comparison to the Bechgaard and BEDT-TTF salts.



18 DBTTF

As a summary, the variable temperature conductivity values of selected organic materials are shown in Figure 1.8.[52] In direct comparison with the more commonly known conducting materials - copper metal and doped polyacetylene - one can clearly see the Peierls transitions of $(TMTSF)_2PF_6$ and TTF-TCNQ, as well as the shifts into superconducting states of the salt $(TMTSF)_2ClO_4$.

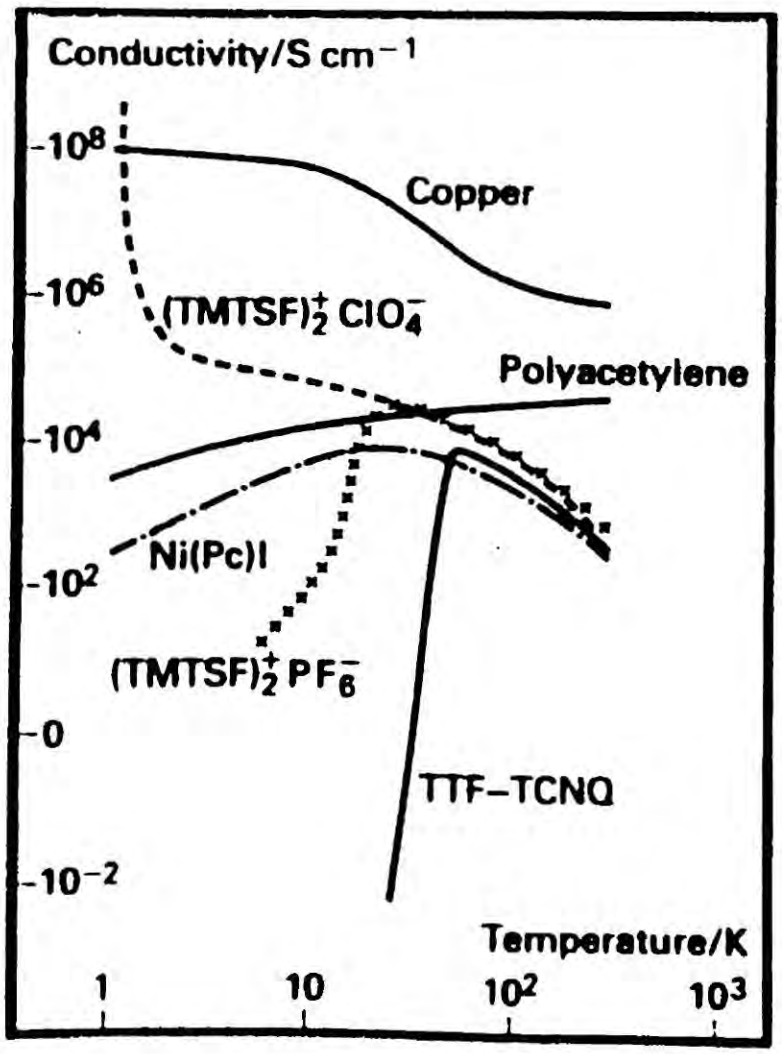


Figure 1.8: Variable temperature conductivity values at ambient pressure for a range of highly conducting materials.

1.1.8.2 THE INTRODUCTION OF SPACER GROUPS BETWEEN THE 1,3-DITHIOLE RING SYSTEMS OF TTF DERIVATIVES

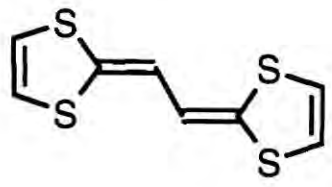
The concept behind the synthesis of vinylogous derivatives of TTF is minimisation of the intramolecular Coulombic repulsion of the dication state, *via* increased separation of the 1,3-dithiole rings.

In 1983, Yoshida *et al.* prepared the donor molecules ethanediylidene-2,2'-bis(1,3-dithiole)[53] **19**, and 1,4-butenediylidene-2,2'-bis(1,3-dithiole)[54] **20**. The redox behaviour of these compounds, and the related dibenzo analogues **21**[55] and **22**[52], have been elucidated by cyclic voltammetry and can be seen in Table 1.2.

In comparison with TTF **1** and DBTTF **18**, donors **19** and **21** display substantially lower first and second oxidation potentials; the difference between the two redox waves, E_2-E_1, is also reduced in the vinylogues. This proves, therefore, that the insertion of Csp^2-derived spacer groups into the central bond of TTF systems, suppresses Coulombic repulsion and promotes the formation of the dication state at lower applied potentials.

The incorporation of a second pair of Csp^2 atoms into the spacer region does not correlate to a further reduction in redox values, but induces the 1,3-dithiole rings to act independently of each other. In both cases, a single two-electron oxidation is observed for molecules **20** and **22** (0.22V and 0.47V, respectively).

Similar results are also seen with donors **23** (independently synthesised by three different groups),[56-58] and **24**.[58] Although BEDT-TTF **11** forms superconducting salts, it is a weaker donor than TTF. The vinylogous derivative **23**, however, displays reduced redox potentials comparable to TTF but with a much lower ΔE value. The same also applies to molecule **24**, which is the first vinylogous donor of its type to be characterised by X-ray crystallography.[58] Donor **24** is essentially planar with a small amount of puckering at the ethylene bridge. This arrangement is in slight contrast to the non-planar structure of BEDT-TTF **11** which exhibits a bowing in the TTF portion of the molecule, and can be seen in Figure 1.9.



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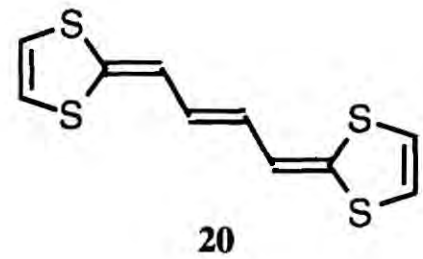

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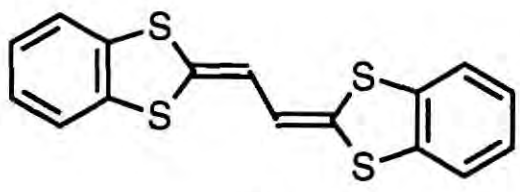

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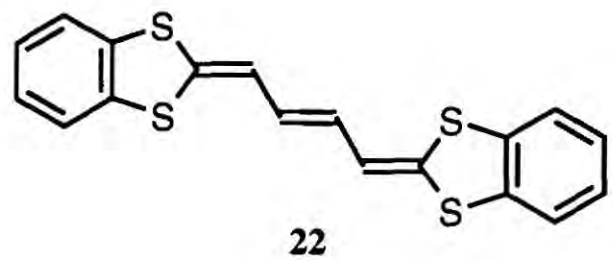

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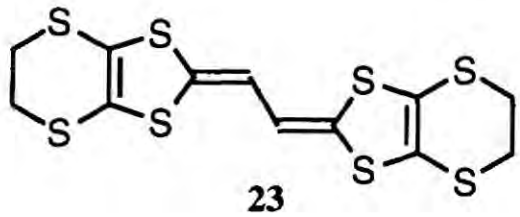
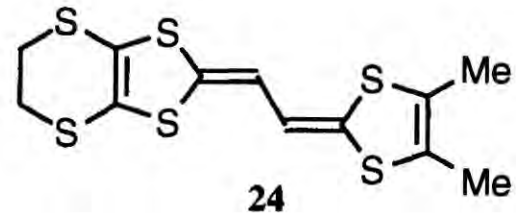


23



24

DONOR	E_1/V	E_2/V	(E_2-E_1)/V
1 TTF[a]	0.34	0.71	0.37
19[a]	0.20	0.36	0.16
20[a]	0.22	---	---
18 DBTTF[a]	0.61	0.93	0.32
21[a]	0.47	0.64	0.17
22[a]	0.47	---	---
1 TTF[b]	0.34	0.78	0.44
11 BEDT-TTF[b]	0.59	0.99	0.40
23[b]	0.48	0.71	0.23
24[b]	0.36	0.62	0.26
25[b]	0.43	---	---
27[b]	0.14	---	---

Table 1.2: Cyclic voltammetric data for TTF **1**, DBTTF **18**, BEDT-TTF **11**, and donors **19-25**. Pt electrode vs. Ag/AgCl, supporting electrolyte Et_4NClO_4 0.1M, 20°C, in (a) CH_2Cl_2, (b) CH_3CN.

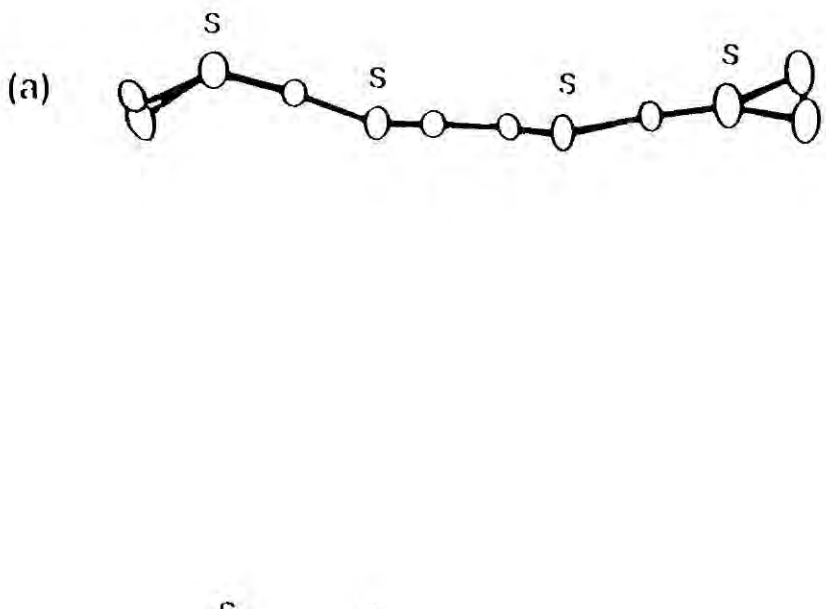
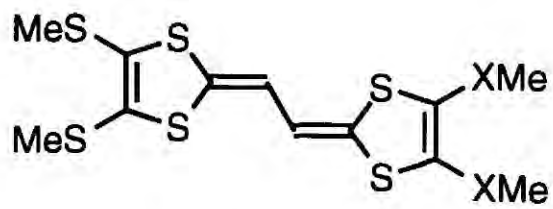


Figure 1.9: Molecular structures of donors (a) BEDT-TTF **11** and (b) molecule **24**.

The molecular structures of vinylogous compounds **25**,[59] and **26**[60] have also been solved. Both compounds are isostructural and stack uniformally with several intermolecular S---S(Se) contacts close to the sum of the van der Waals radii (Figure 1.10a).



25 X = S
26 X = Se

Donor **25** forms a 1:1 CT salt with TCNQ (Figure 1.10b), and in its oxidised state adopts a totally different conformation from its neutral structure. The radical cation (Figure 1.10c) is non-planar with respect to the 1,3-dithiole units showing a dihedral angle of *ca.* 19° between the two five-membered rings. Unfortunately, the 1:1 complex has a mixed-stack structure which leads to low conductivity; the formation and subsequent properties of the vinylogous TTF-TCNQ salts, on the whole, have been rather disappointing.

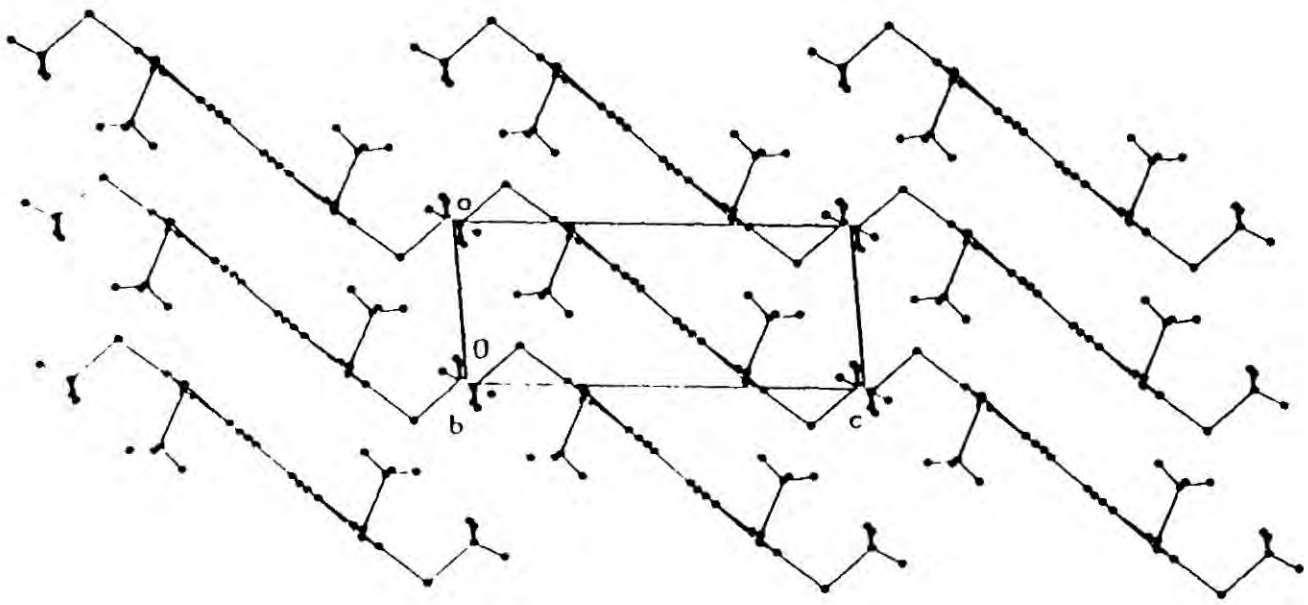


Figure 1.10a: X-ray crystal structure of neutral donor **25**.

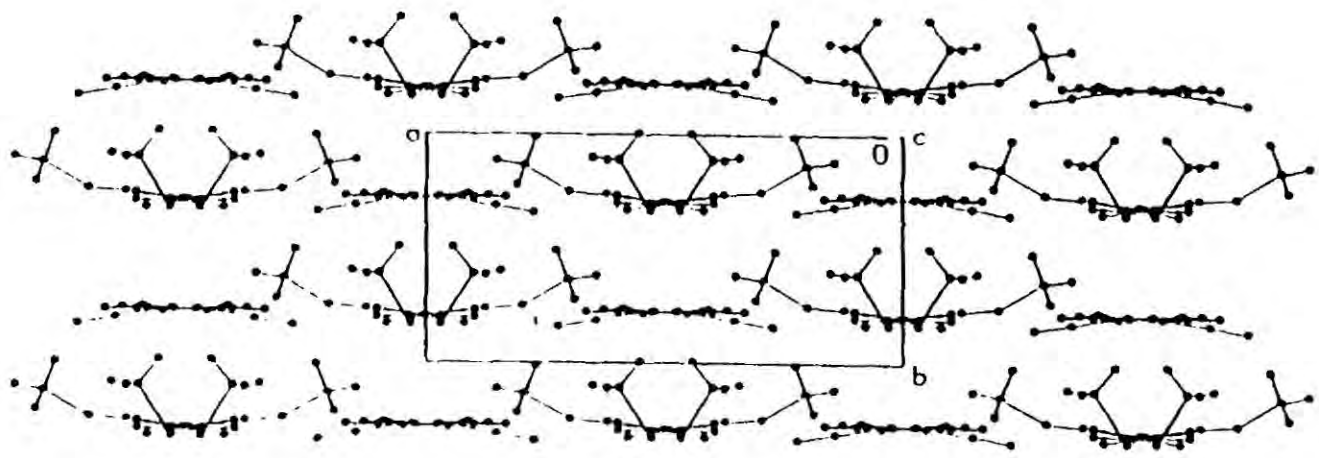


Figure 1.10b: X-ray crystal structure of a 1:1 complex of compound **25** and TCNQ, viewed down the long axes of the molecules.

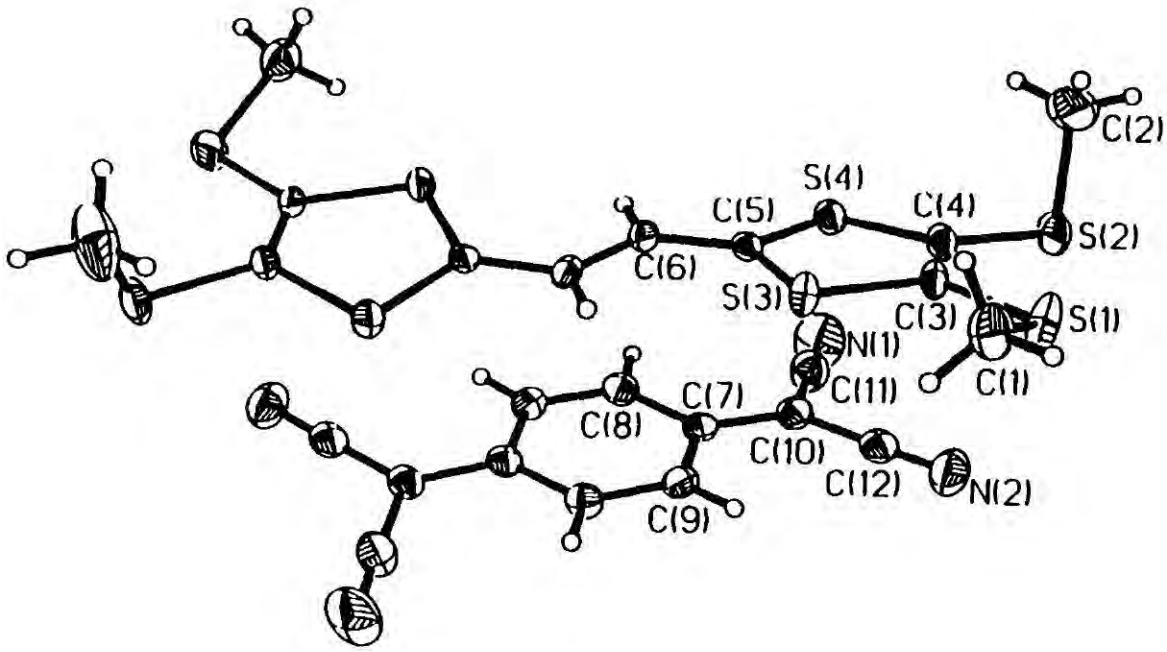


Figure 1.10c: Structure of the cation radical $\mathbf{25}^{+\cdot}$ in the TCNQ complex.

The insertion of aromatic rings between the 1,3-dithiole rings has also been the subject of recent work.[61] In contrast to the flexible structures of vinylogous derivatives, these systems provide more rigid molecules, for the successful formation of crystalline organic conductors.[62]

One of the most interesting donors in this series is molecule **27**,[63] studied in our laboratory.

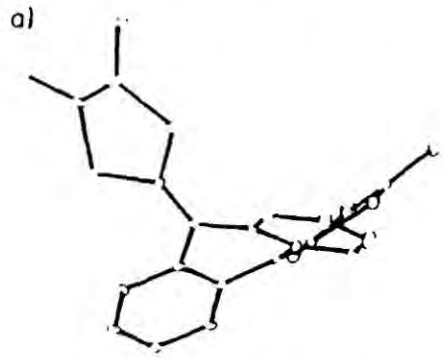
27

From Table 1.2 we can deduce that the anthracene spacer group facilitates a simultaneous two-electron oxidation to the dication state. The oxidation occurs at

+0.34V and is not cleanly reversible, however, reduction of the dication can be detected at +0.07V.

Donor **27** forms a highly conducting 1:4 complex with TCNQ.[64] The X-ray crystal structures of both the neutral donor and the TCNQ complex are shown in Figure 1.11.

In the neutral state, the donor molecule adopts a 'butterfly' configuration [Figure 1.11(a)]. On translation to the dication state in the 1:4 TCNQ complex [Figure 1.11(b)], the 1,3-dithiolium cations become twisted, and are almost orthogonal to the planar anthracene ring with dihedral angles of 86°. The salt is most unusual because it is the first semi-metallic TCNQ complex based on TTF which adopts such a non-planar conformation. The room temperature conductivity of the 1:4 complex is 60Scm^{-1}, and varies only slightly upon cooling to *ca.* 90K. Below this temperature, Peierls distortion rapidly predominates with conductivity becoming negligible at *ca.* 40K.



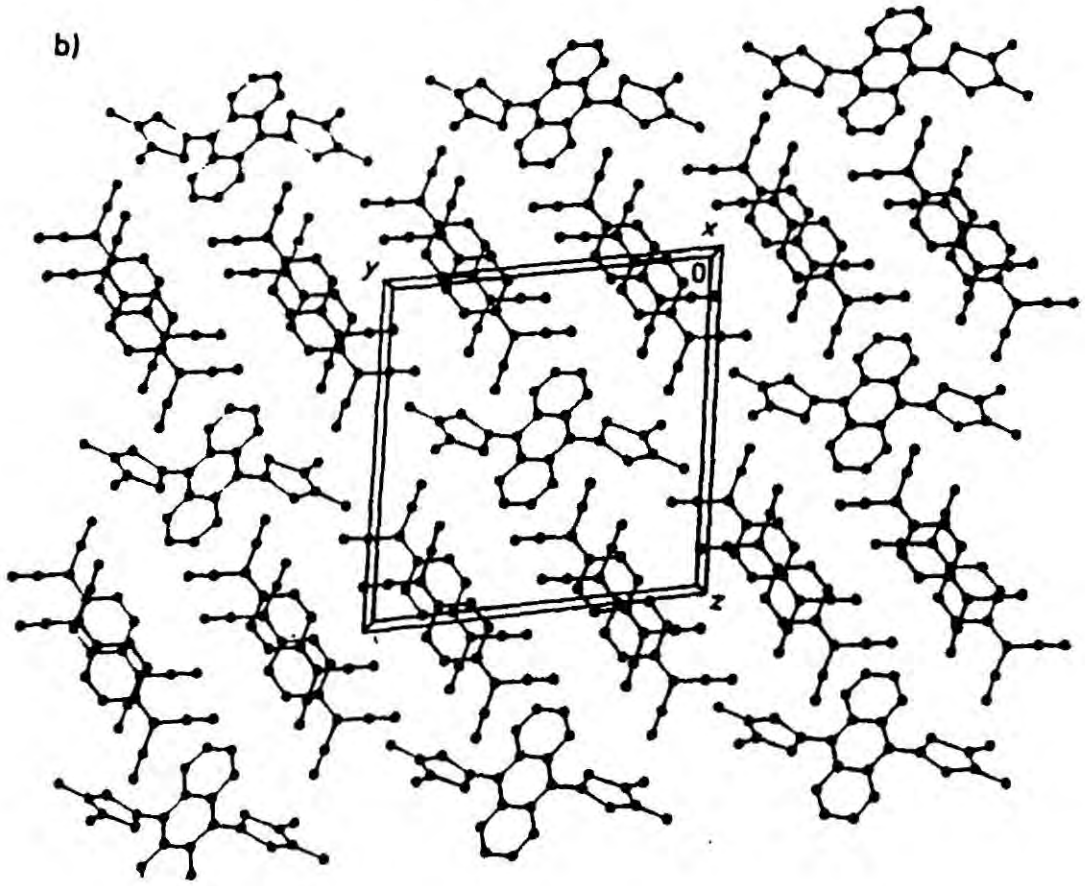


Figure 1.11: X-ray crystal structure of (a) neutral donor molecule **27** and (b) the 1:4 TCNQ complex.

1.2 MOLECULAR-BASED MAGNETS

1.2.1 THE PRINCIPLE OF MOMENTS

Virtually every household in the UK will contain at least one magnetic material in frequent use. Applications of magnets are found in motors and generators, magneto-mechanical equipment (medical implants, frictionless bearings), acoustic devices (loudspeakers, microphones), and information technology (sensors, switches, magnetic resonance imaging, computer hardware/software).[65]

As discussed in Section 1.1.4, there are several different types of conducting materials (superconductors, metals, semiconductors, etc.). Similarly, a material can be classified in terms of magnetism, by examining its behaviour in the presence of a magnetic field. All substances exhibit a magnetic moment, M, upon application of a magnetic field, H, such that $M=\chi H$, where χ is the *magnetic susceptibility* - the degree to which a material responds to the field. Magnetic behaviour arises from the intrinsic spin of an electron, since every electron has a minute magnetic moment. The interaction and comparison with other electron spins on adjacent atoms or molecules is an extremely important factor.

In a closed-shell species each orbital will contain paired electrons with anti-parallel spins, resulting in zero net spin. The overall magnetic moment, therefore, will also be nil. This situation gives rise to a *diamagnet* (Figure 1.12a), where magnetic susceptibility is actually at a negative value.

In an open-shell species containing at least one odd electron per atom/molecule, the bulk electron spins may form into a random arrangement. Inevitably, there will be some net spin which leads to a weak magnetic moment. Such a material is a *paramagnet* (Figure 1.12b).

At sufficiently low temperatures the spins may approach closely enough for inter- or intra-atomic/molecular spin interaction to take place. Subsequent spin alignment can then take place in three different ways:

(i) An *antiferromagnet* will have spins which oppose (Figure 1.12c).

(ii) A *ferrimagnetic* material will have antiferromagnetic ordering, but the number of spins on neighbouring sites will be variable (Figure 1.12d). This results in a low magnetic moment.

(iii) A true *ferromagnet* (Figure 1.12e) will have spins perfectly aligned in parallel fashion throughout the bulk material. A high value of magnetic moment will be seen in the absence of an applied field. *Ferromagnetic coupling* is observed when certain materials transpose to a ferromagnetic state on induction of a low magnetic field. Similarly, a *metamagnet* acts as a more impulsive switch from antiferromagnetism to a ferromagnetic state on application of a comparably higher field.

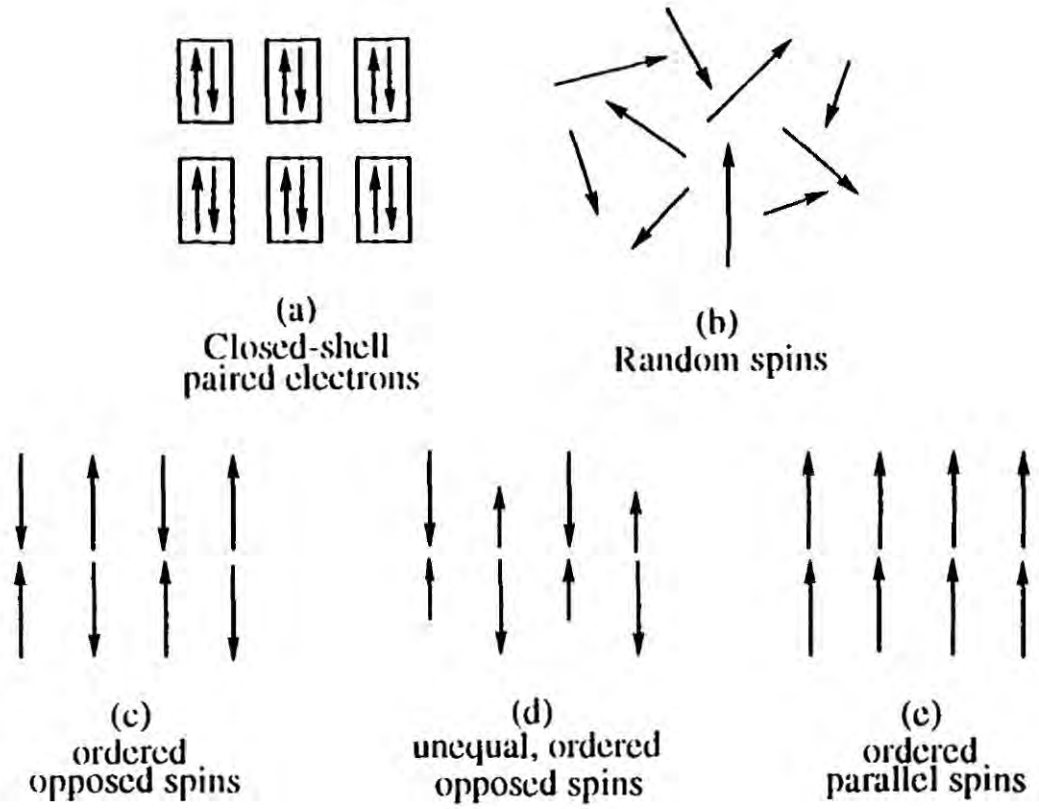


Figure 1.12: two-dimensional spin representations for a) diamagnet, b) paramagnet, c) antiferromagnet, d) ferrimagnet, and e) ferromagnet.

The magnetic behaviour of these different types of materials over a variable field is shown in Figure 1.13.[66]

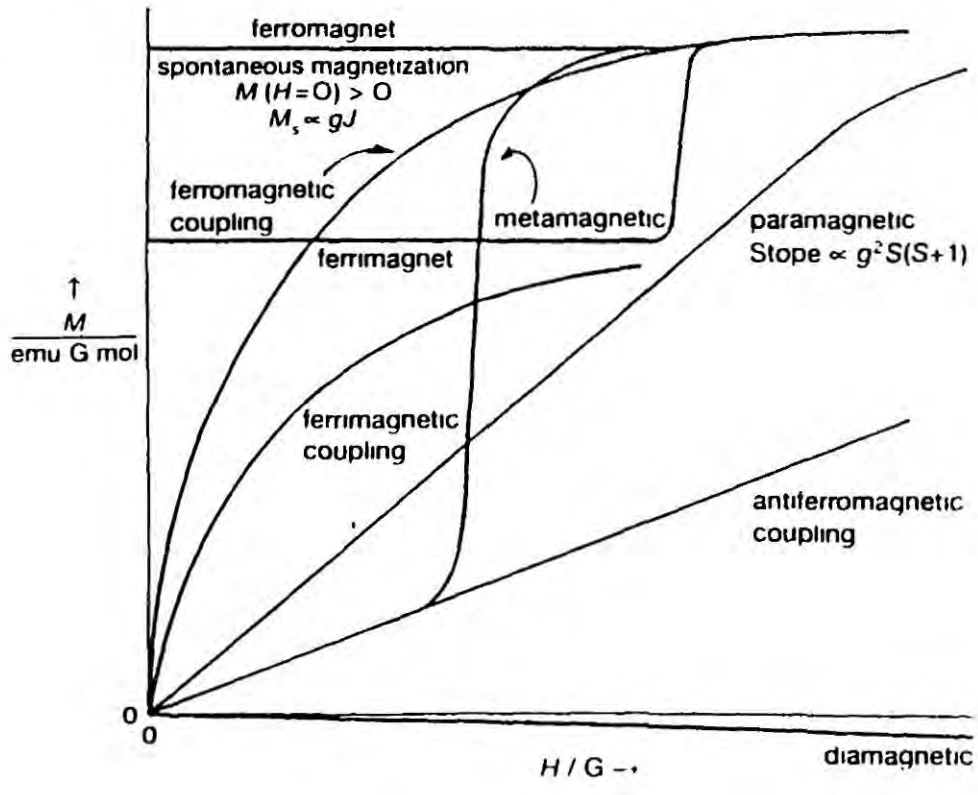


Figure 1.13: Plot of magnetisation (M) as a function of field (H) for several types of magnetic behaviour.

1.2.2 THE MAGNETIC BEHAVIOUR OF METALLOCENES

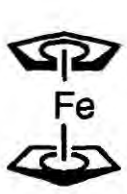
Molecular based ferromagnets have been postulated since the 1960s. Whereas inorganic magnets prepared by metallurgy possess high density d or f orbital metal spin sites, an organic magnet must contain at least one type of spin site based on s and p orbitals. Organometallic compounds may have the freedom to use either type of electron source.

The McConnell model[67] for organic ferromagnetic materials is based upon charge-transfer complexes. Ferromagnetic behaviour requires long range spin order throughout the bulk material. This phenomenon is almost exclusive to three-dimensional interactions. There is a fundamental problem, therefore, in the case of CT salts (which at best are predominantly two-dimensional materials), since there is no secure mechanism to prevent antiferromagnetic alignment of electron spins between each donor-acceptor stack.

There is evidence, however, that non-3D associations suffice in certain circumstances. For example, the complex Rb_2CrCl_4[68] can be broken down to a two-dimensional interacting structure by replacing Rb^+ with bulky alkylammonium cations, yet T_c (Curie temperature - the critical point at which ferromagnetism is observed), is not significantly altered. This suggests that the inclusion of CT salts as potential ferromagnets is feasible, and not exclusively reliant upon spin alignment beyond the two-dimensional level.

From this basis Miller and Epstein developed a range of metallocene CT complexes with various electron acceptors. Of the metallocene family, Group 8 transition metals (Fe, Ru, Os) form the most stable 'sandwich-type' structures. Consisting of an 18π fully-paired electron configuration, they possess labile d-orbital electrons available for donation.

The first of the Group 8 metallocenes, ferrocene **28**, is more difficult to oxidise (by 0.5V) than decamethylferrocene **29**, which forms a CT complex with tetracyanoethylene (TCNE) **30**, whereas ferrocene **28** is too weak a donor to reduce this electron acceptor.[69]



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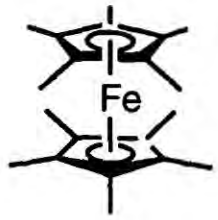

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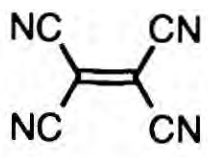


30

Decamethyl derivatives of ruthenium and osmium have provided complexes with TCNE but have been difficult to analyse. The TCNE complex of $[Os^{III}(C_5Me_5)_2]^{+\cdot}$ produces various stoichieometries with low susceptibilities, and the subsequent crystals formed have been inadequate for crystallographic studies.[70] A problem also arises with the ruthenium analogue, where the subsequent radical cation commonly disproportionates to $Ru^{II}(C_5Me_5)_2$ and $[Ru^{IV}(C_5Me_5)(C_5Me_4CH_2)]^+$.[71]

For these reasons, $Fe^{II}(C_5Me_5)_2$ has proved to be the best and most popular candidate for highly magnetic CT salts.

A range of metallocenes, together with a number of different electron acceptors, has provided with excellent examples of CT complexes displaying a range of magnetic behaviour.[65,66] A selection of these is presented in Table 1.3.

DONOR	**MAGNETIC BEHAVIOUR**	**T_C/K**
$Fe^{II}(C_5H_5)_2TCNE$	Diamagnet	---
$Fe^{III}Cp^*_2{}^{\cdot+}[C_3(CN)_5]^{\cdot-}$	Paramagnet	---
$Fe^{III}Cp^*_2{}^{\cdot+}TCNE^{\cdot-}$	Ferromagnet	4.8
$Ni^{III}Cp^*_2{}^{\cdot+}TCNE^{\cdot-}$	Antiferromagnet	---
$Mn^{III}Cp^*_2{}^{\cdot+}TCNE^{\cdot-}$	Ferromagnet	8.8
$Cr^{III}Cp^*_2{}^{\cdot+}TCNE^{\cdot-}$	Ferrimagnet	3.65 (H=0.15G)
$Fe^{III}Cp^*_2{}^{\cdot+}TCNQ^{\cdot-}$	Metamagnet	2.55 (H=1600G)
$Mn^{III}Cp^*_2{}^{\cdot+}TCNQ^{\cdot-}$	Ferromagnetic couple	6.3 (H=50G)
$Cr^{III}Cp^*_2{}^{\cdot+}TCNQ^{\cdot-}$	Ferromagnetic couple	3.3 (H=15G)

Table 1.3: Magnetic behaviour of selected complexes of general formula $[M(Cp/Cp^*)_2][A]$, with critical temperatures (T_c) where applicable; $Cp^*=(C_5Me_5)$.

As seen from Table 1.3, highly magnetic states can be achieved with metallocenes using TCNQ and TCNE as electron acceptors. With respect to T_c, the doublet state decamethylferrocene derivatives are second best only to the triplet state manganese analogues.

1.3 CONCLUSION

A large number of symmetrical and non-symmetrical tetrachalcogenofulvalene derivatives (including the analogous 'stretched' systems), are known to form highly conducting CT materials. Some are even found to be superconducting at below *ca.* 12K. The redox behaviour of the neutral donors is variable and highly dependent upon substituents attached to the periphery of, and within, the fulvalene framework.

In parallel, the metallocenes are also able to form interesting CT complexes. In this case, however, rather than producing conducting salts, they form materials with outstanding magnetic properties. Again, metallocene redox behaviour varies according to substituents.

The study of molecules comprising two different redox centres that are covalently linked is a burgeoning topic within supramolecular chemistry, with applications in molecular electronic devices, sensors, electrocatalysis, and energy conversion.[72] Current research includes the study of redox behaviour between combinations of organic and organometallic components, *e.g.*, bipyridinium cations, quinones, metallocenes, and metal coordinated macrocycles.[73]

It is, therefore, a fascinating challenge to covalently link ferrocene and tetrathiafulvalene derivatives. The successful incorporation of such redox systems into one molecule could ultimately foster CT complexes with novel conducting and magnetic properties.

CHAPTER 2

FUNCTIONALISATION OF TETRATHIAFULVALENE: THE SYNTHESIS OF COVALENTLY LINKED TTF-FERROCENE DERIVATIVES

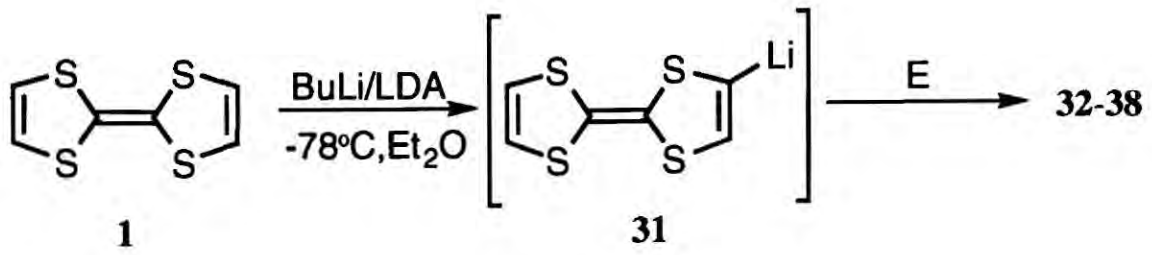
2.1 INTRODUCTION

The functionalisation of TTF is usually achieved by one of two methods. The most direct route is by lithiation of TTF itself, while a more complicated method involves coupling of two 1,3-dithiole-2-one (or 2-thione) units.

This chapter briefly reviews the synthesis of functionalised TTF systems by the above methods, focussing on those derivatives that we have used extensively, and then reports the successful attachment of ferrocene units to the reactive TTF derivatives developed in Durham.

2.2 LITHIATION OF TTF

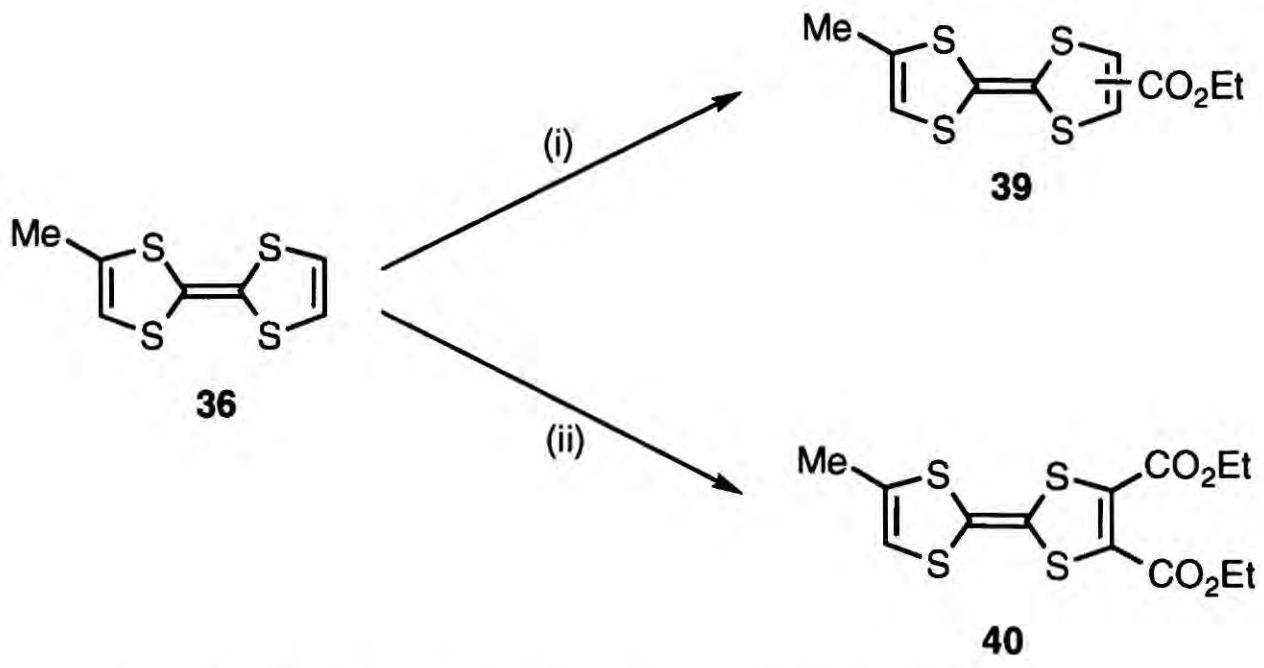
Green first demonstrated that the hydrogen atoms of TTF are sufficiently acidic for metallation to take place (using equimolar amounts of BuLi or LDA),[74] thereby pioneering the chemistry of tetrathiafulvalenyllithium (TTFLi) **31**. This species is stable under nitrogen, at temperatures below -70°C in ether or THF and is highly susceptible to electrophilic attack. The reactivity of anion **31** was investigated by Green, who presented a number of substituted products in reasonable yields (30-80%; Scheme 2.1).[74c]



Scheme 2.1:

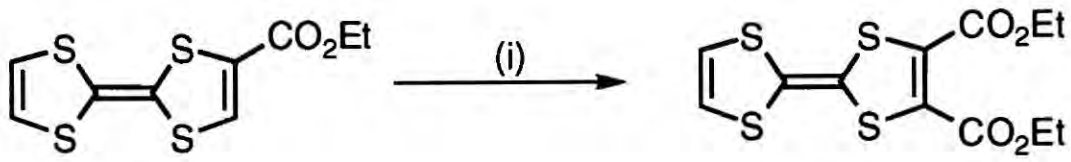
Electrophilic Reagent (E)	Reaction Product	Yield (%)
DMF	TTF-CHO **32**	44
$ClCO_2Et$	TTF-CO_2Et **33**	50
CO_2	TTF-CO_2H **34**	60
MeC(O)Cl	TTF-C(O)Me **35**	67
Me_2SO_4	TTF-Me **36**	80
HCHO	TTF-CH_2OH **37**	34
$Et_3O^+PF_6^-$	TTF-Et **38**	*ca.* 45

Lithiation of substituted TTF derivatives is dependent upon the side-chain substituents.[74c] Green proved that an electron donating component, such as a methyl group, will reduce the acidity of the adjacent hydrogen on the same dithiole ring. Subsequently, metallation, followed by substitution, will take place on the other ring. Using ethylchloroformate as the electrophile, monolithiation of methyltetrathiafulvalene **36** (Scheme 2.2), afforded compound **39** (35%), while dilithiation of **36** with two equivalents of LDA gave compound **40** (30%).



Scheme 2.2: (i) LDA, $ClCO_2Et$ (1 equiv.); (ii) LDA, $ClCO_2Et$ (2 equiv.).

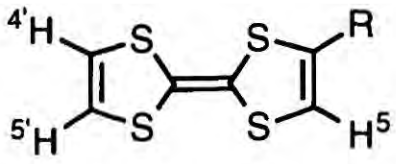
An electron withdrawing substituent will increase the acidity of the adjacent proton. For example, substitution takes place on the same ring when ethylchloroformate is reacted with the lithiated derivative of compound **33**, to give derivative **41** (33%; Scheme 2.3).



33 **41**

Scheme 2.3: (i) LDA (1 equiv.), $ClCO_2Et$.

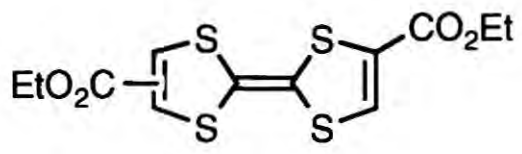
We have used the computer program CAMEO to examine the effect that a range of substituents on the TTF frame has on the pK_a values of the remaining protons. It has been shown previously that there is agreement to within 1-2 pK_a units between calculated and experimental values for protons on unsaturated sites adjacent to sulfur.[75] The calculated data for TTF derivatives are collated in Table 2.1 It can be seen that attachment of an electron withdrawing ester or acyl substituent increases the acidity of the adjacent proton by 3 pK_a units; a bromine atom or a methylthio group has less effect, but, nonetheless, the data for these compounds are consistent with deprotonation being favoured at the adjacent site, giving rise to observed 4,5-disubstituted products. According to CAMEO, however, a methyl substituent on TTF does not change any of the pK_a values of the remaining protons.



R	5-H	4'-H	5'-H
H	48	48	48
Me	48	48	48
CO_2Me	45	48	48
C(O)Me	45	48	48
Br	47	48	48
SMe	47	48	48

Table 2.1: pK_a values of hydrogen atoms in TTF derivatives, calculated using the computer program CAMEO.

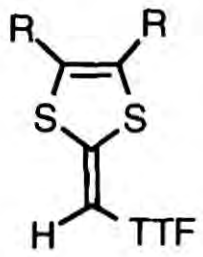
At temperatures above -70°C, TTFLi **31** disproportionates to a mixture of TTF and mono-, di-, tri- and tetra-lithiated TTF species. Even at -78°C, small amounts of multi-substituted products are formed. Green found that addition of two equivalents of LDA at -78°C gave the 4,4'(5')-disubstituted adduct **42** with ethylchloroformate. The 4,5-disubstituted product was not observed.



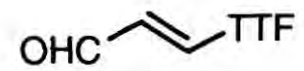
42

The above results indicate the problems that are frequently encountered during the lithiation of TTF. For optimum yields of mono-substituted derivatives one must strictly adhere to certain conditions: the addition of a precise equimolar amount of LDA or BuLi is vital; the reaction temperature must be kept below -70°C under vigorously anhydrous conditions; the concentration of the ethereal solution should also be sufficiently dilute, to prevent precipitation of TTF on cooling to -70°C, which would result in a higher ratio of LDA (or ^{n}BuLi):TTF, leading to multi-substituted products.

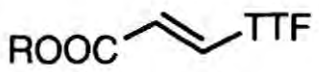
A more profitable route to aldehyde **32**, developed recently in our laboratory, utilises *N*-methylformanilide as the formylating agent, rather than DMF, resulting in a yield of 82%.[76] TTF-carboxaldehyde **32** is highly reactive towards Wittig and Wittig-Horner species; a selection of corresponding derivatives is shown below.



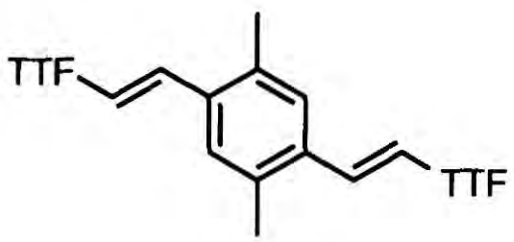
R=H, Me, SMe
R-R=S$(CH_2)_2$S
(60-90%)[77]



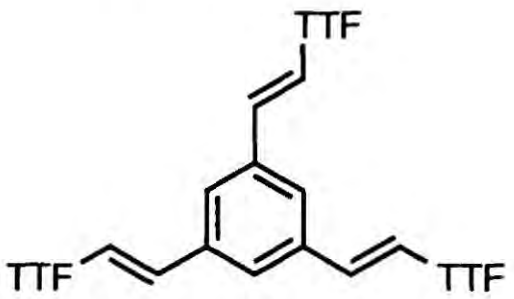
(62%)[76]



R=Me (89%)[76]
R=$C_{16}H_{33}$ (76%)[76]

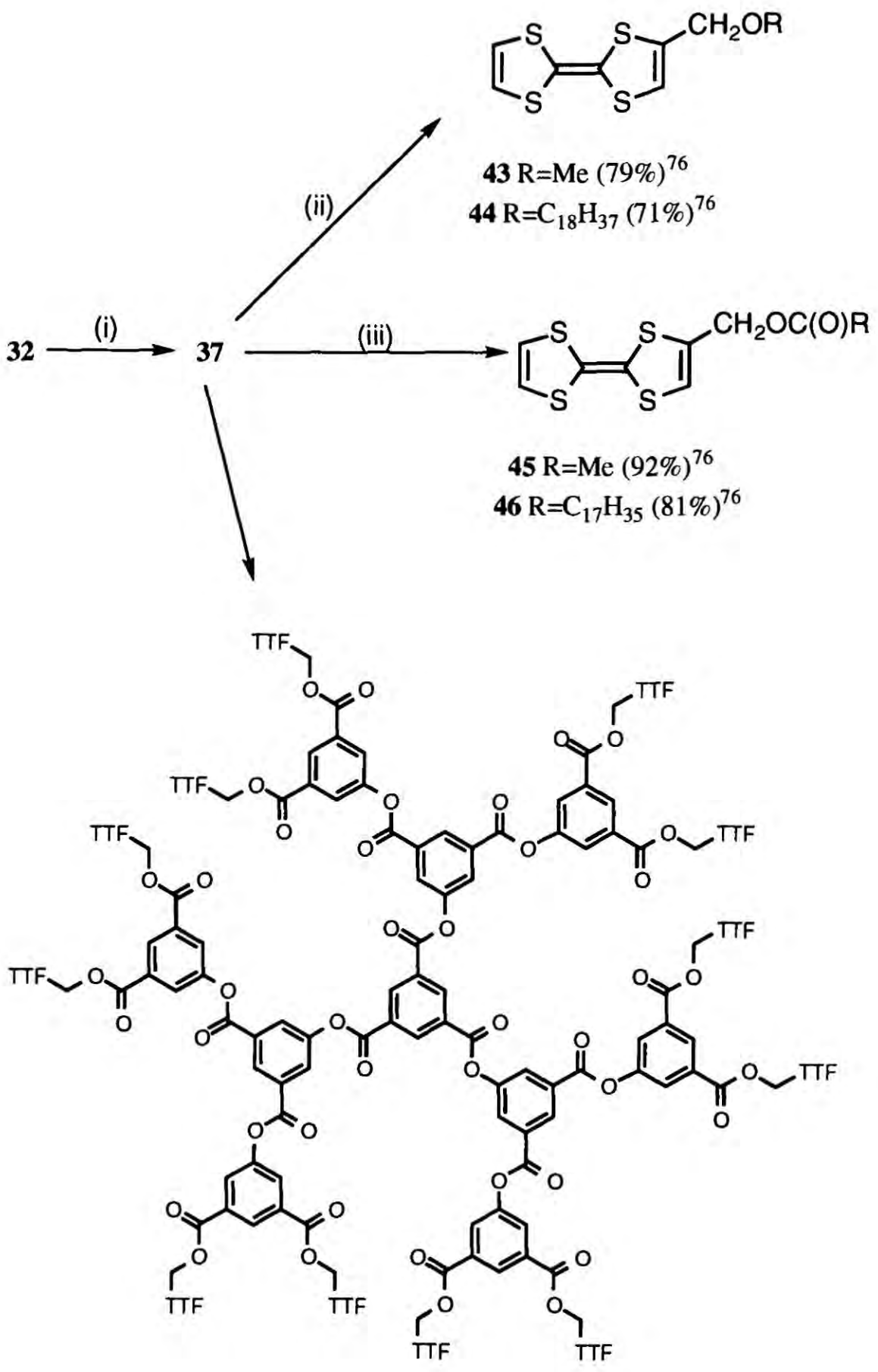


(74%)[78]



(53%)[79]

Reduction of **32** with sodium borohydride affords the versatile tetrathiafulvalenylmethanol **37**, with an overall yield (75%) much higher than Green's one-pot synthesis (34%) involving formaldehyde and TTFLi **31**. As expected compound **37** undergoes classical Williamson syntheses (*e.g.* to yield **43** and **44**),[76] and reacts well with acid chlorides (*e.g.* to yield **45** and **46**).[76] The most elaborate of these ester derivatives, which was synthesised very recently, is the third generation dendrimer **47**, containing 12 TTF units (Scheme 2.4).[80]



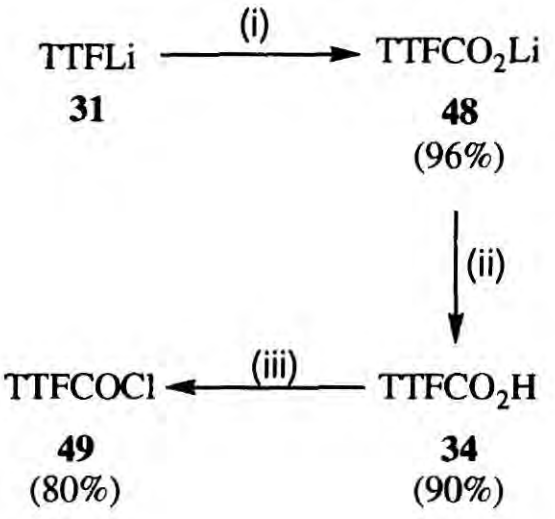
43 R=Me (79%)[76]
44 R=$C_{18}H_{37}$ (71%)[76]

45 R=Me (92%)[76]
46 R=$C_{17}H_{35}$ (81%)[76]

47 (32%)[80]

Scheme 2.4: (i) $NaBH_4$, IPA, EtOH; (ii) NaH, PhMe, RI; (iii) RC(O)Cl, NEt_3.

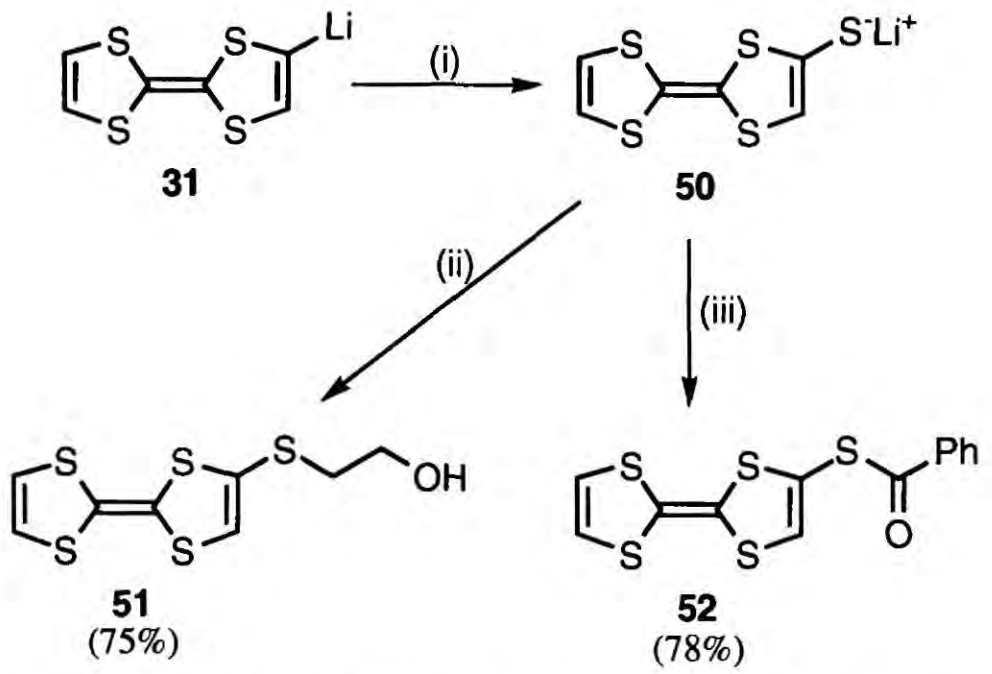
An improvement in the yield of TTF-carboxylic acid **34** (86% from **31** on a multi-gram scale), has also been achieved recently by isolating the lithium carboxylate salt **48**.[76] Acid chloride **49** is thus now available as another reactive TTF building block[81] (Scheme 2.5).



Scheme 2.5: (i) CO_2; (ii) aq. HCl; (iii) oxalyl chloride, PhMe, MeCN, DMF.

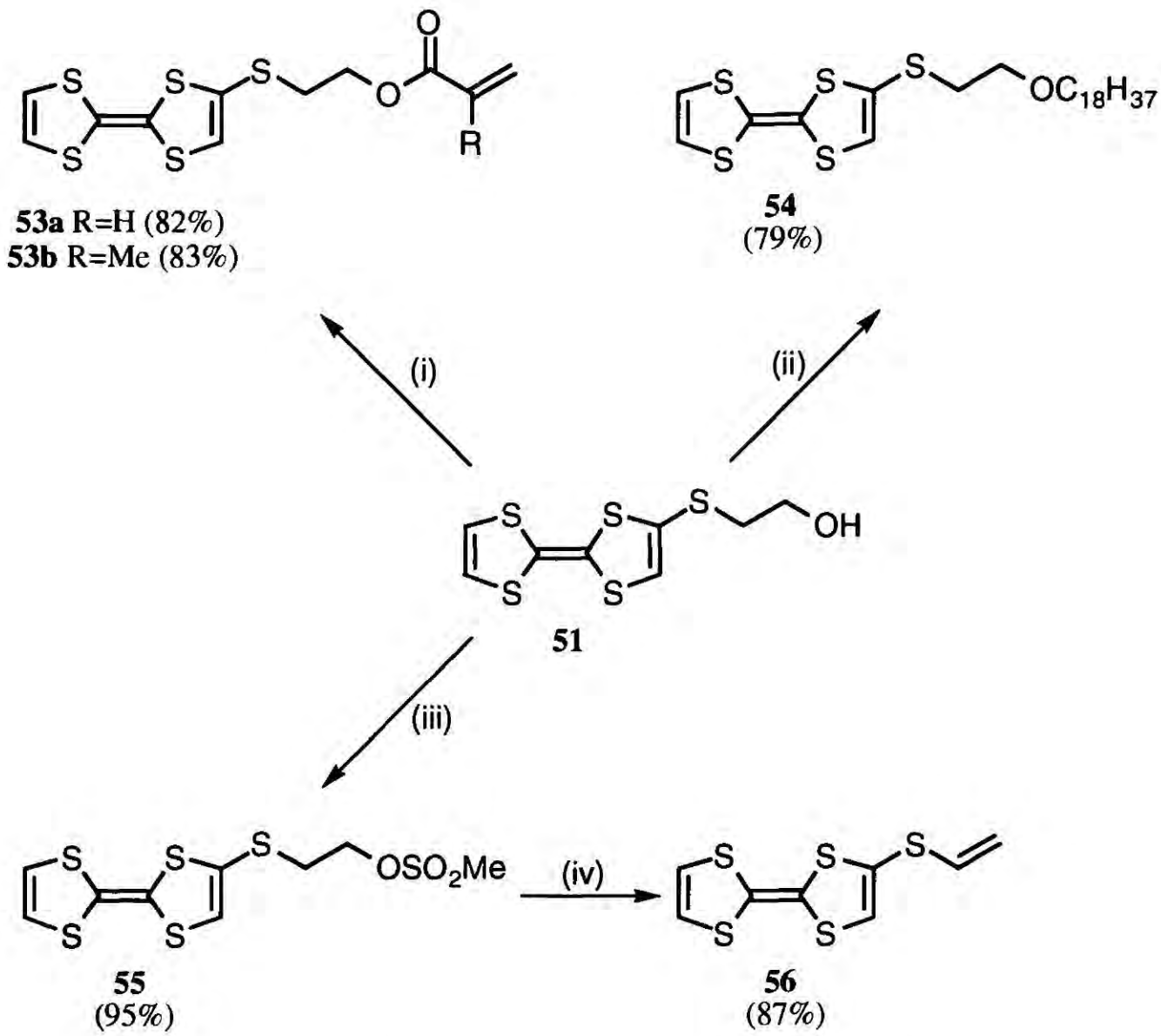
2.3 CHALCOGENATION OF TTF

The insertion of sulfur into TTFLi **31** affords TTF-thiolate **50**, which is a more reactive species than **31**. Indeed, the thiolate anion **50** reacts with alkyl halides (whereas **31** does not): alkylation and acylation of **50** yield **51** and **52**, respectively[82] (Scheme 2.6), both of which are synthetically versatile TTF derivatives[83-85] (see Scheme 2.7 for reactions of **51**). It is noteworthy that **51** is an analogue of **37**.



Scheme 2.6: (i) Elemental sulfur, -78°C, 8h; (ii) bromoethanol; (iii) benzoyl chloride.

Compound **51**, generated from **50** and bromoethanol, is a synthetic analogue to alcohol **37**, but can be prepared in identical yield by a one-pot reaction. Again, the reactivity of this alcohol has been extensively explored; preliminary examples are shown in Scheme 2.7.



53a R=H (82%)
53b R=Me (83%)

54
(79%)

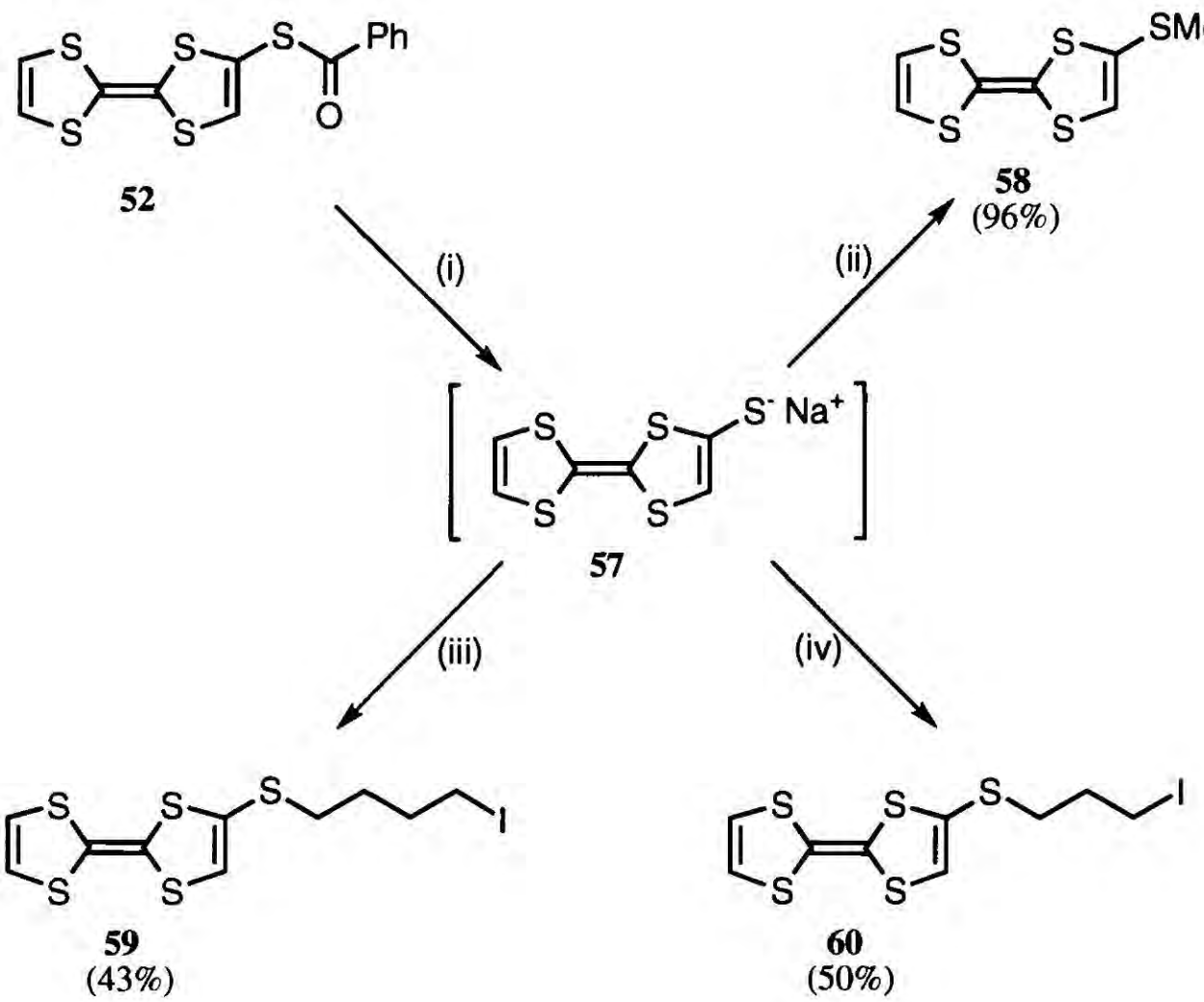
51

55
(95%)

56
(87%)

Scheme 2.7: (i) $CH_2CRC(O)Cl$, NEt_3, dioxane, 20°C, 2h;
(ii) Na, PhMe, $C_{18}H_{37}I$, 20°C; (iii) $MeSO_2Cl$, NEt_3, dioxane, 20°C, 2h;
(iv) NaOEt, EtOH, 20°C, 10h.

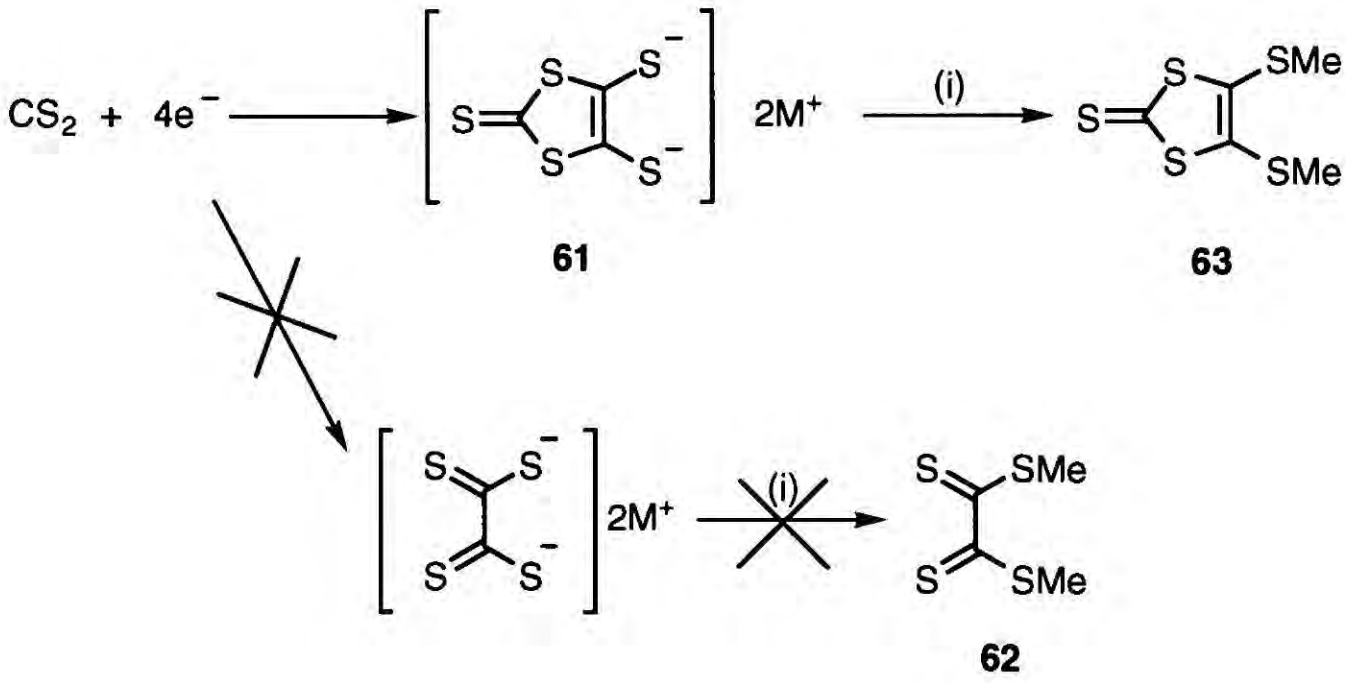
Thioester **52** is an important compound as upon the addition of sodium ethoxide in ethanol at -10°C, derivative **52** can be deprotected to the sodium salt of TTF-thiolate **57**. Compound **52**, therefore, serves as a shelf stable equivalent of TTF-thiolate **50**; examples of its synthetic use are the syntheses of molecules **58-60**[84] shown in Scheme 2.8.



Scheme 2.8: (i) NaOEt, EtOH, -10°C, 1h; (ii) MeI; (iii) $I(CH_2)_4I$; (iv) $I(CH_2)_3I$.

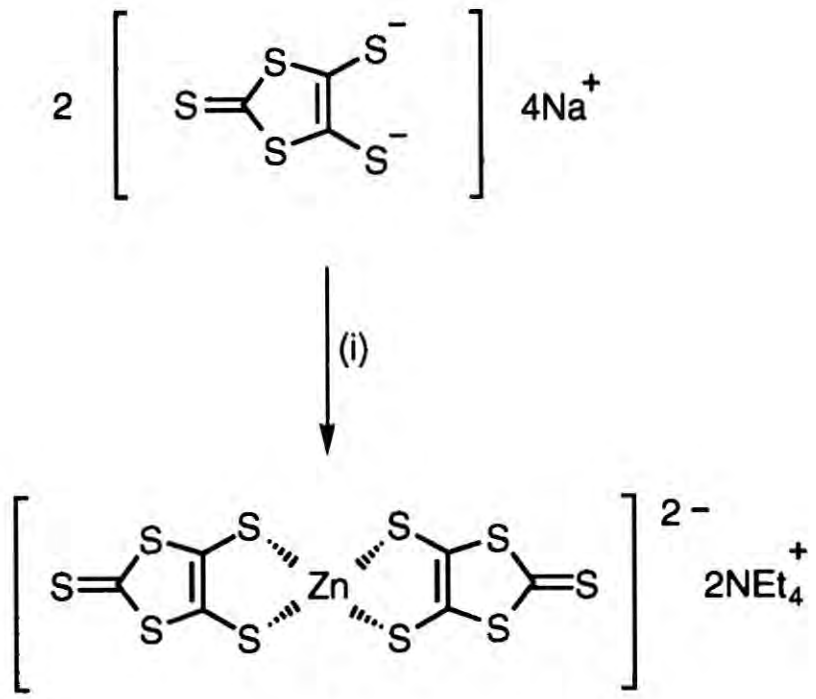
2.4 USE OF THE ZINCATE COMPLEX FOR THE SYNTHESIS OF FUNCTIONALISED TTF DERIVATIVES

In 1927, Fetkenheuer examined the chemical reduction of carbon disulfide by sodium metal.[86] The major product, trapped by alkylation with methylchloride, was assigned as dimethyl tetrathioxalate **62**. The precedence for this conclusion arose from direct comparison of the analogous reaction performed by Kolbe[87] in 1868: using carbon dioxide and sodium metal, Kolbe synthesised oxalic acid *via* its oxalate intermediate. It was not until 1974 that Wawzonek *et al.*,[88] using an electrochemical reduction, correctly identified the product as 4,5-di(methylthio)-1,3-dithiole-2-thione **63** (Scheme 2.9).



Scheme 2.9: (i) MeCl.

Dithiolate intermediate **61** was subsequently isolated by Steimecke *et al.*,[89] as the zincate complex **64** (70% yield; Scheme 2.10). Complex **64** is a shelf stable source of dithiolate **61**.



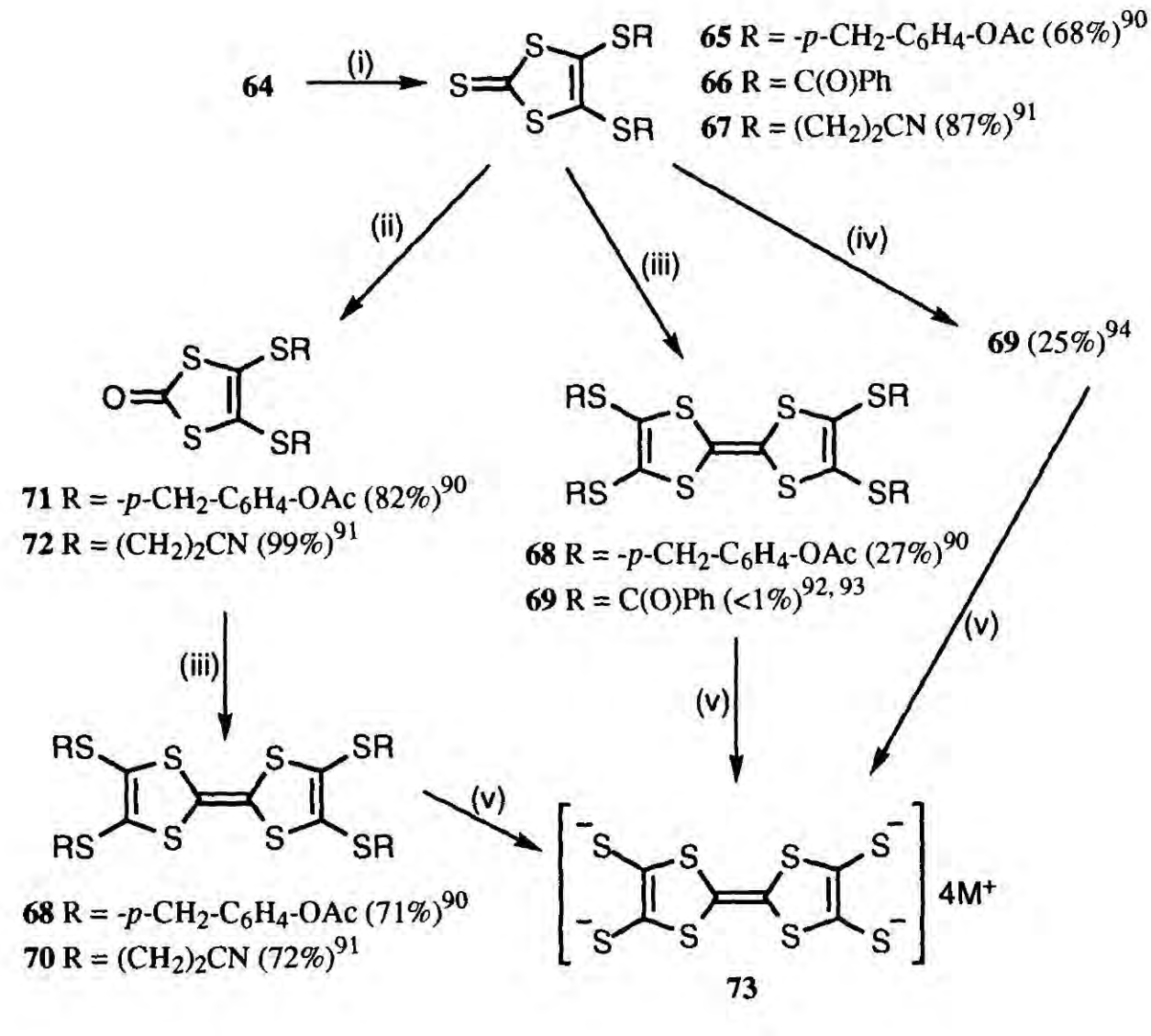
64

Scheme 2.10: (i) $ZnCl_2$, NEt_4Br.

Zincate complex **64** can be alkylated or acylated to give, for example, compounds **65-67**. Coupling of the thione species can be performed by using alkyl phosphites or dicobalt octacarbonyl, at *ca.* 60°C (Scheme 2.11). The choice of coupling reagent depends upon the thioalkyl substituents, and yields can vary from zero to *ca.* 80%. Thione **66** couples in the presence of triethyl phosphite to give TTF derivative **69**, but only in a yield less than 1%, whereas the use of $Co_2(CO)_8$ gives the same product in 25% yield.

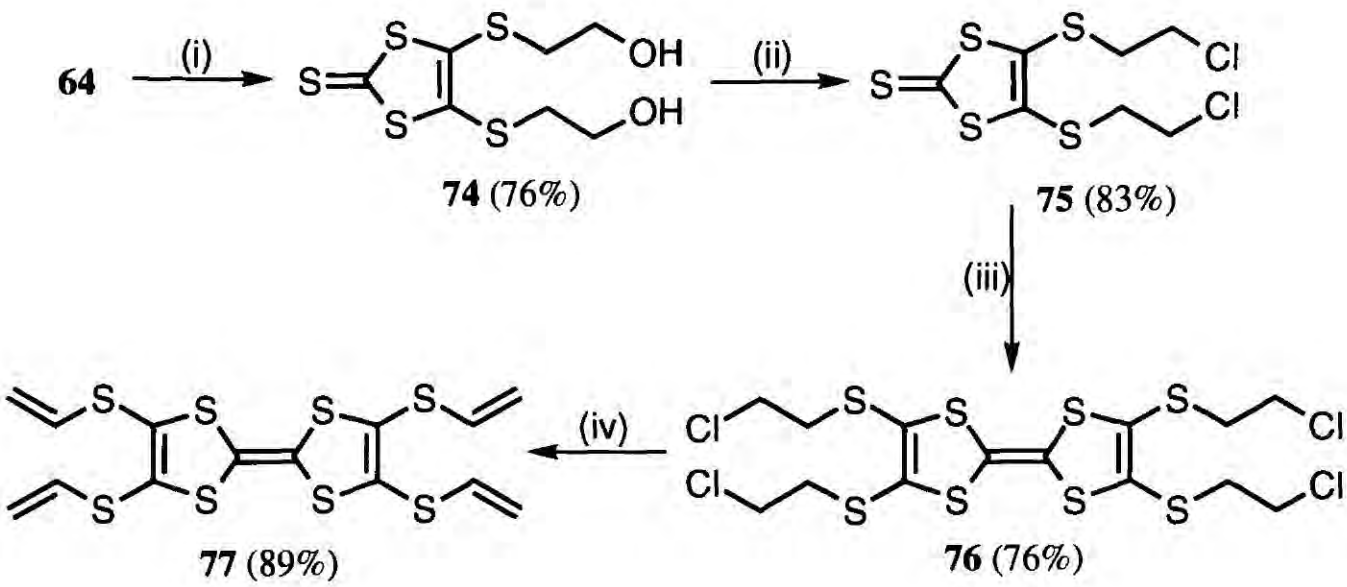
Transformation of the thione functionality to a ketone, using mercuric acetate, may lead to a more reactive dithiole species. Thiones **65** and **67** have been converted to ketones **71** and **72** in excellent yields (82% and 99%, respectively). Coupling of dithiole **72** with $P(OEt)_3$ gives compound **70** in 72% yield. A similar result is seen with ketone **71** (giving derivative **68** in 71% yield), whereas thione analogue **65** gives **68** in only 27% yield.

Deprotection of TTF derivatives **68-70** under basic conditions, affords the highly reactive tetrathiolate-TTF species **73**. Although the same intermediate can be generated directly from TTF, at -78°C, with four equivalents of LDA and elemental sulfur (tetraselenolate and tetratellurolate can also be prepared with elemental selenium and tellurium, respectively),[95] the longer route is much more economical and can be carried out easily in multigram quantities.



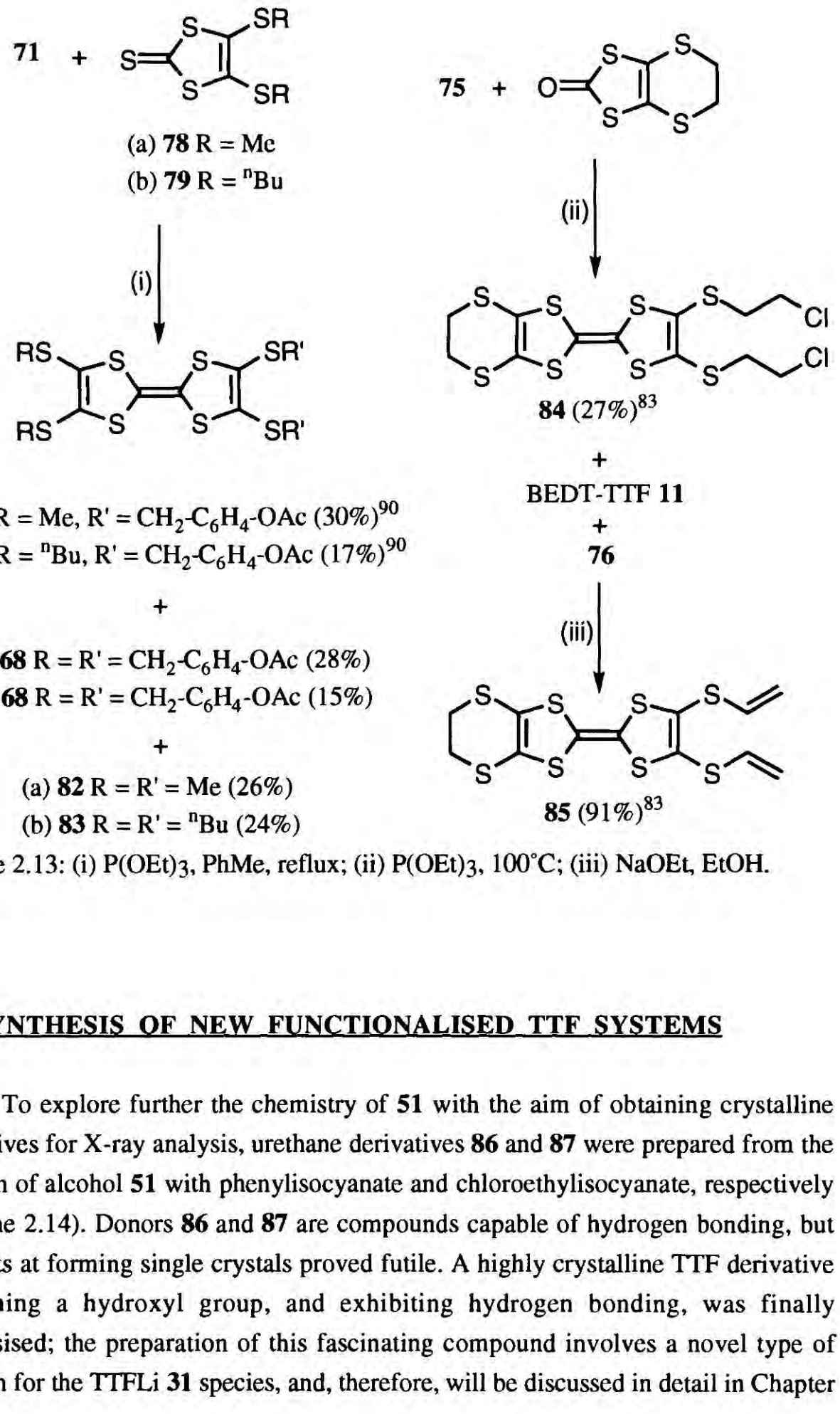
Scheme 2.11: (i) RX, MeCN or $Me_2C(O)$; (ii) $Hg(OAc)_2$; (iii) $P(OEt)_3$; (iv) $Co_2(CO)_8$; (v) Base.

Other functionalised TTF systems derived from coupling reactions include compounds **76** and **77** (Scheme 2.12).[83] The coupling of thione **74**, however, does not take place; this is a common feature for other alcohol containing dithiole units.



Scheme 2.12: (i) $Br(CH_2)_2OH$, $Me_2C(O)$, reflux, 10 h; (ii) $SOCl_2$, DCM, 0°C, 0.5 h, then reflux; (iii) $P(OEt)_3$; (iv) NaOEt, EtOH, 20°C, 10 h.

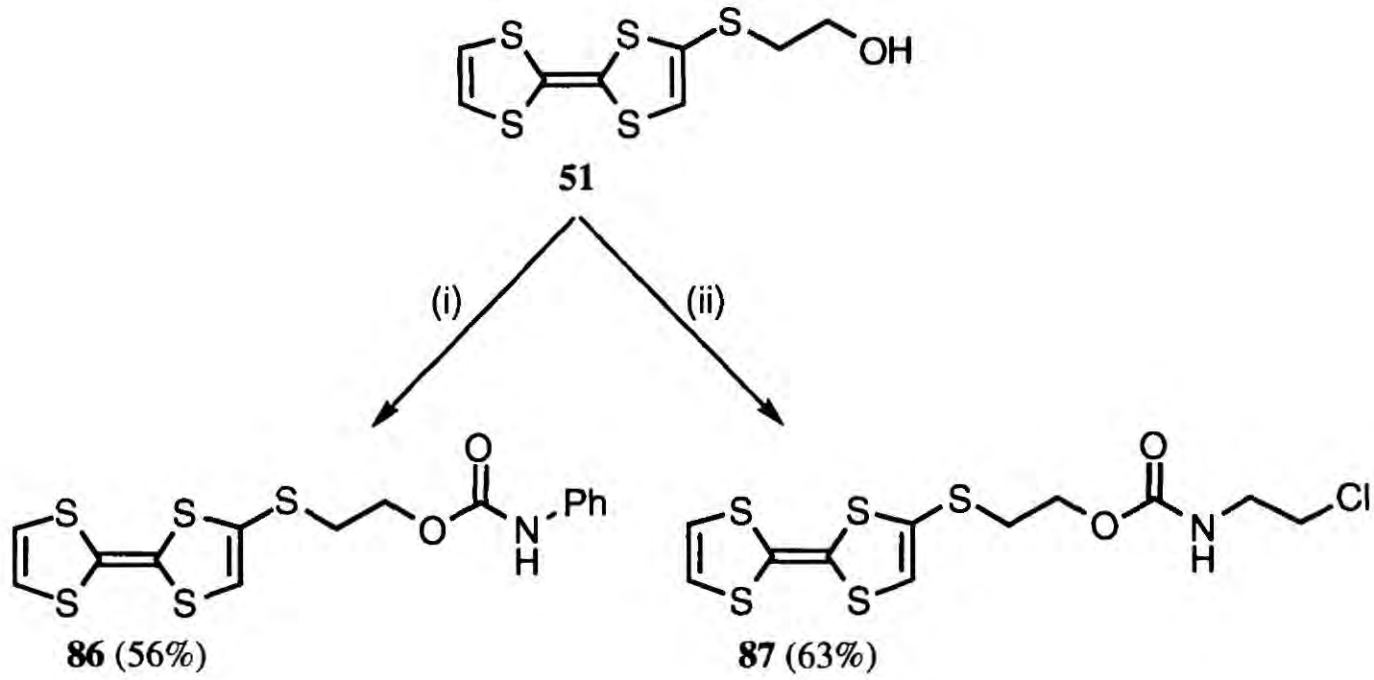
Unsymmetrical, functionalised TTF derivatives are more difficult to obtain by the cross-coupling of two different thione (or ketone) dithiole species. Due to inevitable self-coupling reactions competing with cross-coupling, separation of the desired product is often a demanding task. Relevant examples of cross-coupling are shown in Scheme 2.13. Compared to the self-coupling reactions seen in Scheme 2.11, the yields of the cross-coupled products, **80**, **81** and **84**, are greatly reduced.[83,90] The component ratios of the resulting mixtures are also variable, and are dependent upon the thioalkyl substituents.



Scheme 2.13: (i) $P(OEt)_3$, PhMe, reflux; (ii) $P(OEt)_3$, 100°C; (iii) NaOEt, EtOH.

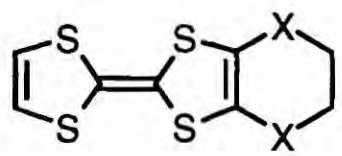
2.5 SYNTHESIS OF NEW FUNCTIONALISED TTF SYSTEMS

To explore further the chemistry of **51** with the aim of obtaining crystalline derivatives for X-ray analysis, urethane derivatives **86** and **87** were prepared from the reaction of alcohol **51** with phenylisocyanate and chloroethylisocyanate, respectively (Scheme 2.14). Donors **86** and **87** are compounds capable of hydrogen bonding, but attempts at forming single crystals proved futile. A highly crystalline TTF derivative containing a hydroxyl group, and exhibiting hydrogen bonding, was finally synthesised; the preparation of this fascinating compound involves a novel type of reaction for the TTFLi **31** species, and, therefore, will be discussed in detail in Chapter 5.

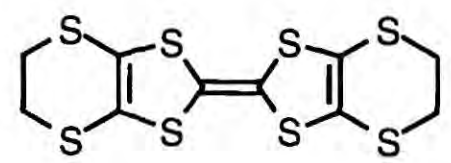


Scheme 2.14: (i) PhNCO, NEt_3, DCM, 20°C; (ii) $Cl(CH_2)_2NCO$, NEt_3, DCM, 20°C.

The reactions of TTF anion **31**, with elemental sulfur or selenium (1.5 equivalents), followed by the addition of 1,2-dibromoethane (0.5 equivalents) formed the known donors EDT-TTF **88** and EDS-TTF **89**, respectively, in optimised yields of 10-20%.[85] Varying the molar ratios of either LDA, sulfur or dibromoethane, did not improve the yield of EDT-TTF **88**. For instance, the molar ratio of 1:1:2:1 for TTF, LDA, S_8 and dibromoethane gave no EDT-TTF **88**; a mixture of unreacted TTF and BEDT-TTF **11** was obtained instead.



88 X = S (EDT-TTF)
89 X = Se (EDS-TTF)

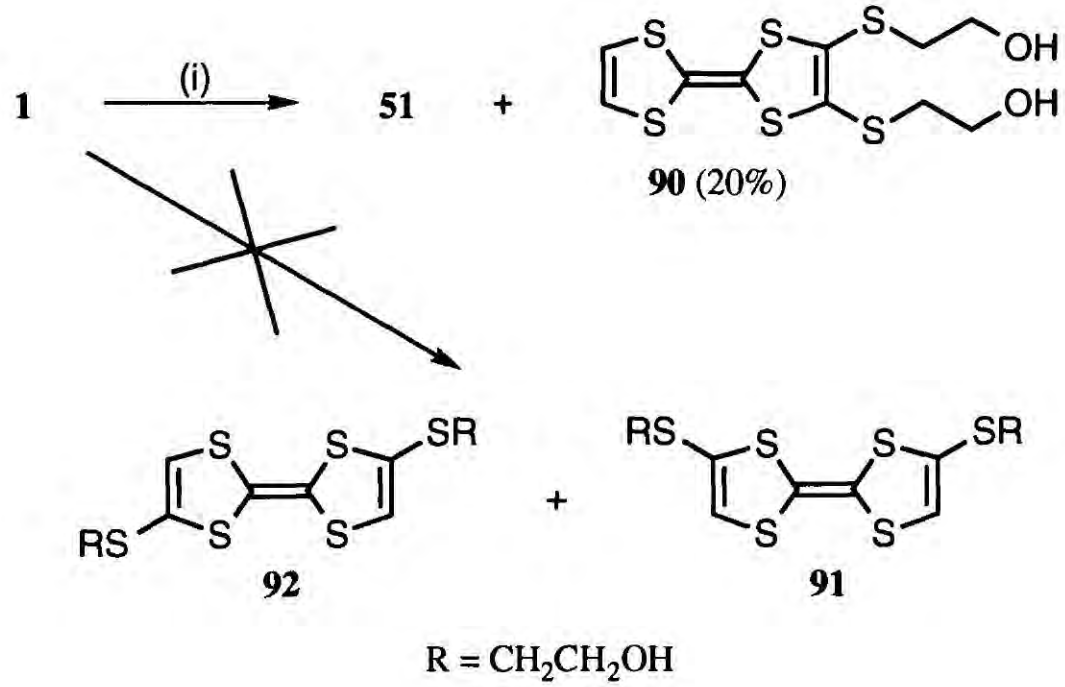


11 BEDT-TTF

Evidently, a new one-pot route to the unsymmetrical donors **88** and **89** has been recognised, and although the yield is only modest, it is considerably shorter than the previous method involving phosphite-mediated cross-coupling of the two 1,3-dithiole half units.[96]

On route to alcohol **51**, a new minor product **90** was isolated and by varying the ratios of the reactants an optimum yield of 20% was obtained (Scheme 2.15).

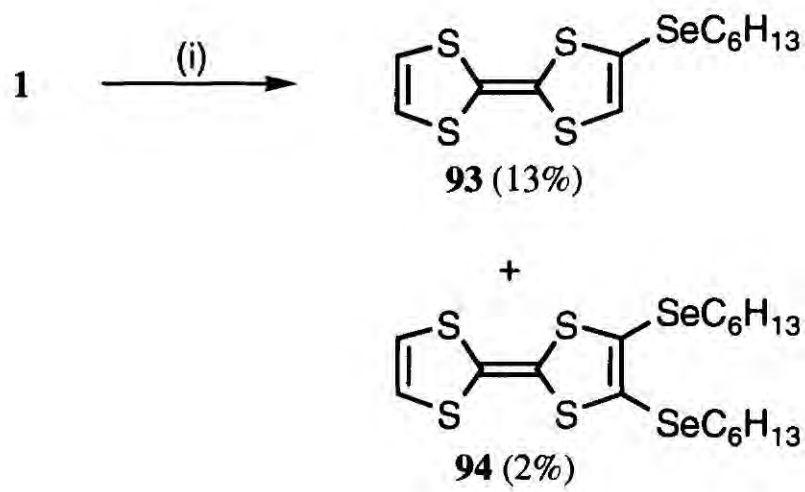
Surprisingly, regioisometric disubstituted products **91** and **92** were not detected in the reaction mixture (TLC and ^{1}H NMR spectroscopic evidence).



Scheme 2.15: (i) LDA, sulfur, bromoethanol (1:3:10, relative to TTF), Et_2O, -78°C.

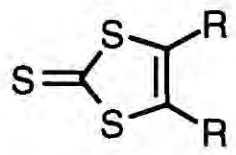
The structure of **90** as the 4,5-isomer was inferred from the ^{1}H NMR spectrum, which showed a singlet for the two TTF protons at δ6.35, whereas the TTF proton adjacent to the pendant group on alcohol **51** is shifted downfield to *ca.* δ6.45. Further evidence for structure **90** was provided by ^{13}C NMR data: inequivalence of the central alkene carbon atoms of the TTF frame is unique to the 4,5-isomer; they are observed at δ_c116.9 and δ_c104.5.

The disubstituted by-product obtained during the formation of hexylseleno-TTF **93**, was likewise assigned structure **94** (Scheme 2.16). The mass spectroscopic fragmentation pattern of compounds **90** and **94** was also consistent with the two substituents being on the same 1,3-dithiole ring.

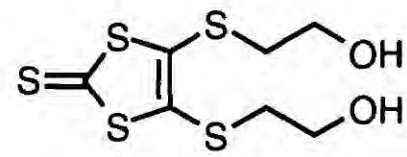


Scheme 2.16: (i) LDA, selenium, hexyltosylate, -78°C, Et_2O.

We recognised the potential of dialcohol **90** as a building block for new disubstituted TTF systems, and, therefore, sought conclusive proof of its structure from an unambiguous synthesis. As previously mentioned (Section 2.4), phosphite or dicobalt octacarbonyl coupling does not proceed with hydroxyl-containing species, *e.g.* **74**, so direct reaction of **95a** with **74** was futile. Several protected forms of compound **74** were therefore investigated.

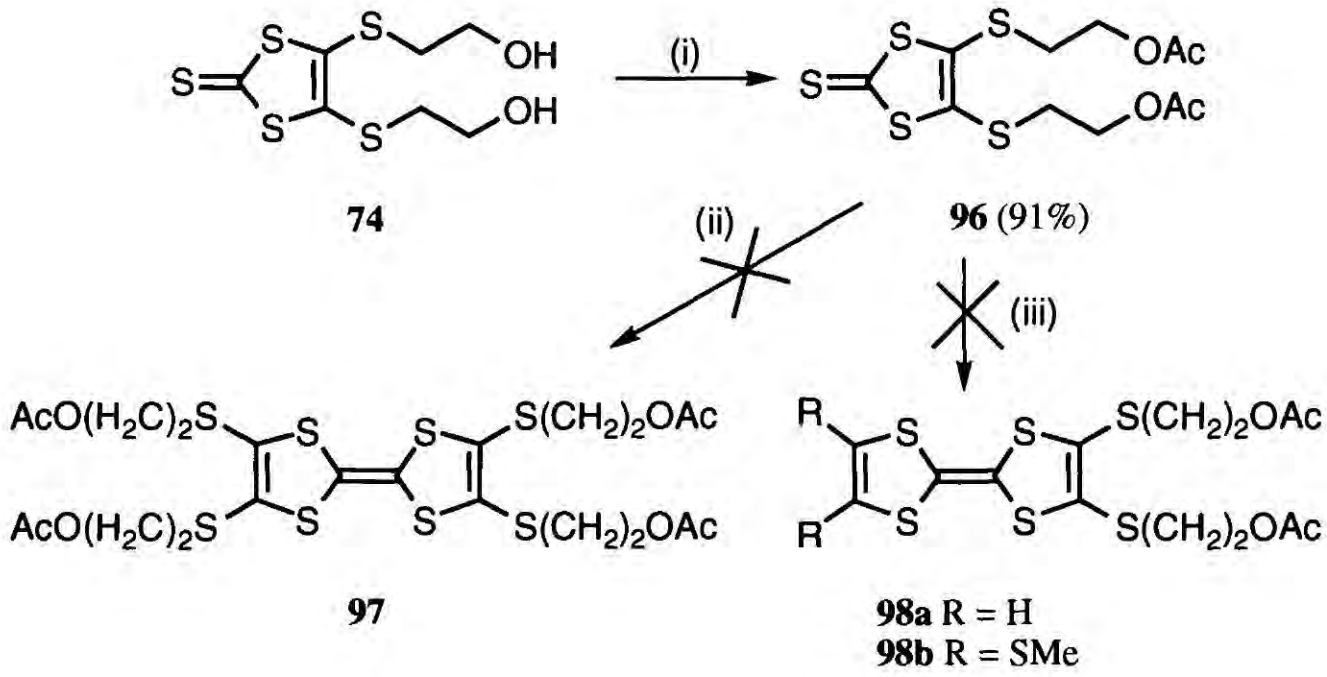


95a R = H
95b R = SMe



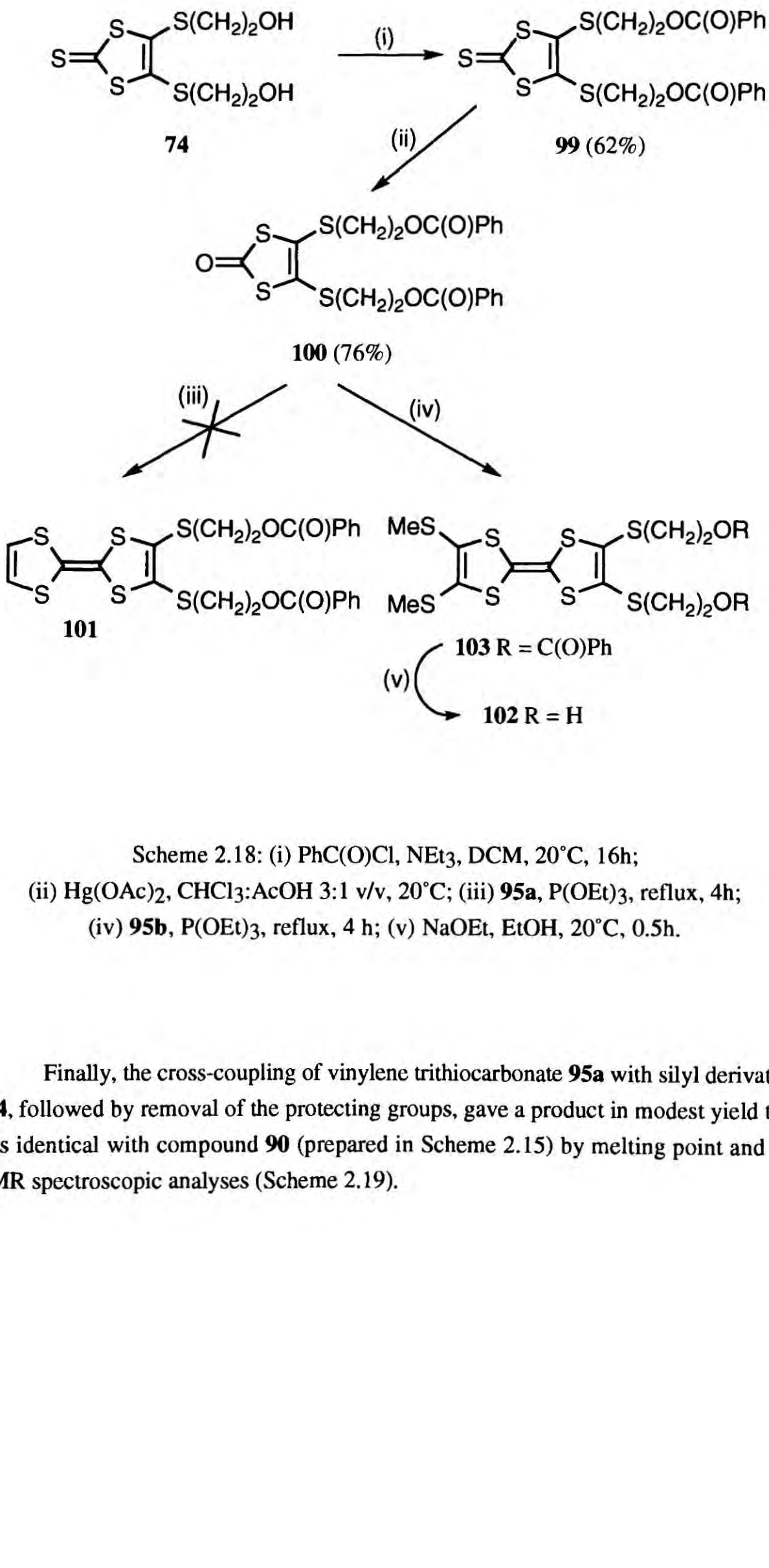
74

Diester **96** was prepared by the reaction of diol **74** with acetyl chloride. Coupling of **96** with triethyl phosphite failed to produce tetraester **97**, and, together with thiones **95a** or **95b**, the related cross-coupled diesters **98a** and **98b** were not obtained (Scheme 2.17).



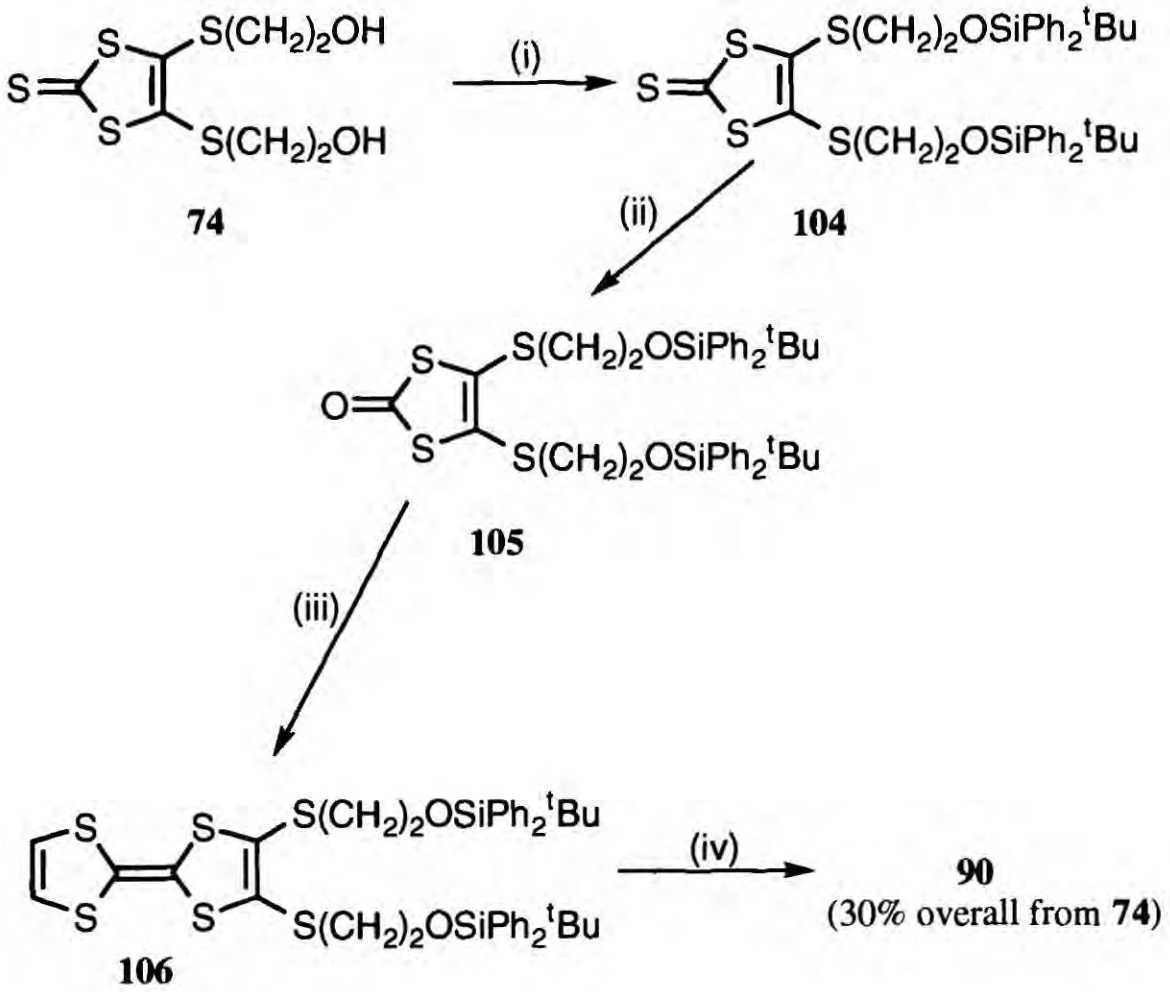
Scheme 2.17: (i) AcCl, DCM, NEt_3, 16h; (ii) $P(OEt)_3$, reflux, 45min., (iii) **95a** or **95b**, $P(OEt)_3$, reflux, 45min.

Attempts were made using $Co_2(CO)_8$ as the coupling reagent, but again the desired targets **97**, **98a** and **98b** were not achieved. This problem was overcome, however, by the use of the corresponding benzoyl ester **99** which was synthesised from **74** and benzoyl chloride (Scheme 2.18). Phosphite cross-coupling with vinylene trithiocarbonate **95a** and ketone **100** failed to produce TTF-derivative **101**. Diol **102**, however, was obtained from the hydrolysis of diester **103**: the latter being synthesised from the phosphite-mediated cross-coupling of **95b** and ketone **100** (15% yield).



Scheme 2.18: (i) $PhC(O)Cl$, NEt_3, DCM, 20°C, 16h;
(ii) $Hg(OAc)_2$, $CHCl_3$:AcOH 3:1 v/v, 20°C; (iii) **95a**, $P(OEt)_3$, reflux, 4h;
(iv) **95b**, $P(OEt)_3$, reflux, 4 h; (v) NaOEt, EtOH, 20°C, 0.5h.

Finally, the cross-coupling of vinylene trithiocarbonate **95a** with silyl derivative **104**, followed by removal of the protecting groups, gave a product in modest yield that was identical with compound **90** (prepared in Scheme 2.15) by melting point and ^1H NMR spectroscopic analyses (Scheme 2.19).



Scheme 2.19: (i) TBDPSiCl, DMF, imidazole, 20°C 16h; (ii) $Hg(OAc)_2$, $CHCl_3$:AcOH 1:3 v/v, 20°C; (iii) **95a**, $P(OEt)_3$, 60°C, 16h; (iv) Bu_4NF, THF, 20°C.

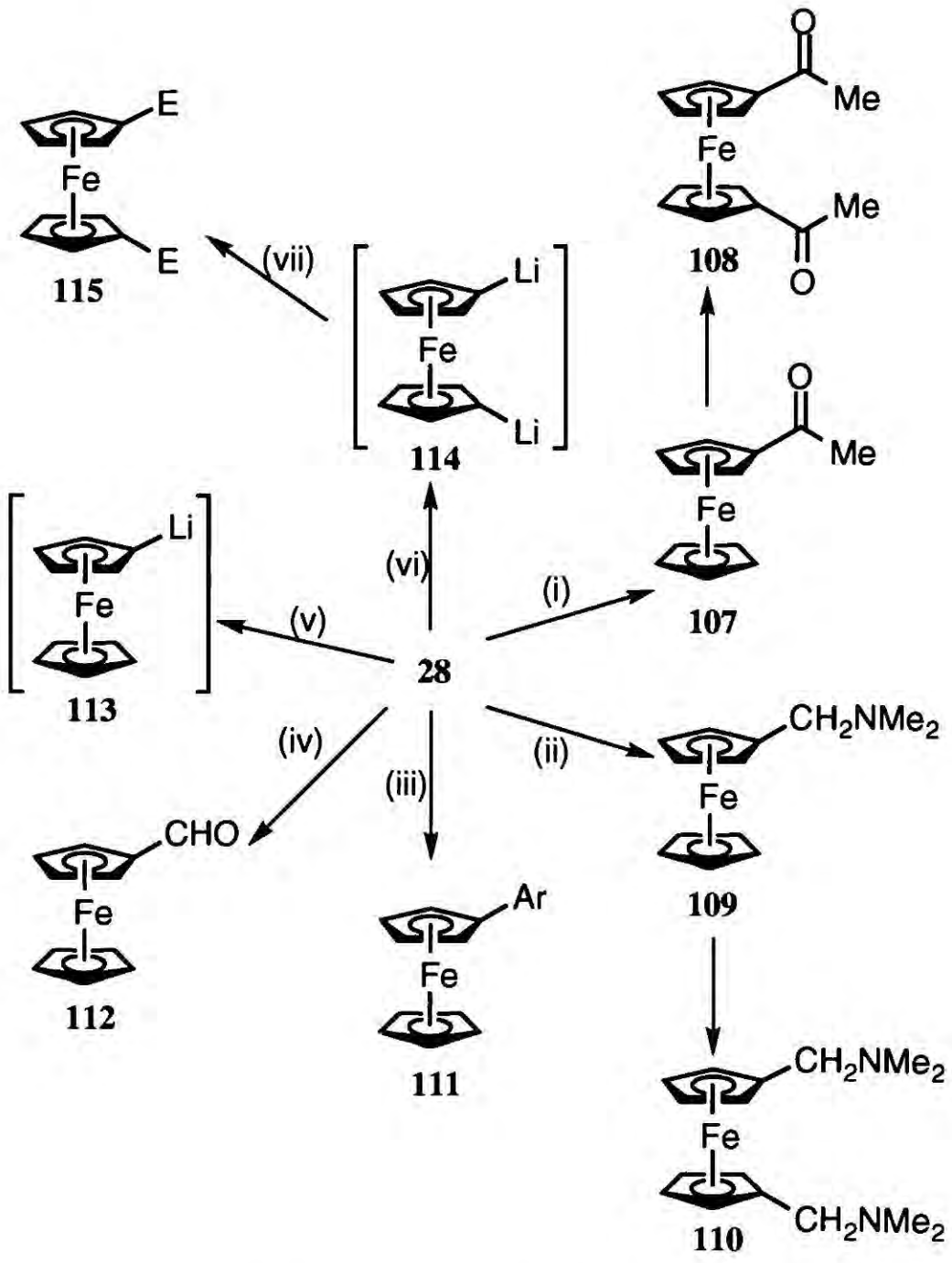
The mechanism for the formation of the disubstituted products **88-90** and **94** directly from TTF is unclear. Disproportionation of TTFLi **31** may occur to yield transient dianion species, however, Green stated[74] that 4,4'(5')-disubstituted products should predominate. An alternative, and perhaps more likely mechanism does not involve dianion species, but, instead, alkylation of thiolate **50** (and its selenolate analogue) occurs prior to the second deprotonation and chalcogenation of the TTF system. The directing influence of an alkylthio- or alkylseleno-substituent on further substitution onto the TTF ring has not been investigated previously, although Becker *et al.* assigned a different substitution pattern, namely the 4,4'- or 4,5'-regioisomer, to a bis(ethyltelluro)TTF derivative.[95a]

From the CAMEO results presented in Table 2.1, methylthioTTF would favour a second substitution at the 5-position (*i.e.* on the same ring). Further studies with the CAMEO program gave similar predictions for ethylthioTTF and TTF-alcohol **51** (pK_a values: 5-H = 47, 4'-H = 48, and 5'-H = 48, in both cases). The formation of the 4,5-disubstituted compounds **88-90** and **94** is, therefore, consistent with these results. It is

also likely that lithium coordination to the mono-chalcogenated species plays a role in directing the second metallation to the adjacent site.

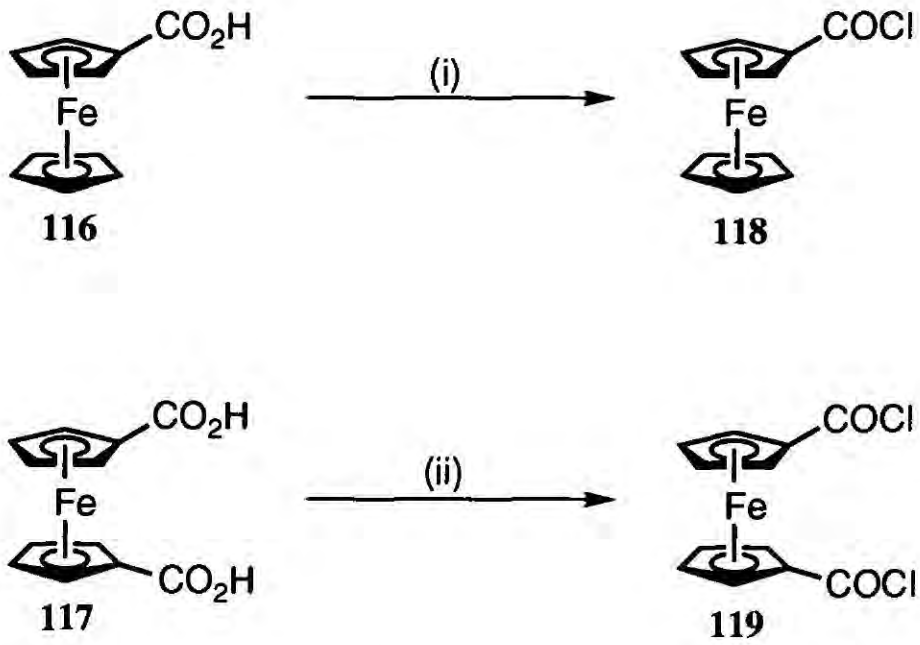
2.6 COVALENTLY LINKED TTF-FERROCENE SYSTEMS

The first synthesis of ferrocene **28** was reported in 1951 by two independent groups: Kealey and Pauson,[97] and Miller, Tebboth and Tremaine.[98] It was discovered soon after that this fascinating stable complex could undergo classical organic reactions typical of aromatic species. With a reactivity greater than that of benzene, and more akin to toluene, ferrocene **28** is able to perform, for example, standard Friedel-Crafts and Mannich reactions, electrophilic substitution, Vilsmeier formylation and metallation (Scheme 2.20).



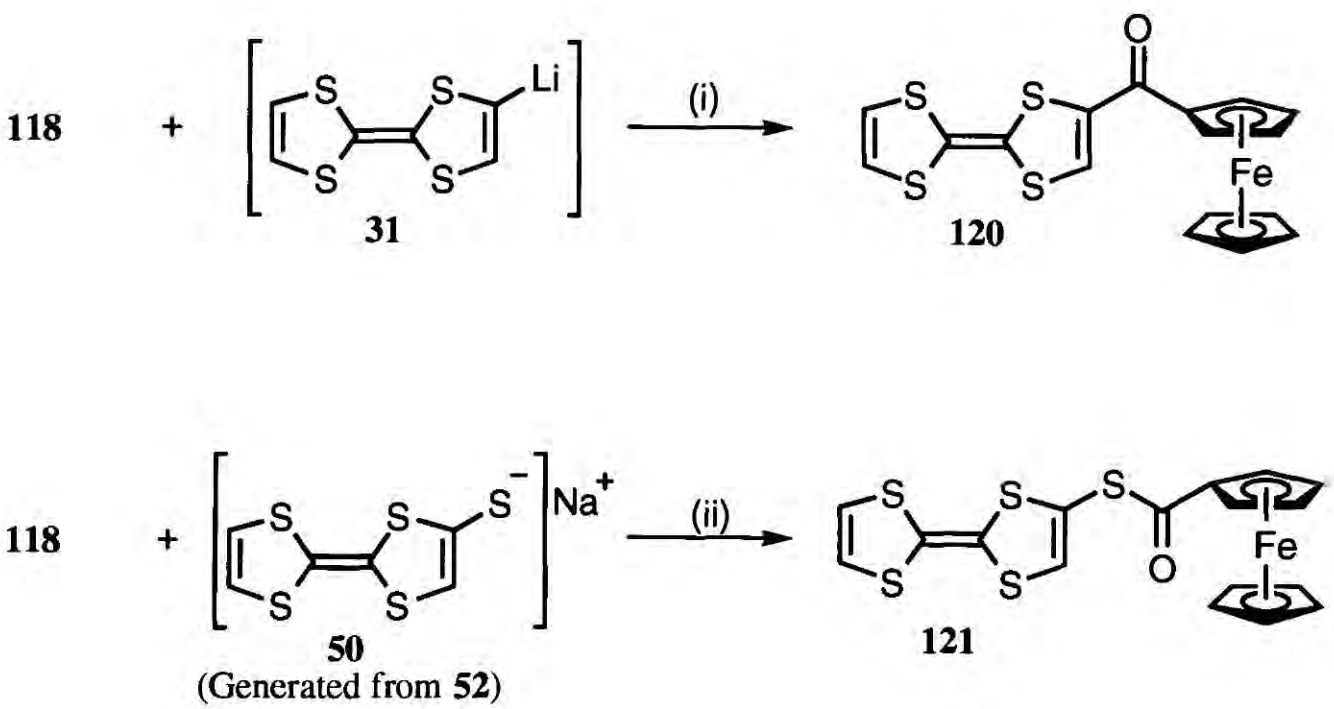
Scheme 2.20: (i) Ac_2O, BF_3;[99] (ii) $Me_2NCH_2CH_2NMe_2$, H_3PO_4, AcOH;[100] (iii) ArN_2^+; (iv) DMF, $POCl_3$;[99] (v) ^tBuLi; (vi) BuLi, TMEDA (or PMDT);[101] (vii) electrophile (E^+).

Our first attempts to synthesise covalently linked TTF-ferrocene systems involved the preparation of ferrocenylacyl chlorides **118** and **119** from commercially available ferrocenyl mono- and di-carboxylic acids **116** and **117**, respectively (Scheme 2.21).



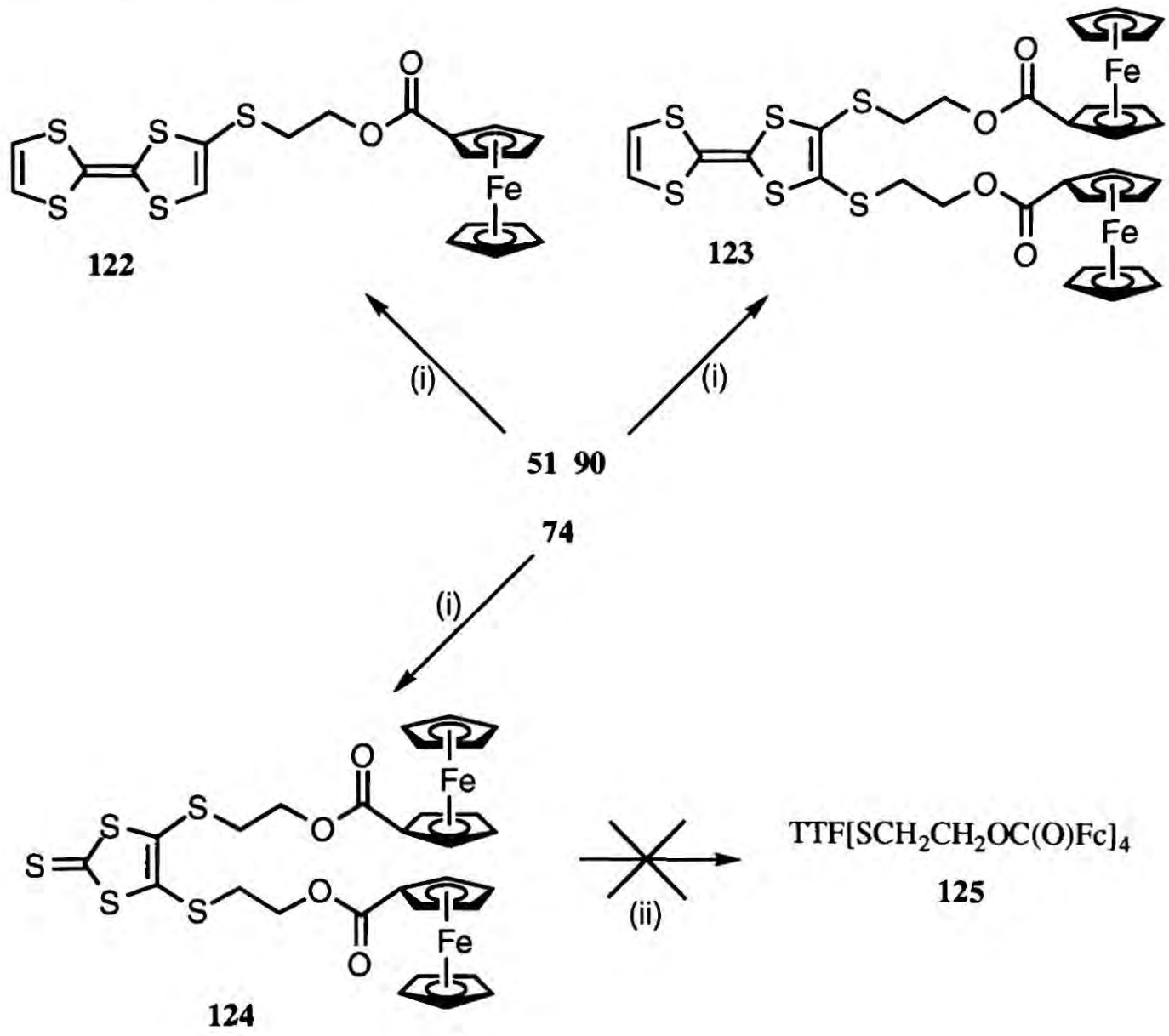
Scheme 2.21: (i) PCl_5, PhMe;[102] (ii) oxalyl chloride, pyridine, DCM.[103]

Acyl chloride **118** was reacted with TTFLi **31**, and also with TTF-thiolate **50** (*via* benzoyl derivative **52**), to give ketone **120** and thioester **121** (12% and 27%, respectively; Scheme 2.22).



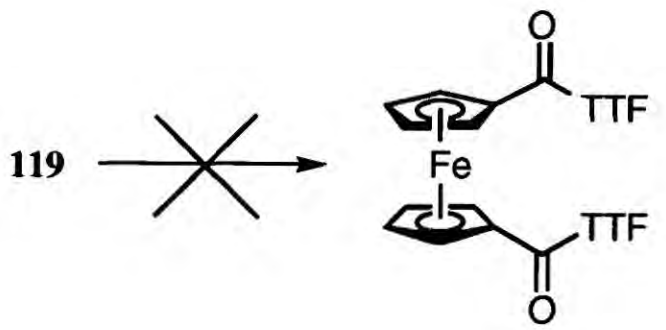
Scheme 2.22: (i) -78°C, Et_2O; (ii) -10°C, EtOH.

Monosubstituted acid chloride **118** was reacted with TTF alcohols **51** and **90**, and also with thione **74**, to form esters **122-124** (80%, 60% and 64%, respectively; Scheme 2.23). Unfortunately, the attempted coupling of half-unit **124** with phosphite or dicobaltoctacarbonyl did not furnish the expected tetraester **125**; an intractable mixture was obtained.



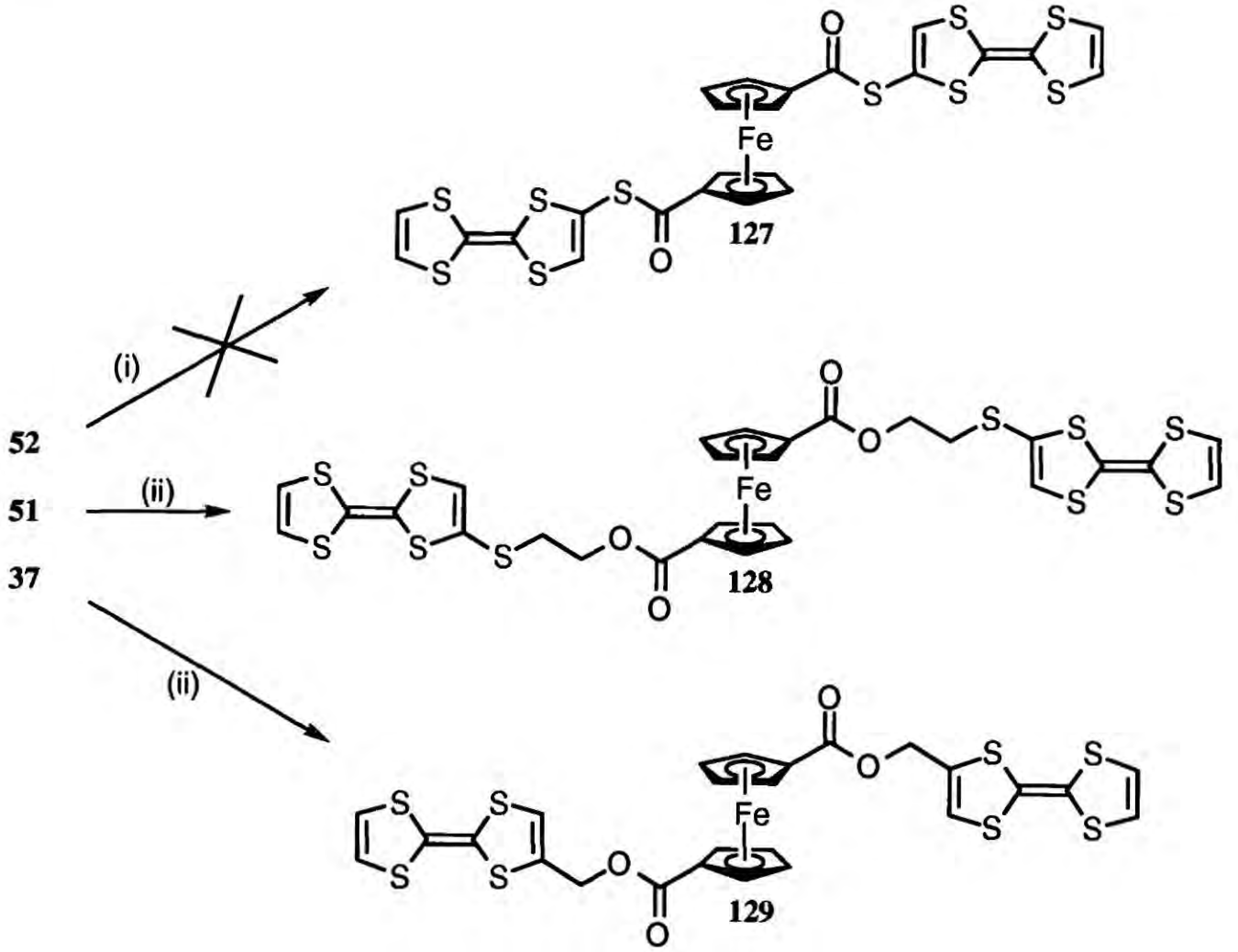
Scheme 2.23: (i) FcC(O)Cl **118**, NEt_3, DCM; (ii) $POEt_3$ or $Co_2(CO)_8$.

Given the low yield of **120** (Scheme 2.22), the synthesis of 1,1'-bis(TTF-carboxy)ferrocene **126** (from acyl chloride **119** and TTFLi **31**) was abandoned.



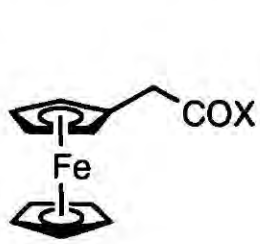
126

Reaction of diacid chloride **119** with benzoylthio-TTF **52** did not afford compound **127**, however, alcohols **51** and **37** provided TTF-σ-ferrocene-σ-TTF triad systems **128** and **129** (20%, and 65%, respectively; Scheme 2.24).

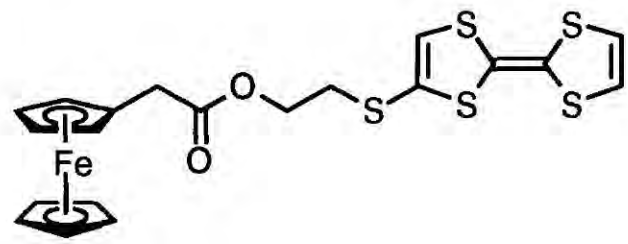


Scheme 2.24: (i) NaOEt, EtOH, -10°C, 0.5 h, then $Fc(COCl)_2$ **119**;
(ii) $Fc(COCl)_2$ **119**, NEt_3, DCM, 20°C.

Alcohol **51** was also reacted with ferroceneacetyl chloride **131**, which was prepared from commercially available ferroceneacetic acid **130**. TTF-derivative **132**, with an extended spacer unit between the redox species, was isolated in low yield (8%), as an orange, waxy solid (mass spectroscopy, NMR and IR evidence). Surprisingly the compound decomposed over a short period of time. It was the only TTF-ferrocene derivative found to be unstable under ambient conditions, perhaps due to the presence of trace amounts of impurities.

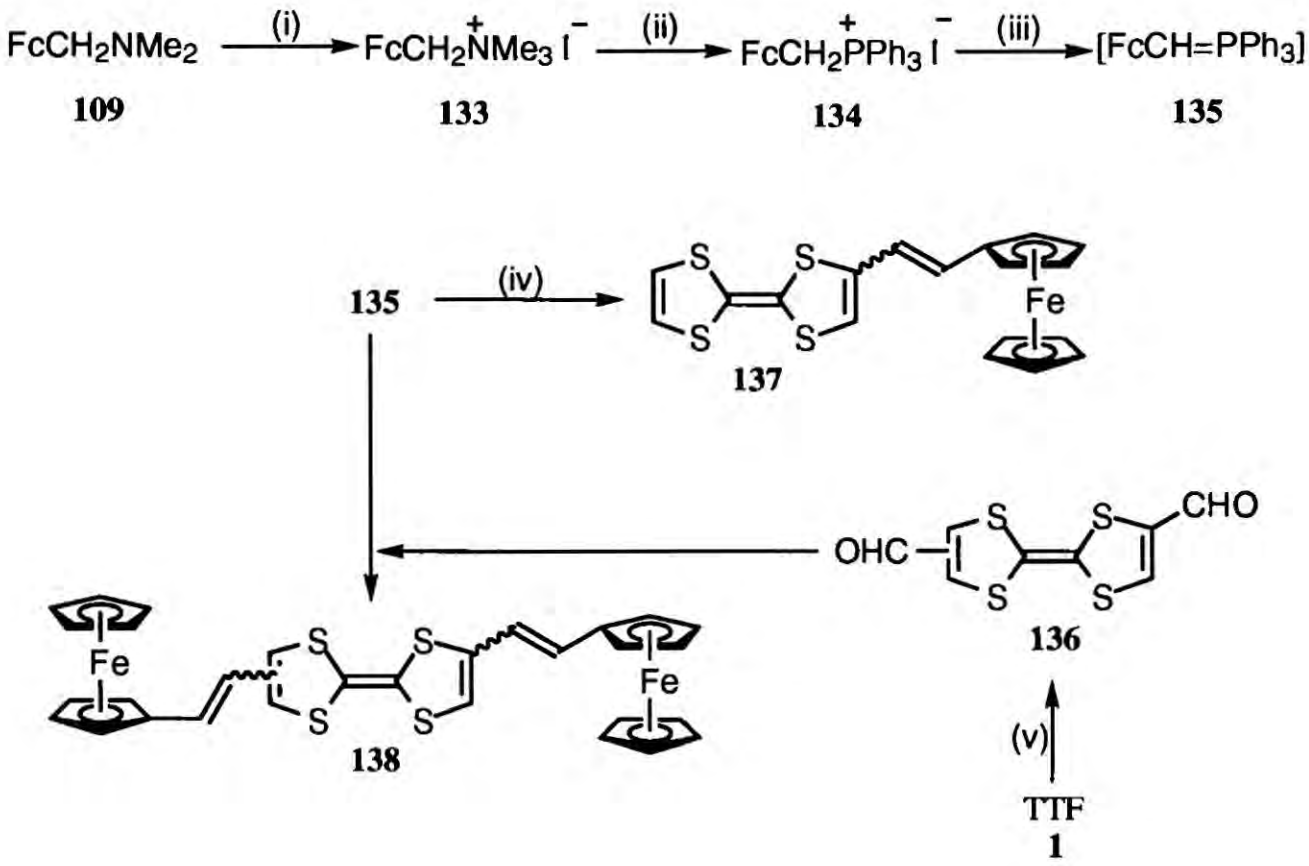


130 X = OH
131 X = Cl

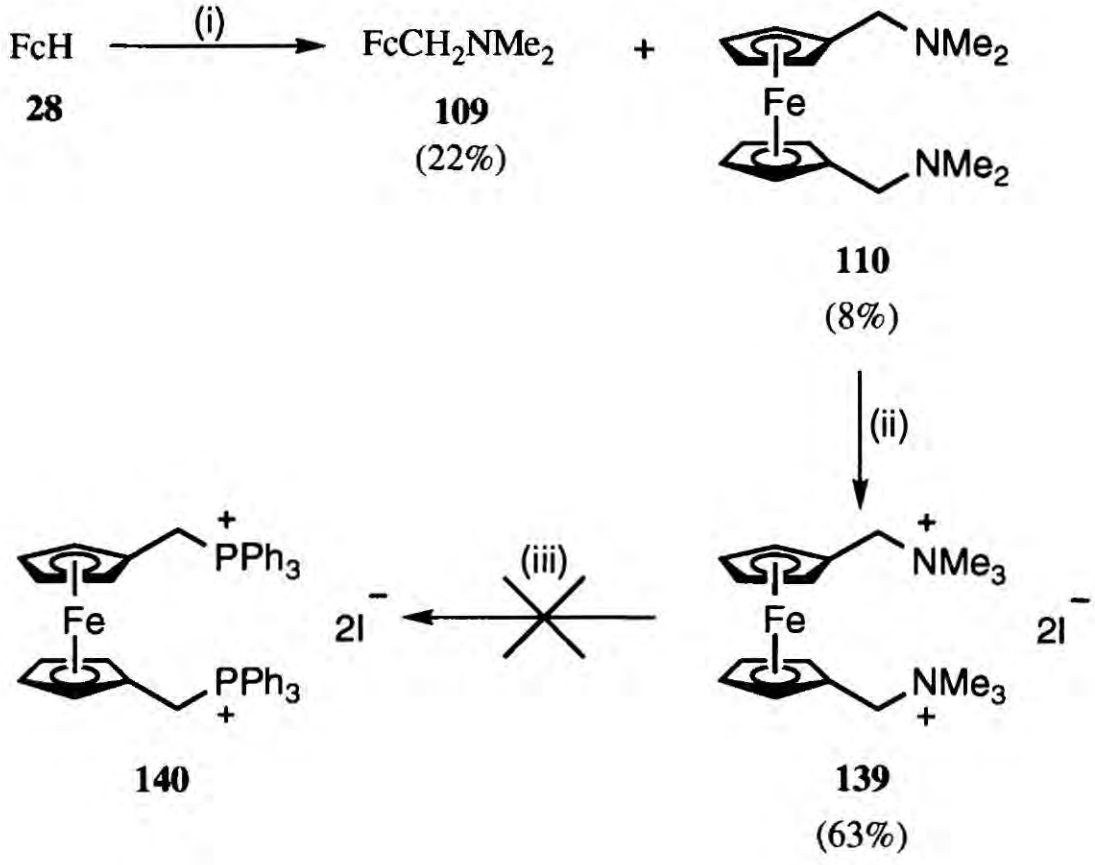


132

To obtain ferrocene-π-TTF derivatives linked *via* a conjugated spacer unit, the versatile ferrocene Wittig salt **134**[104] was prepared (Scheme 2.25). Reaction of the ylide intermediate **135** with TTF-carboxaldehyde **32**, and the previously unknown dicarboxaldehyde **136** (known to be a mixture of 4,4'- and 4,5'-isomers from incontrovertible ^{1}H NMR spectroscopic data), afforded mixtures of the ethene bridged *cis/trans* derivatives, **137** and **138**, respectively. The many isomers of compound **138** proved to be inseparable; the *trans*-isomer of **137**, however, was isolated pure by fractional recrystallisation from toluene with an overall yield of 58%.

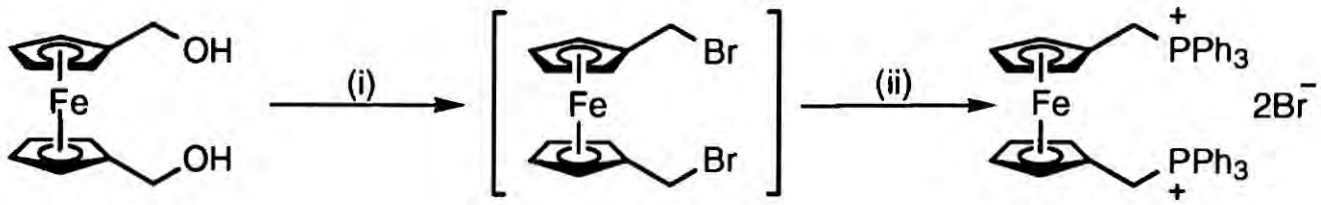


Scheme 2.25: (i) MeI, MeCN, 0°C; (ii) PPh_3, EtOH, reflux; (iii) ^nBuLi, THF, 20°C; (iv) TTFCHO **32**; (v) LDA (4 equiv.), Me(Ph)NCHO (2 equiv.), Et_2O, -78°C (40%).



Scheme 2.26: (i) $Me_2NCH_2NMe_2$, H_3PO_4, AcOH, 115°C, 20h; (ii) MeI, MeCN, 0°C; (iii) PPh_3, EtOH, reflux.

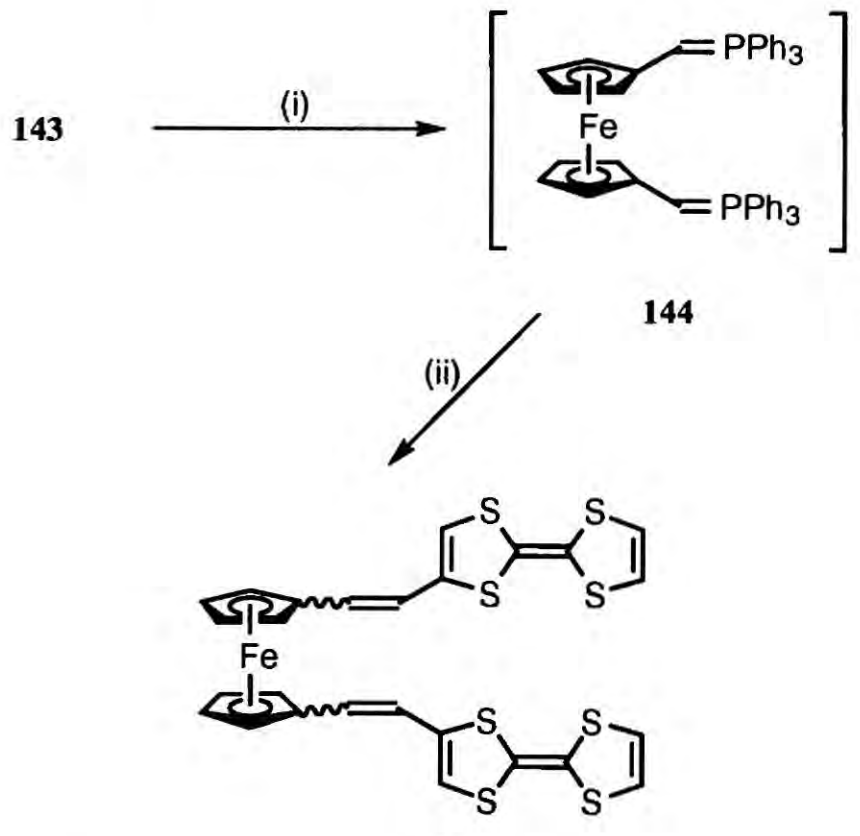
The preparation of 1,1'-disubstituted ferrocenyl diphosphonium salt **140** was attempted in the first instance from the known diamine derivative **110**[105] (Scheme 2.26). Diammonium salt **139** was isolated in 63% yield; nucleophilic substitution by triphenylphosphine, however, did not take place and compound **139** was recovered. The dibromide analogue of **140** was reported by Beer *et al.*,[106] and was synthesised from the unstable dibromide derivative **142**,[107] which was prepared in turn from 1,1'-bis(hydroxymethyl)ferrocene **141**[108] (Scheme 2.27).



141 **142** **143**

Scheme 2.27: (i) PBr_3, Et_2O, 0°C, 6 h; (ii) PPh_3, 16 h.

Treatment of **143** with two equivalents of butyllithium afforded the bisylide **144**[106], which was trapped with TTF-carboxaldehyde **32** (Scheme 2.28). From the ^1H NMR spectrum of the resulting TTF-ferrocene derivative **145**, a mixture of three isomers is evident. Neither chromatographic nor recrystallisation techniques were able to separate the *trans-trans*, *cis-trans* and *cis-cis* isomers.



145

Scheme 2.28: (i) ^nBuLi (2 equiv.), THF, 20°C; (ii) TTF-CHO **32**.

2.7 CV DATA AND DISCUSSION

Starting from functionalised ferrocene and TTF derivatives, the generation of a series of new covalently linked TTF-ferrocene compounds has been achieved. Between the redox centres of these molecules are spacer groups of varying lengths; additionally, the intramolecular TTF:ferrocene ratios have been varied: *viz.* 1:1 (**120-122**, **132** and **137**), 1:2 (**123** and **138**), and 2:1 (**128**, **129** and **145**). These criteria have provided us with a fascinating collection of novel redox active species, which have been investigated in detail by cyclic voltammetry. The data for these compounds, together with those of other relevant redox-active species are collated in Table 2.3, with a selection of voltamograms presented in Figure 2.1.

With the above TTF-ferrocene compounds the reversible electron transfer oxidations taking place correspond to: TTF $\rightarrow$ $TTF^{+\cdot}$, $TTF^{+\cdot} \rightarrow TTF^{2+}$, and ferrocene $\rightarrow$ ferricinium. In all cases the first oxidation is assigned to TTF $\rightarrow$ $TTF^{+\cdot}$, since non-ferrocene containing TTF derivatives (*e.g.* **51**, **86**, **90**, **102**), exhibit only a slight change in their redox potential, compared to TTF **1**. In contrast, substituted ferrocene derivatives (*e.g.* **116**), usually display a significant increase in redox potential.

Identification of $TTF^{+\cdot} \rightarrow TTF^{2+}$ and ferrocene $\rightarrow$ ferricinium oxidations requires a more thoughtful approach, with speculative conclusions relying heavily upon model compounds. Results show that the functionalised TTF compounds **51** and **90** possess very similar redox values to TTF **1** and are only slightly higher (by *ca.* 0.08V in both cases). The data on molecule **86** represent the covalent incorporation of a non-redox active moiety into compound **51**. The difference between the redox values of **51** and **86** are negligible; we should be able to conclude, therefore, that any increase in TTF redox potentials arising from the inclusion of a second different redox active centre into a derivative of **51**, will be directly due to the second redox species. TTF-ferrocene **122** displays its first oxidation at 0.47V, which is 0.05V higher than for **51**. If the ferrocene unit is responsible for this effect, then we can assume the second oxidation of TTF is seen as the redox wave at 0.80V.

In contrast, the TTF units of compounds **120** and **121** have been largely unaffected by the closely linked ferrocene species: both **120** and **121** have almost identical $E_1^{1/2}$ and $E_2^{1/2}$ values to their respective non-ferrocene containing model compounds **147** and **52**. The redox wave corresponding to ferrocene in compound **121** has been lost (as expected), in the broad two electron wave at *ca.* 0.83V, but the ferrocene $\rightarrow$ ferricinium value for species **120** has been raised to 0.90V - on this occasion an effect of the TTF unit on the metallocene.

Molecule	Formula	$E_1^{1/2}$(V)	$E_2^{1/2}$(V)	$E_3^{1/2}$(V)
1	TTF	0.34[a]	0.71[a]	---
28	FcH	0.36[a]	---	---
51	$TTFS(CH_2)_2OH$	0.42[a]	0.78[a]	---
52	TTFSC(O)Ph	0.45[b]	0.81[b]	---
86	$TTFS(CH_2)_2OC(O)NH(CH_2)_2Cl$	0.43[a]	0.79[a]	---
90	$TTF[S(CH_2)_2OH]_2$	0.45[a]	0.78[a]	---
102	$(MeS)_2TTF[S(CH_2)_2OH]_2$	0.49[b]	0.79[b]	---
115	$FcCO_2H$	0.79[ae]	---	---
120	TTFC(O)Fc	0.48[a] 0.38[b]	0.82[a] 0.73[b]	0.90[a] 0.88[b]
121	TTFSC(O)Fc	0.45[a] 0.45[b]	0.83[a] 0.73[bc]	---
122	$TTFS(CH_2)_2OC(O)Fc$	0.35[a] 0.47[b]	0.73[a] 0.61[b]	0.80[a] 0.75[b]
123	$TTF[S(CH_2)_2OC(O)Fc]_2$	0.53[a] 0.45[b]	0.75[a] 0.62[bd]	0.83[a] 0.82[b]
124	see page 53	0.77[a]	---	---
128	$Fc[C(O)O(CH_2)_2STTF]_2$	0.41[a] 0.37[bd]	0.73[a] 0.71[bd]	0.77[a] 0.85[b]
129	$Fc[C(O)OCH_2TTF]_2$	0.50[b]	0.73[b]	---
132	$FcCH_2C(O)O(CH_2)_2STTF$	0.46[a]	0.87[a]	---
137	*trans*-$TTF(CH)_2Fc$	0.41[a] 0.26[b]	0.62[a] 0.44[b]	0.92[a] 0.77[b]
138	$TTF[(CH)_2Fc]_2$	0.38[b]	0.53[bd]	0.91[b]
145	$Fc[(CH)_2TTF]_2$	0.40[bd]	0.71[b]	0.79[bd]
146	$Fc(CH)_2Fc$	0.34[b]	0.55[b]	---
Vinylferrocene	$FcCHCH_2$	0.43[b]	---	---
147	TTFC(O)Me	0.47[a]	0.83[a]	---
150	see page 61	0.63[b]	---	---

Table 2.3: Cyclic voltammetric data; Pt working electrode, Pt gauze counter electrode, Ag/AgCl reference electrode, 0.2 mol dm^{-3} $^nBu_4N^+PF_6^-$, 10^{-4} mol dm^{-3} compound in dry acetonitrile[a] or dry dichloromethane[b], under nitrogen or argon at 20°C, with iR compensation. All waves represent a reversible, one electron process except where indicated. [c] Broad two electron wave. [d] Two electron wave. [e] Irreversible wave.

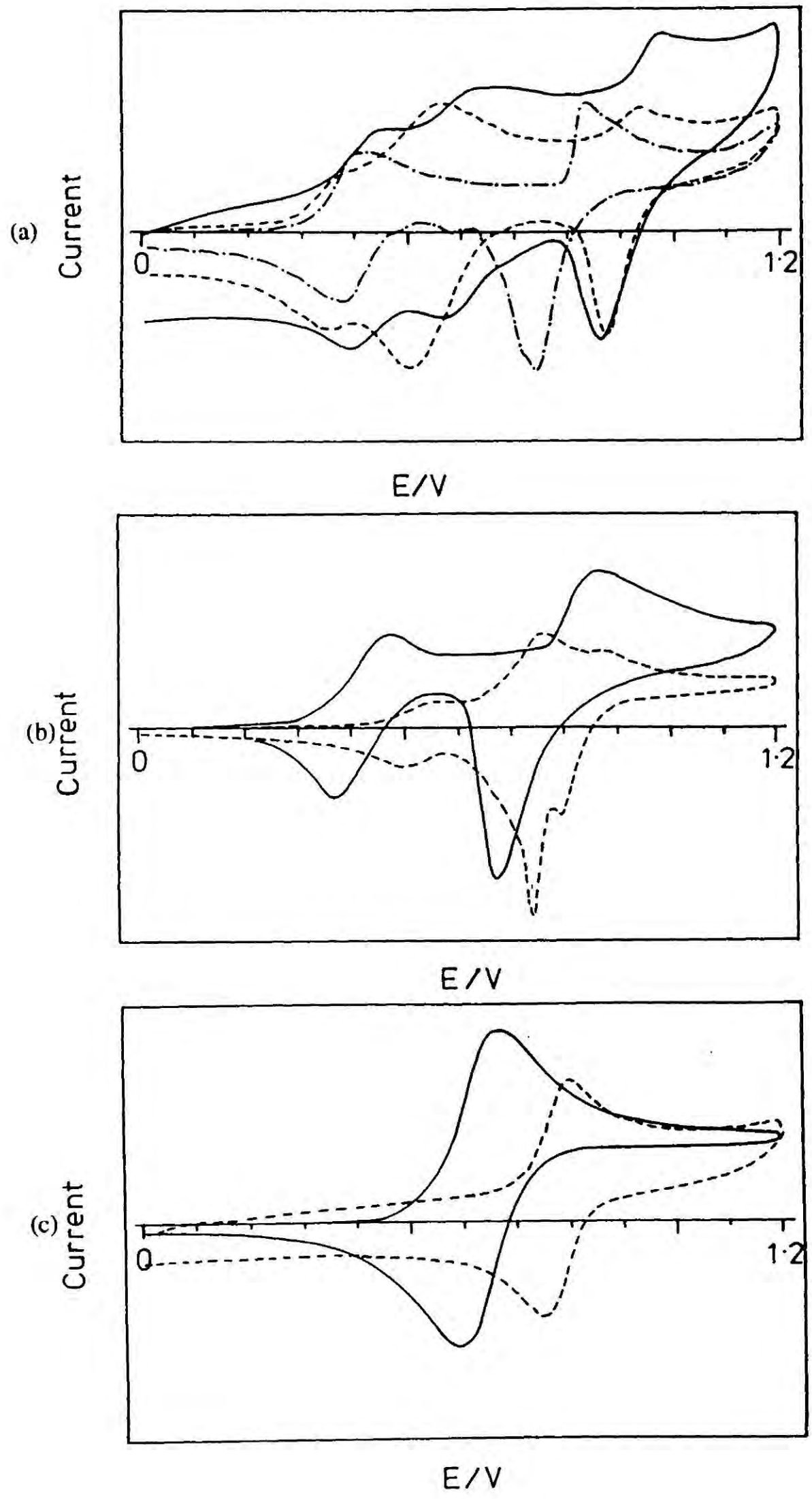
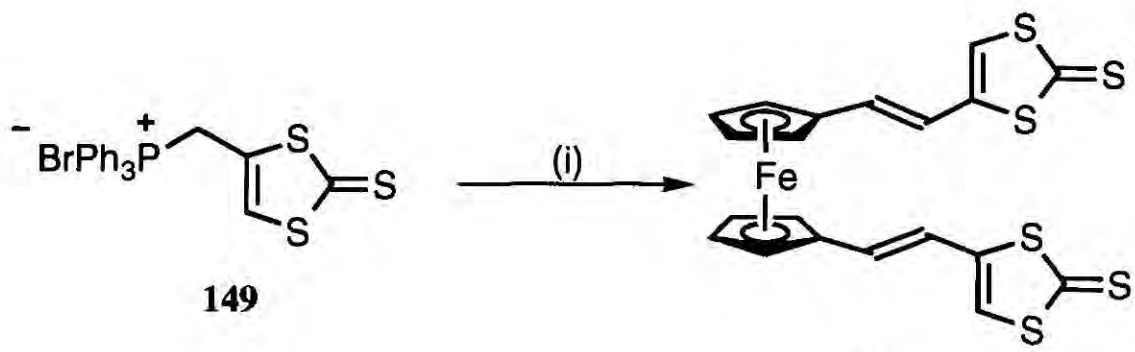


Figure 2.1: Cyclic voltammograms of compounds (a) **137** [——], **138** [----] and **145** [–·–·–]; (b) **123** [----] and **128** [——]; (c) **124** [----] and **150** [——].

For the elucidation of the redox behaviour of TTF-ferrocene derivative **123** we have used the model compound **124**, which does not contain the TTF system. Assuming that TTF does not affect the ferrocene portion of species **123** (as was the case in **122**), the second oxidation of this compound should be attributed to the formation of the ferricinium cation. Again, as for **122**, and by comparison with compound **90**, the ferrocene units appear to have raised the redox potentials of the TTF species in compound **123**.

Similar conclusions to those above can be made for esters **128**, **129** and **132**. The assignment of oxidation values for compound **137**, however, is a greater challenge and is not assisted by the model compound **146** (known to be the *trans* -configuration from X-ray crystallographic evidence; see Appendix 1.8). The redox behaviour of diferrocene **146** is quite unlike the substituted ferrocene systems previously encountered, with $E_1^{1/2}$ and $E_2^{1/2}$ values as low as 0.34V and 0.55V. The accurate assignment of oxidation potentials for **137** is virtually impossible from these results, but if one focuses on the redox value for vinylferrocene (0.43V), then the second redox wave of **137** could be attributed to ferrocene. Further proof of this deduction is gained from the data for compound **138**: firstly, the second wave indicates a two electron process; secondly, the values for $E_1^{1/2}$ and $E_2^{1/2}$ are very close together ($\Delta E = 0.15V$) - Coulombic repulsion would not allow the two acting redox centres responsible for these values to be the 1,3-dithiole rings of a common TTF unit.

To elucidate the redox behaviour of compound **145**, the bis(1,3-dithiole-2-thione)ferrocene species **150** was synthesised from 1,1'-ferrocene dicarboxaldehyde[109] **148** and Wittig salt **149**[110] (67% yield, Scheme 2.29). The redox wave corresponding to ferrocene → ferricinium in compound **150** (0.63V), can be seen at 0.71V in species **145**; in the latter case, the positive shift in the redox potential can be attributed to Coulombic repulsion of the radical cation TTF species, which is absent in derivative **150**.



149 **150**

Scheme 2.29: (i) ^{n}BuLi, THF, -78°C, 2h, then $Fc(CHO)_2$ **148**.

In conclusion, we can see that when TTF and ferrocene are incorporated into the same molecule some interaction is observed in the redox properties, albeit in an unpredictable way. Furthermore, the attainment of multiply charged species can be achieved within reasonably low potential limits, ranging from 0.26V to 0.92V. The assignment of specific redox activity has been discussed; the reader must take into perspective, however, that unambiguous proof of these conclusions has not been achieved, and that the observations made are 'best-fit' representations.

CHAPTER 3

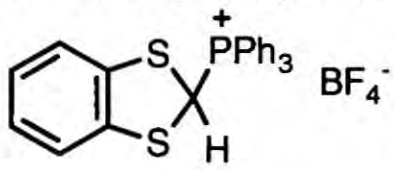
THE SYNTHESIS AND REDOX BEHAVIOUR OF EXTENDED TTF-SYSTEMS INCORPORATING FERROCENYL UNITS

3.1 INTRODUCTION

TTF systems bearing peripherally attached ferrocene units have been discussed in Chapter 2. The synthesis of two further types of TTF-ferrocene compounds has been achieved, and involves the insertion of ferrocene components into the central C-C π-conjugated regions of extended TTF species. The two structural types consist of: (i) dithiole units which are linked by a π-conjugated bridge system comprising a ferrocene molecule; (ii) vinylogous TTF systems with ferrocene units pendant to the central ethene bridges. Both families of compounds will be discussed separately.

3.2 EXTENDED TTF DERIVATIVES LINKED BY FERROCENE

Highly versatile building blocks for vinylogous TTF systems are the phosphonium salts (**151**, **152**) and phosphonates (**153**, **154**) of 1,3-dithiole species. These units readily undergo Wittig and Wittig-Horner reactions respectively, in good yields, with suitable carbonyl compounds.



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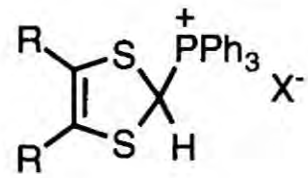

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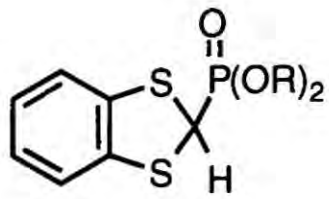

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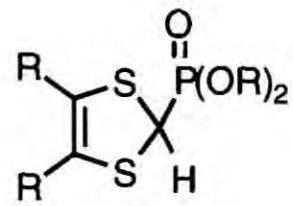
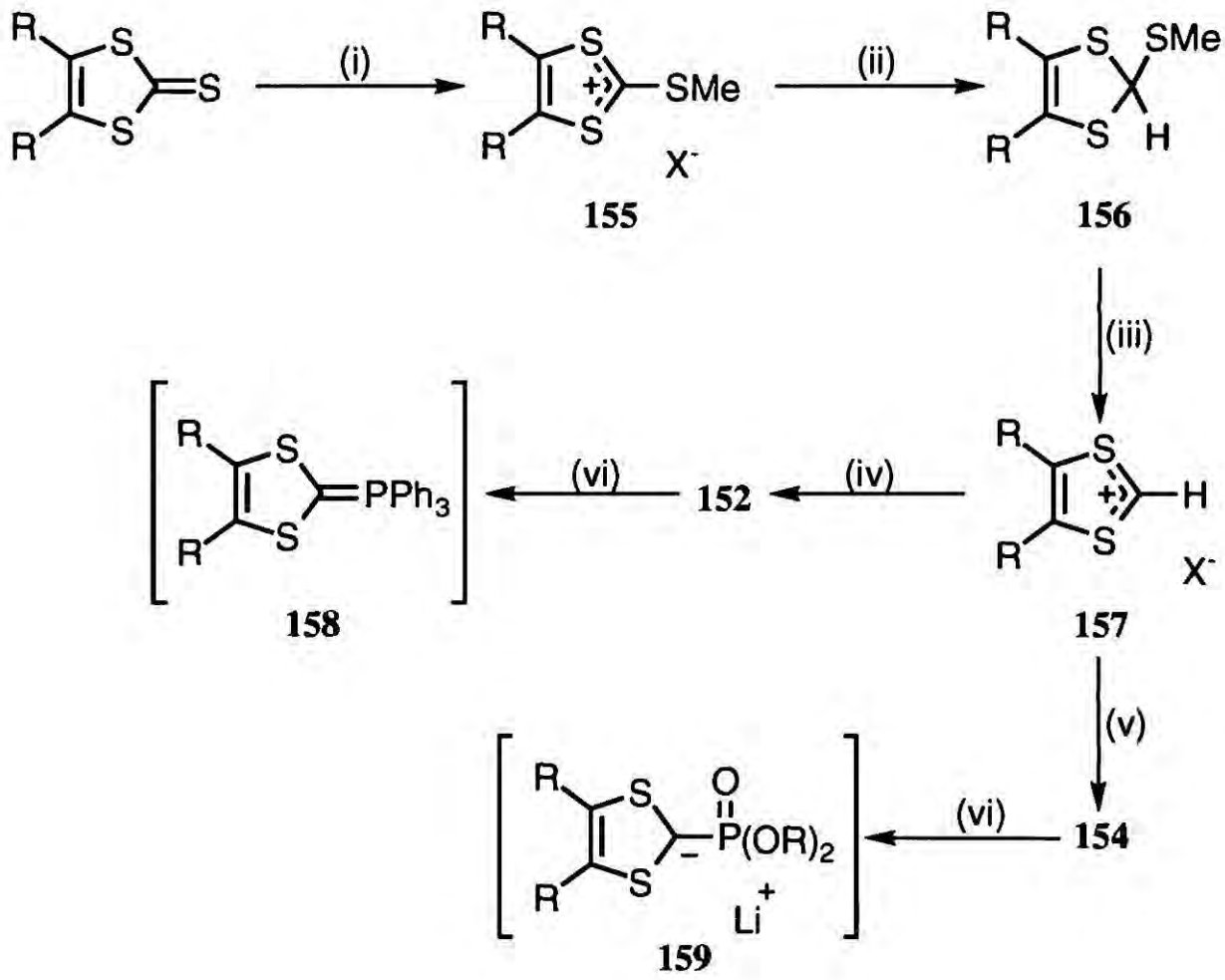


154

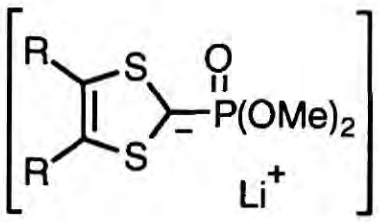
The first synthesis of a dithiole phosphonium salt was by Gonella and Cava[111] (compound **151**), while the first phosphonate analogue was prepared by Akiba *et*

al.[112] (compound **153**). A range of similar species (general formula **152** and **154**) have since been developed by several independent groups. A wide choice of reagents are available for the synthesis of the Wittig and Wittig-Horner precursors. Beginning with the relevant 1,3-dithiole-2-thione (Scheme 3.1), methylation followed by reduction of the resulting dithiolium cation **155**, gives the sulfide species **156**. Protonation of **156** results in dithiolium salt **157**, which can then be treated with either triphenylphosphine or trialkylphosphite to furnish the phosphonium salt **152** and phosphonate compound **154**, respectively. Deprotonation of these species (usually by ^{n}BuLi) generates the phosphorus ylide **158** or the phosphonate anion **159**, the latter being more reactive towards aldehydes and ketones. In our laboratory we have favoured dimethylsulphate, sodium borohydride and tetrafluoroboric acid as the preferred reagents for steps (i)-(iii), Scheme 3.1.

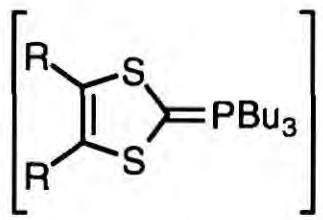


Scheme 3.1. General synthesis of 1,3-dithiole Wittig and Wittig-Horner reagents: (i) MeX, MeCN/DCM; (ii) hydride, ^{i}PrOH, MeCN; (iii) HX, MeCN; (iv) PPh_3, MeCN; (v) $P(OR)_3$, NaI, MeCN; (vi) Base, -78°C, Et_2O/THF.

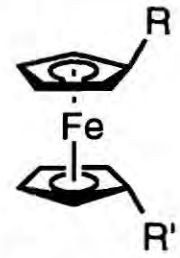
Via the generation of phosphonate anions **160-162** and ylide **163**, compounds **164-172** have been synthesised (60-80% yield) from commercially available ferrocene derivatives **108** and **112**, and the known dicarboxaldehyde **148**.



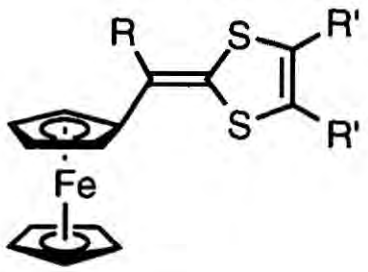
160 R = H
161 R = Me
162 R = SMe



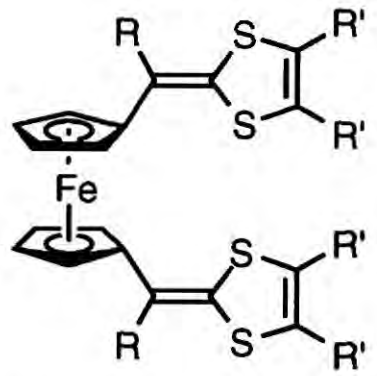
163 R = CO_2Me



108 R = R' = C(O)Me
112 R = CHO, R' = H
148 R = R' = CHO



164 R = R' = H
165 R = H, R' = Me
166 R = H, R' = SMe
167 R = H, R' = CO_2Me



168 R = H, R' = CO_2Me
169 R = H, R' = Me
170 R = Me, R' = Me
171 R = Me, R' = H
172 R = Me, R' = SMe

Compounds **168-172**, therefore, represent a novel form of 'stretched'-TTF systems. The X-ray crystal structure of derivative **171** has been solved and is shown in Figures 3.1a and 3.1b. The molecule is situated around a two-fold crystallographic axis, with the cyclopentadienyl rings parallel to within 1.3° and staggered by 17.6°. The entire molecule is remarkably non-planar, being twisted by 26.0° around the C(1)-C(8) axis and by *ca.* 3.4° around the C(6)=C(8) double bond.

The electrochemical properties of compound **164-172** will be discussed at the end of this chapter.

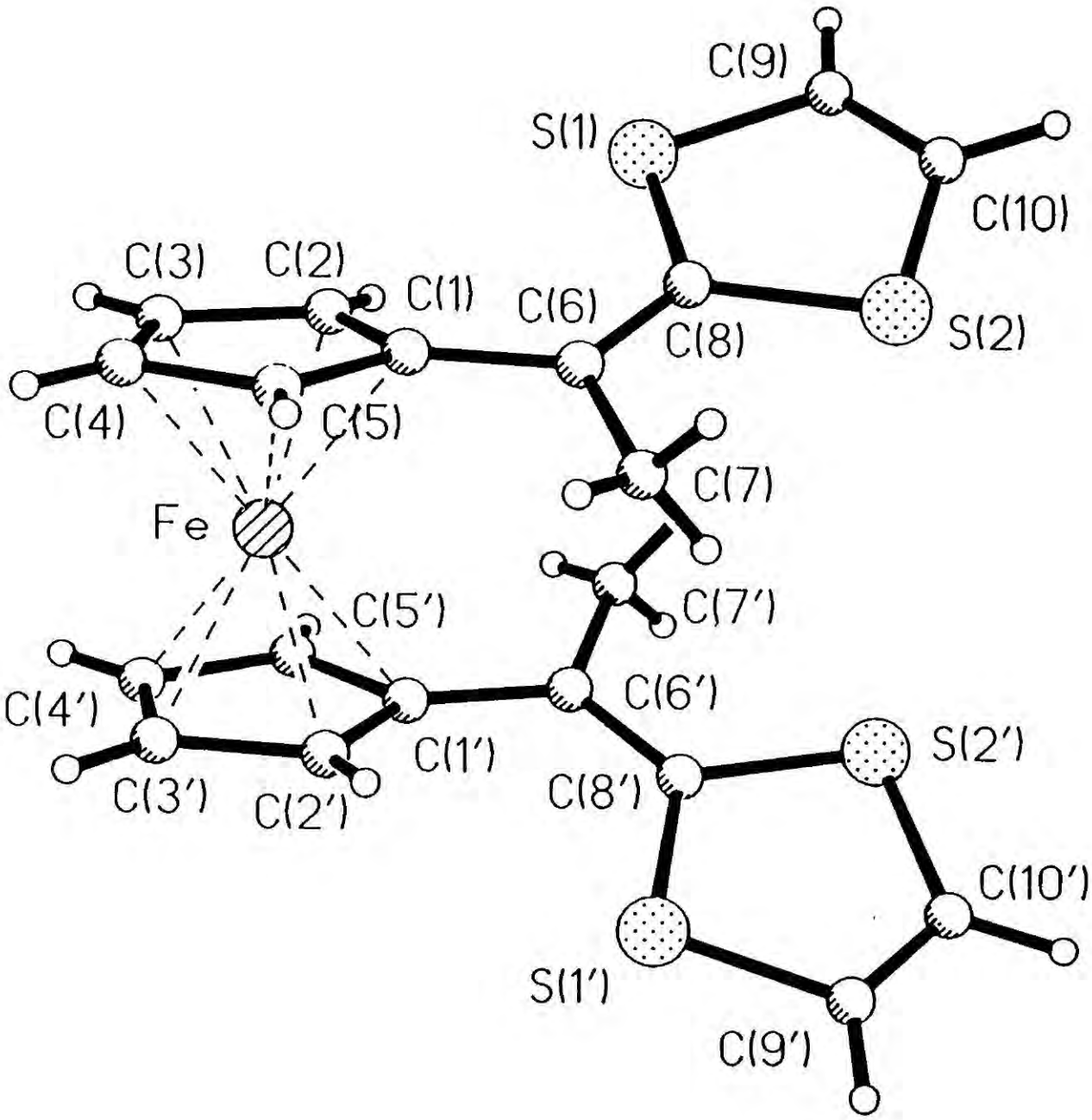


Figure 3.1a: X-ray molecular structure of **171** with crystallographic numbering scheme.

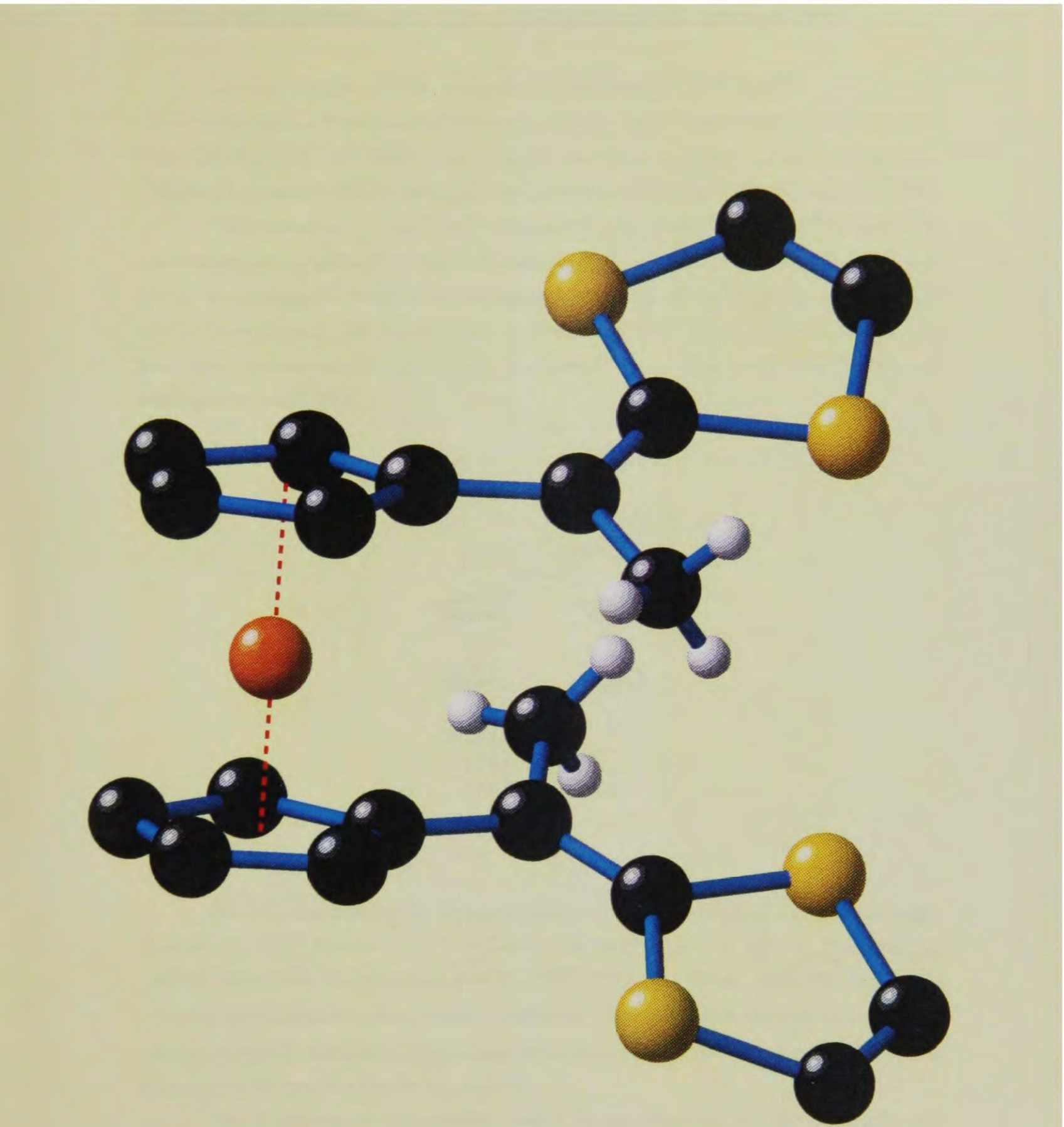
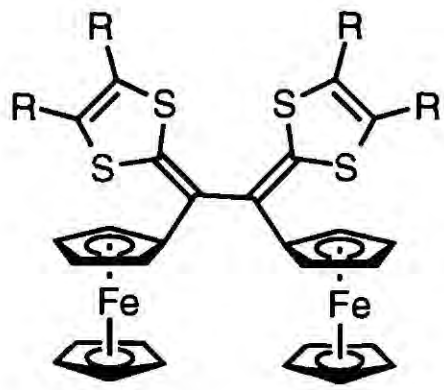


Figure 3.1b: X-Ray molecular structure of **171**.

3.3 VINYLOGOUS TTF DERIVATIVES BEARING FERROCENE UNITS PERIPHERAL TO THE CENTRAL ETHYLENE BONDS

During routine NMR analysis of compound **165** a dark orange solid crystallised from a deuterated chloroform solution. The material was clearly different from **165** by TLC and NMR data. Indeed, the mass spectrum of the new product indicated a mass of 654 for the compound, whereas derivative **165** has a mass of 328.

The structure of this new compound was shown to be **173** by X-ray crystallography (Figure 3.2). Figure 3.2 shows that the two ferrocene units are in fact *cis* to the central C-C bond, with the cyclopentadienyl rings facing away from each other. Consequently, the dimerisation of compound **165** under acidic conditions was attempted in earnest (HCl in ether), and proceeded in 60% yield with the loss of hydrogen to yield **173**.



173 R = Me
174 R = H
175 R = CO_2Me

Similar dimerisation of systems containing the 1,3-dithiole-2-ylidene unit has been observed by Daub *et al.*,[113] however, the mechanism for this reaction remains unclear. Treatment of compound **164** with $HCl.Et_2O$ gave dimer **174** (50% yield), yet **175** was not obtained, under similar conditions, from **167**. It would seem, therefore, that the electron withdrawing/donating effects of the R substituents may have some influence in the mechanism for this reaction.

The synthesis of compounds **168-174** has achieved for the first time the attachment of a second different redox-active species to the central region of π-extended TTF systems. Further attempts at synthesising related compounds have produced a series of fascinating products. The study of dendralenes and their unusual cross-conjugated properties have attracted much attention in recent years.[114-117] The

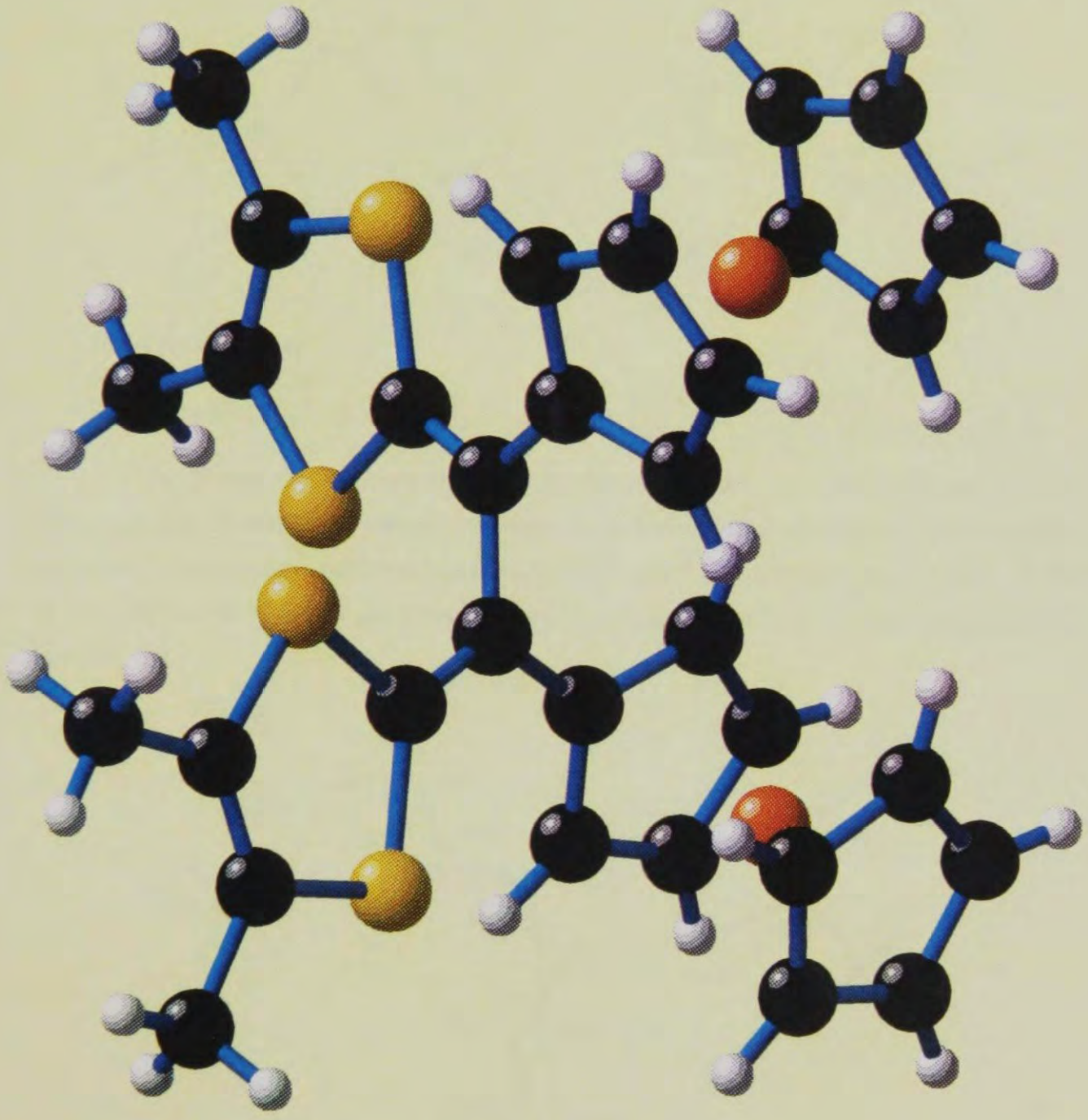
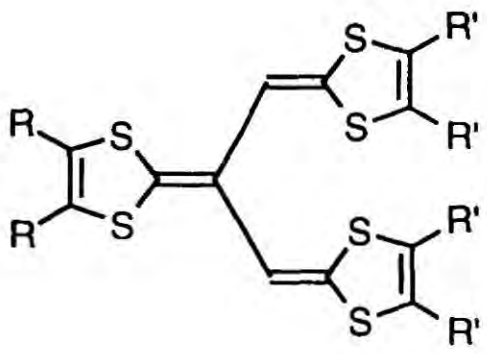


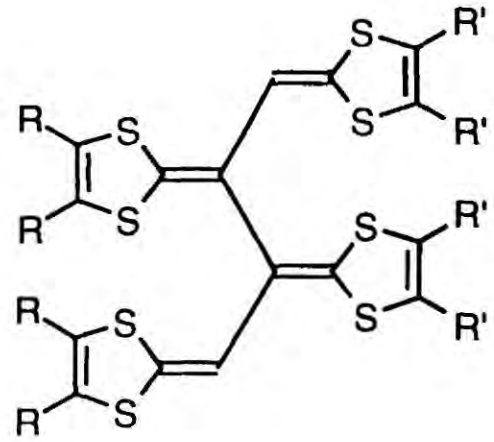
Figure 3.2: X-Ray molecular structure of **173**.

inclusion of redox-active groups into dendralene systems is extremely rare, but is of particular interest if they are able to form stable cross-conjugated radicals.[115] It has been suggested that the controlled electron propagation within these species could be used for the development of soliton switches in molecular electronic devices.[118]

A series of [3]- and[4]-dendralenes, **176a-176c** and **177a-177b** comprising 1,3-dithiole groups, has been synthesised previously in our laboratory.[119]



176a R = R' = Me
176b R = R' = SMe
176c R = Me, R'-R' = S-$(CH_2)_2$-S



177a R = R' = SMe
177b R = Me, R'-R' = S-$(CH_2)_2$-S

The X-ray crystal structure of compound **176a** is shown in Figure 3.3.[119] Ring systems A and B are almost coplanar with a dihedral angle of 8.8°, whilst ring C is virtually orthogonal (dihedral angles of 80.0° and 81.7° with respect to rings A and B). Compounds **176-177** produced interesting CV data which will be considered in section 3.4.

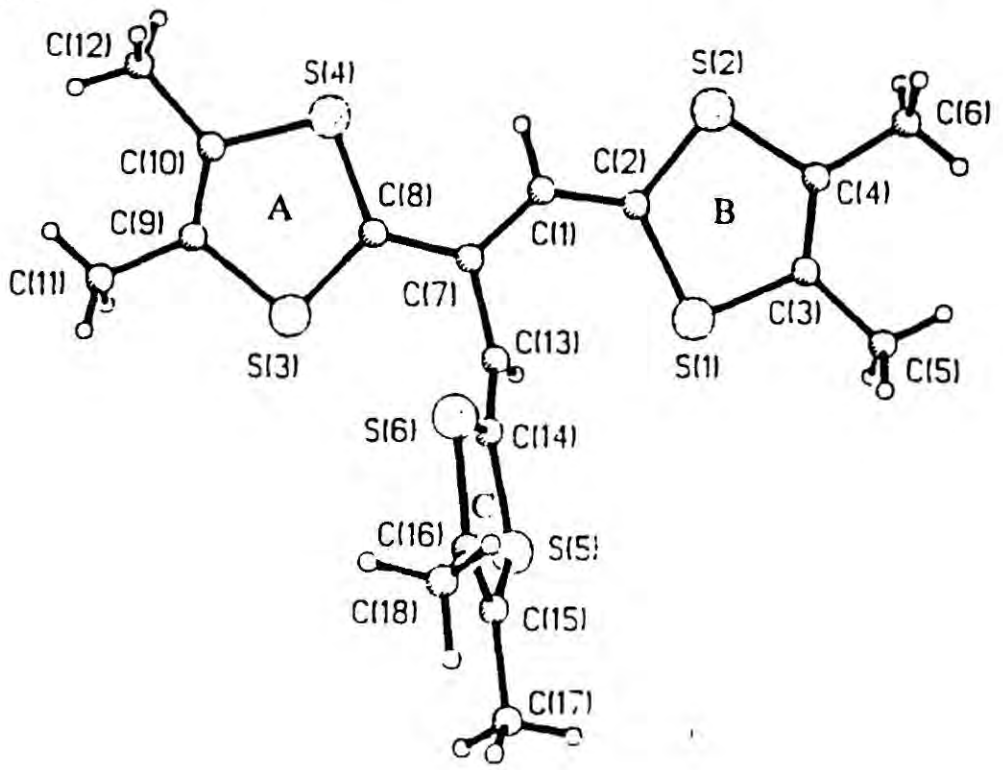
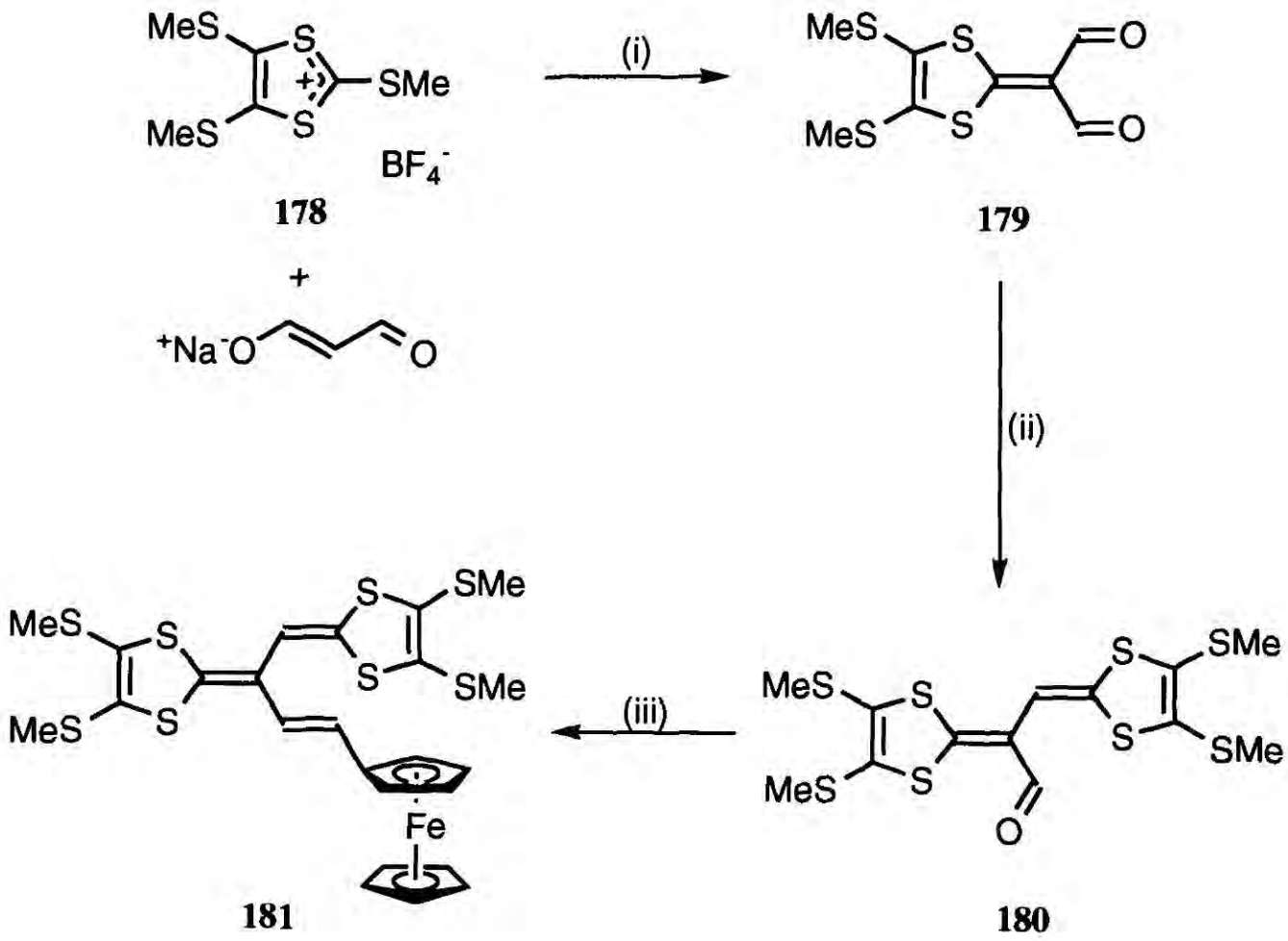


Figure 3.3: X-ray crystal structure of compound **176a**.

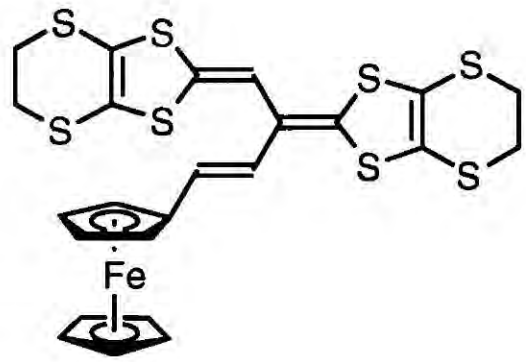
Analogous [3]- and [4]-dendralenes, with ferrocene units substituting one or more of the dithiole rings, were our targets, with a view to a comparison of structural and electrochemical properties with compounds **176-177**.

The first of the extended TTF-ferrocene dendralenes to be synthesised was compound **181**: a [3]-dendralene (Scheme 3.2). Dithiolium salt **178** was reacted with the sodium salt of malonaldehyde to form dialdehyde **179**. From the addition of **179** to dithiole phosphonate anion **162**, aldehyde **180** was produced in 30% yield.[120] Aldehyde **180** was finally reacted with ferrocenyl Wittig reagent **134** to afford the 2:1 mixed dithiole-ferrocene **181** in 54% yield.



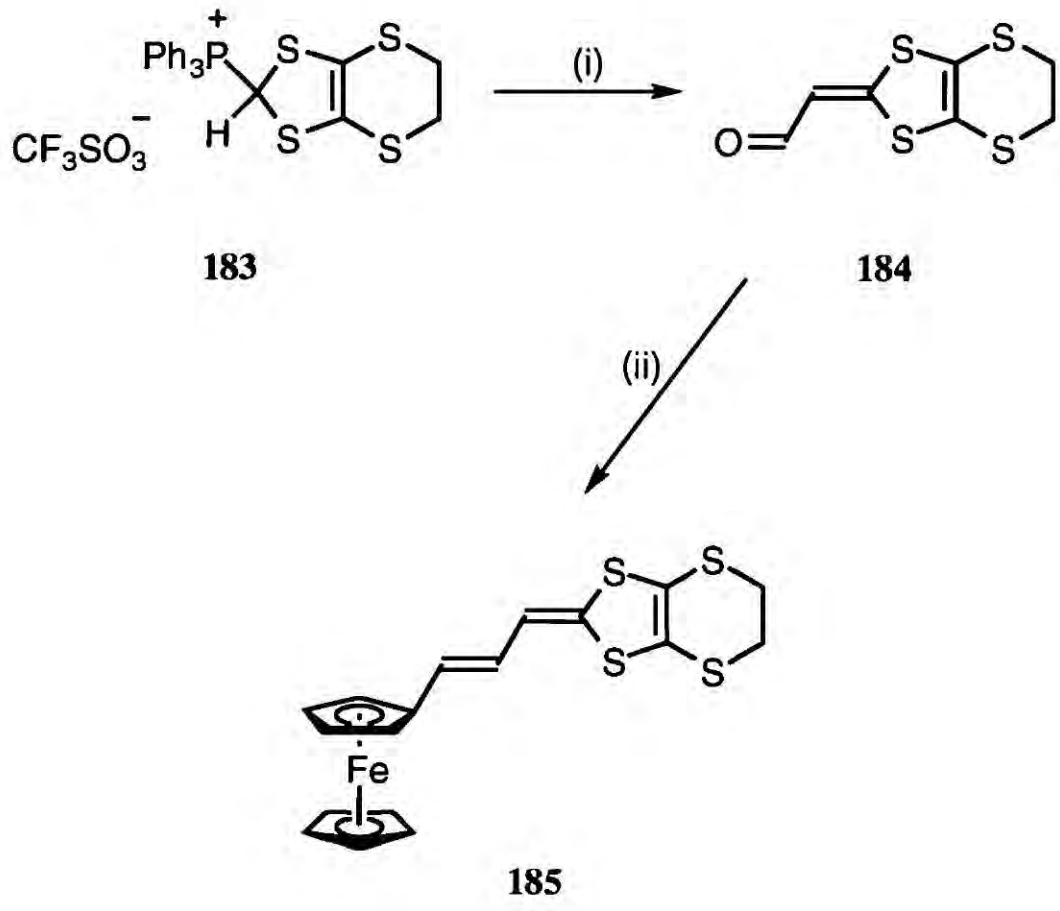
Scheme 3.2: (i) MeCN, 20°C; (ii) **162**, ^{n}BuLi, THF, -78°C;
(iii) $FcCH_2PPh_3^+I^-$ **134**, BuLi, THF, 20°C.

The low yield of step (ii) (Scheme 3.2), is due to the competitive formation of the tris(dithiole) compound **176b**. An improved route to analogous compound **182** was attempted using different methodology.



182

Dithiole derivative **184** can be synthesised from glyoxal and phosphonium salt **183** (Scheme 3.3).[121] Reaction of ferrocenyl phosphonium salt **134** with aldehyde **184** gave ferrocene-dithiole species **185** in 64% yield.



183 **184** **185**

Scheme 3.3: (i) NEt_3, 40% glyoxal in water, MeCN, 20°C;
(ii) $FcCH_2PPh_3^+I^-$ **134**, ^nBuLi, THF, 20°C.

Recrystallisation of compound **185** from dichloromethane produced the crystalline *trans*-isomer, whose structure was determined by X-ray crystallography and

is shown in Figure 3.4. The conjugated portion of the molecule, comprising the 1,3-dithiole ring and the cyclopentadienyl ring is essentially planar. The crystal packing diagram of **185** (Figure 3.5) shows marked S···S intermolecular contacts which are shorter than the sum of the S···S van der Waal's radii (3.6Å), indicating a close-packed structure.

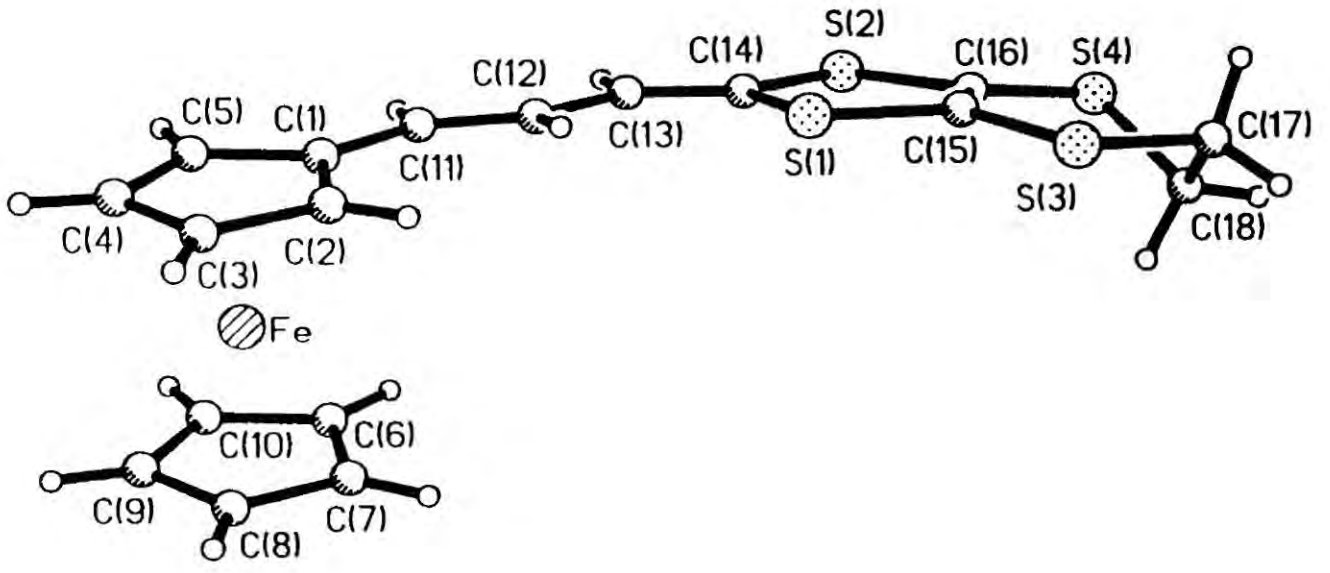


Figure 3.4: X-ray molecular structure of compound **185**.

Functionalisation of molecule **185** using Yoshida's method[115] for the Vilsmeier formylation of ylidenes (Scheme 3.4), gave compound **186** in 73% yield. Aldehyde **186** which is analogous to tetrathiomethyl derivative **180**, has been derived by a different method in a much higher yield. Reaction of **186** with phosphonate anion **188**, prepared from Wittig-Horner reagent **187**, afforded the 2:1 dithiole-ferrocene [3]-dendralene **182** in 83% yield.

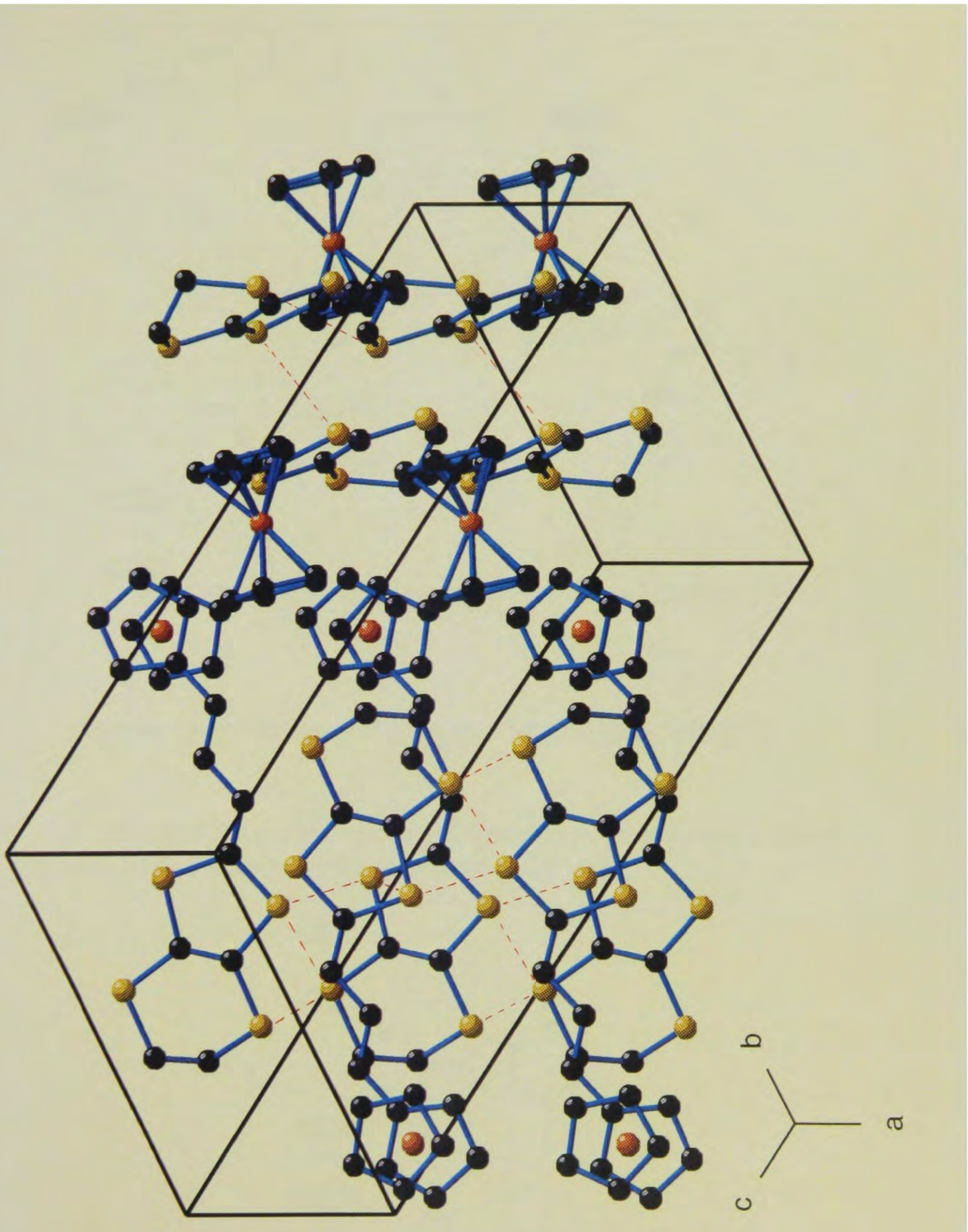
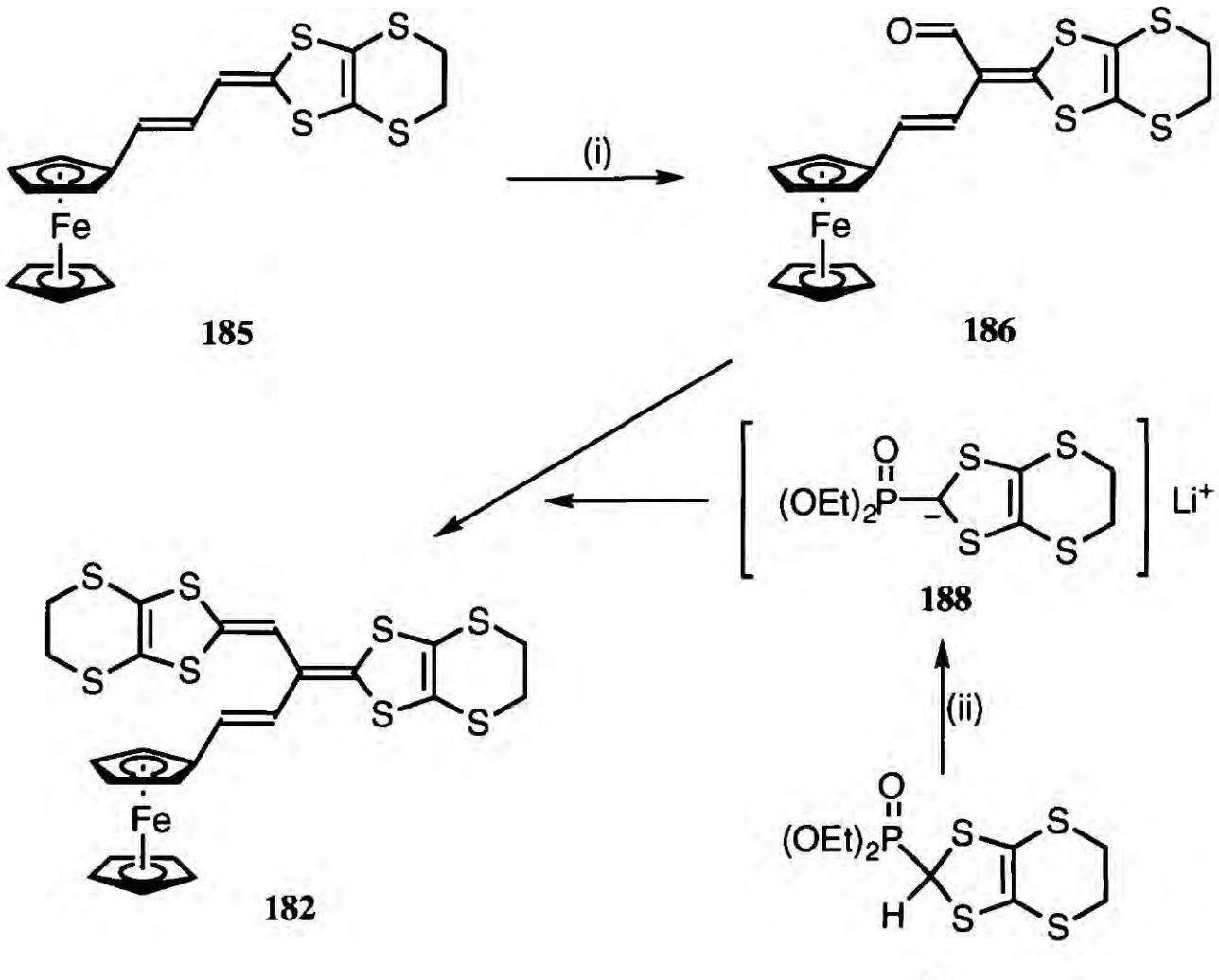
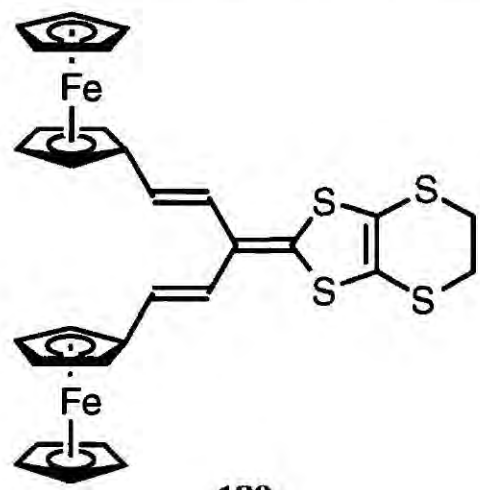


Figure 3.5: X-Ray crystallographic packing diagram of **185**.



Scheme 3.4: (i) DMF, oxalyl chloride, 0°C, 15min; (ii) ^{n}BuLi, THF, -78°C.

Aldehyde **186** was also reacted with ferrocenyl phosphorus ylide of **134** to give the 1:2 dithiole ferrocene [3]-dendralene **189** in 72% yield.



189

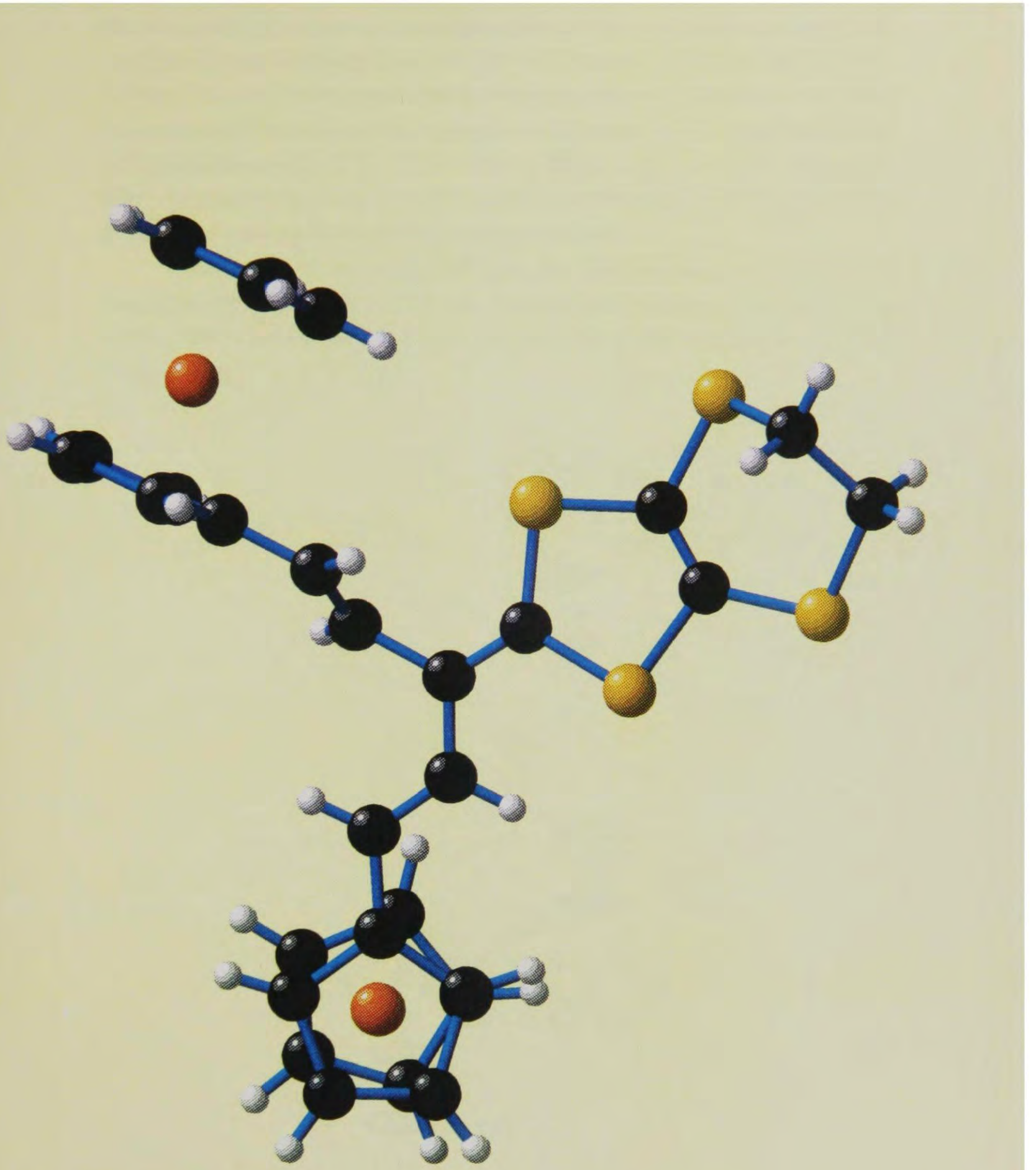
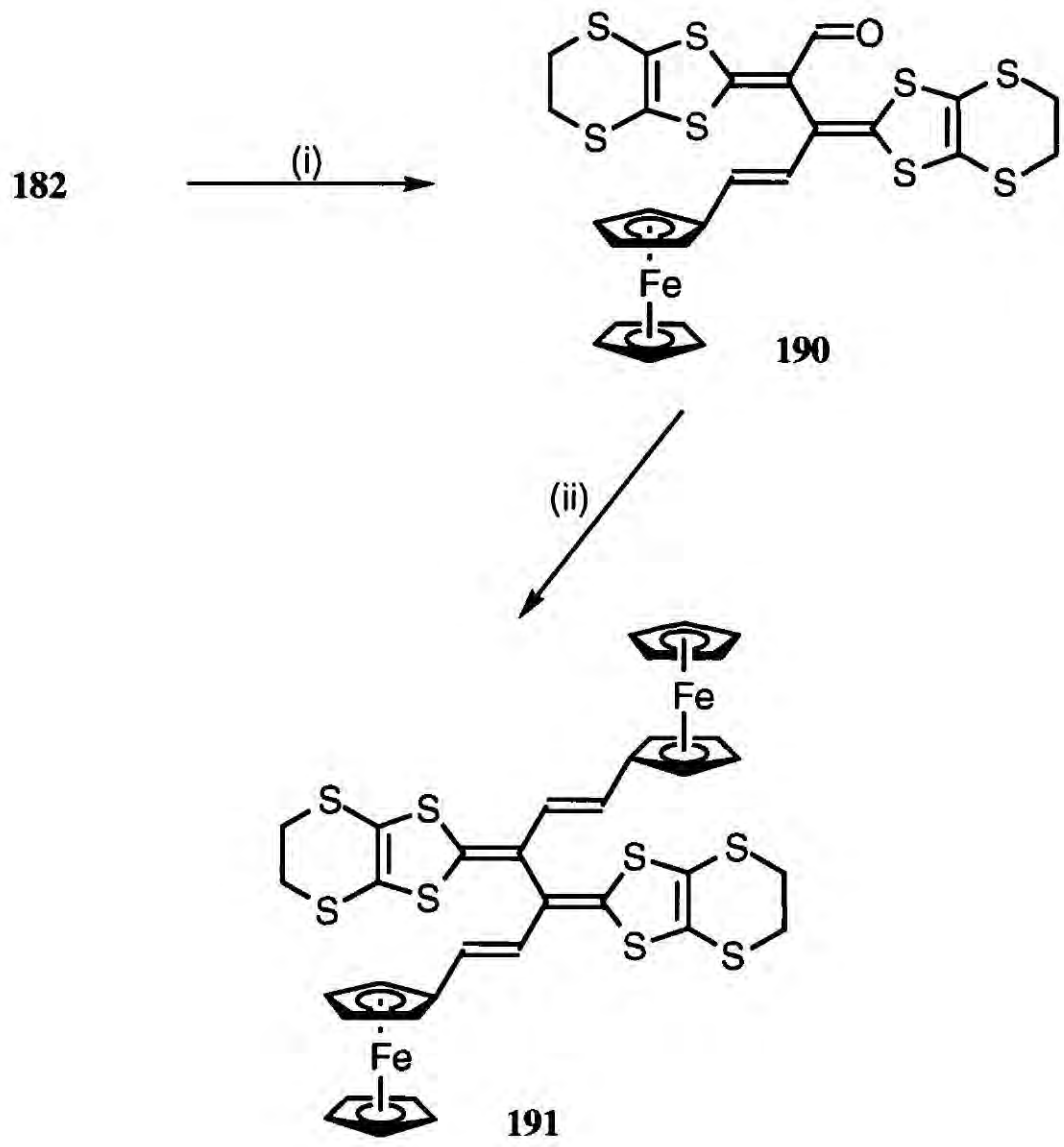


Figure 3.6: X-Ray molecular structure of **189**.

A mixture of isomers was observed in the ^{1}H NMR spectrum of compound **189**. Recrystallisation from dichloromethane-hexane afforded the all-*trans* isomer; the configuration was confirmed from its X-ray crystallographic structure which is shown in Figure 3.6. The [3]-dendralene **189** is remarkably similar in structure to the related tris(dithiole)-[3]-dendralene **176a**: conjugation and planarity are favoured between one cyclopentadienyl ring and the dithiole ring of **189** (as seen in the X-ray structure of **185**). The plane of the second ferrocene unit is also orthogonal to the remainder of the molecule, as is the third dithiole ring in compound **176a**.

Formylation of compound **182** gave the functionalised and unstable [3]-dendralene **190** (71% yield) which was isolated and reacted with ferrocene Wittig reagent **134** to afford the 2:2 dithiole-ferrocene [4]-dendralene **191** in 65% yield (Scheme 3.5).



Scheme 3.5: (i) DMF, oxalyl chloride, 0°C, 15min; (ii) **134**, ^{n}BuLi, THF, -78°C.

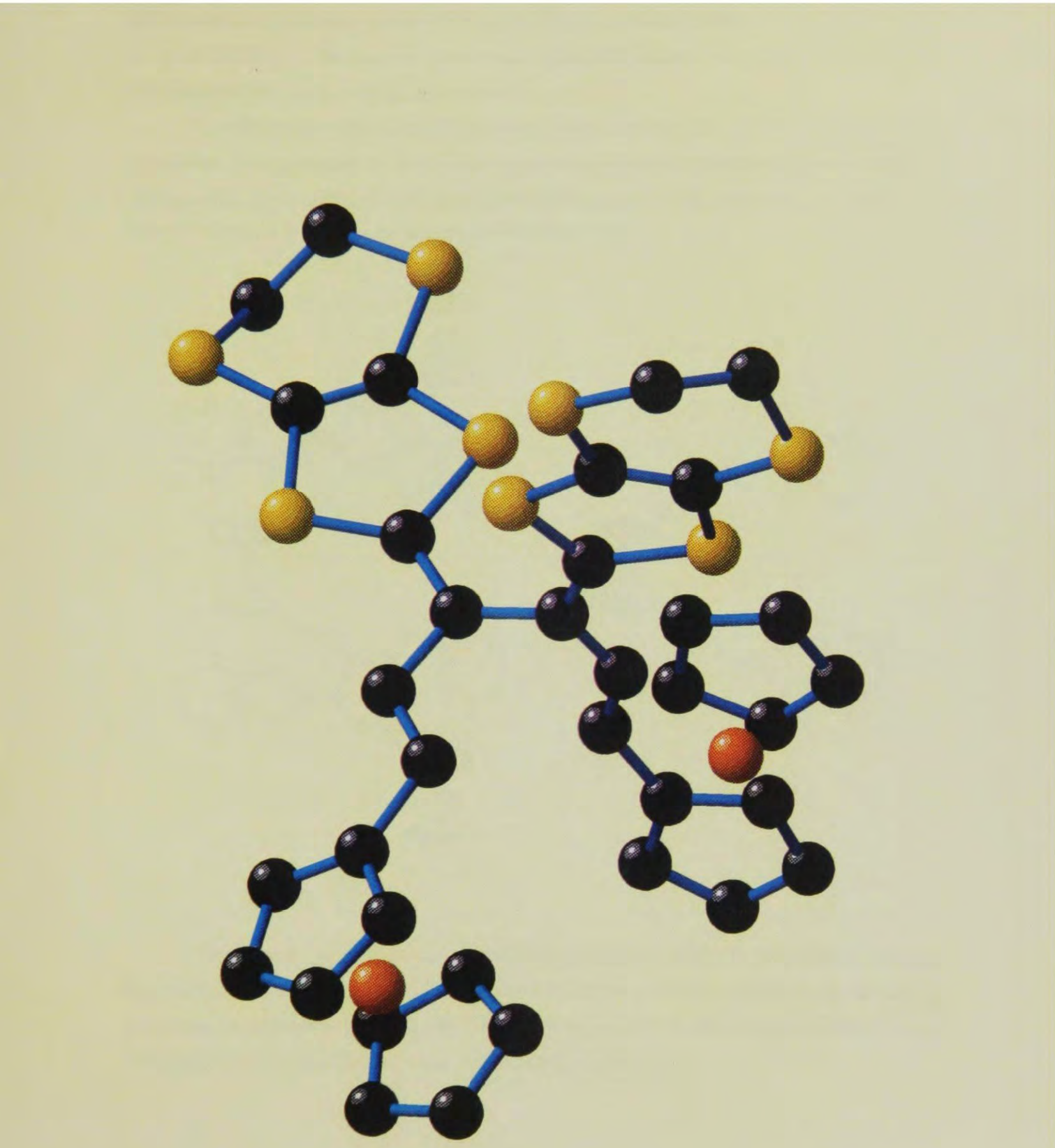
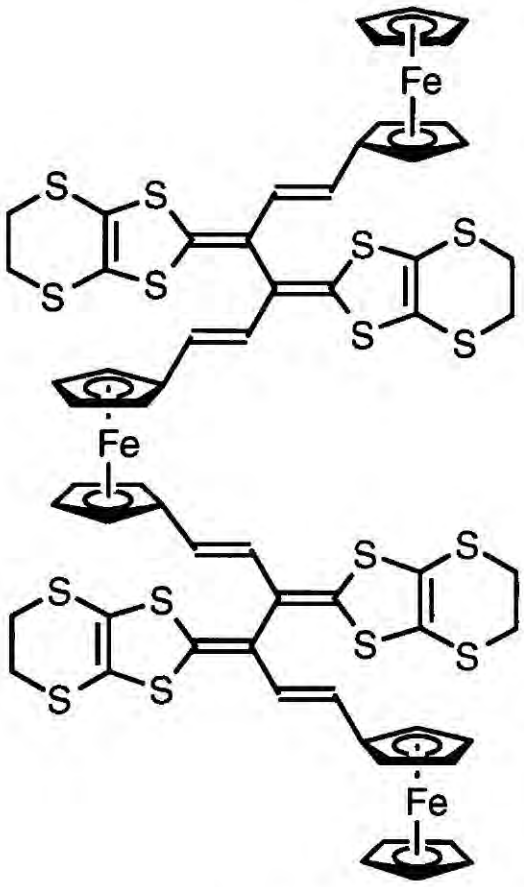


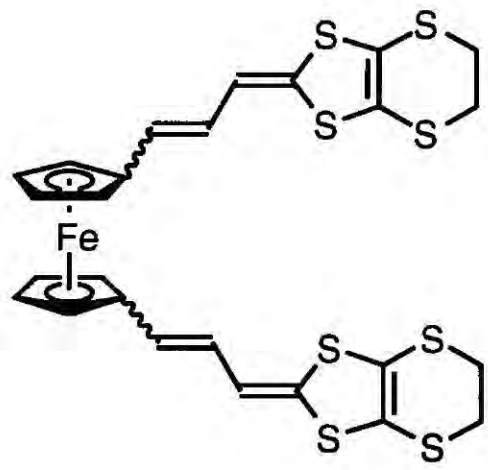
Figure 3.7: X-Ray molecular structure of **191**.

Once again, the all-*trans* isomer was isolated by recrystallisation from dichloromethane-hexane, and confirmed by X-ray crystallography (Figure 3.7). Due to the poor quality of the crystal, however, a detailed discussion of bond lengths and angles cannot be made with good accuracy.

1,1'-Bis{[4]-dendralenyl}ferrocene **192** was another of our intended target molecules. The synthesis of disubstituted ferrocene-dithiole species **193** was achieved (33% yield), by treating ferrocenyl diphosphonium salt **143** with two equivalents of ^{n}BuLi, followed by addition of dithiole aldehyde **184**.



192



193

Unfortunately, in this case, the all-*trans* isomer could not be isolated. Indeed, the formylation of compound **193** produced a further mixture of isomers as shown by a number of aldehyde peaks in the ^{1}H NMR spectrum. Further steps leading to the formation of a [4]-dendralene were subsequently abandoned.

3.4 CV DATA AND DISCUSSION

In this chapter we have presented a series of 1,3-dithiole-ferrocene species; the spacer groups between the two different redox centres are composed of either one or three sp^2 carbon atoms. The CV data obtained (Table 3.1), indicate that the length of the bridging species has some effect upon the redox properties of these compounds. A selection of voltammograms are shown in Figure 3.8.

Dithiole-ferrocenes **164** and **166** both give $E_1^{1/2}$ values at 0.33V and 0.42V, and $E_2^{1/2}$ at 0.75V and 0.85V, respectively. Compound **185** has a similar initial redox value (0.33V), but the second oxidation takes place more readily ($E_2^{1/2}$ = 0.49V). There are two possible reasons for this, assuming that the oxidation of the 1,3-dithiole-ylidene sub-unit precedes that of ferrocene: (i) Coulombic repulsion may inhibit the formation of the ferricinium cation, and , therefore, will be more difficult to achieve for the more compact systems **164** and **166**; (ii) delocalisation of the radical cation of the primary oxidised species may extend to the cyclopentadienyl ring, resulting in a decrease of electron density within the ferrocene moiety. In the latter case delocalisation may be more pronounced (with respect to **185**), in the Cp rings of species **164** and **166** due to the shorter spacer groups of these compounds. The first explanation, however, is the most likely and preferred hypothesis.

Compounds **169-171** display two single-electron reversible oxidations and a third irreversible oxidation at 1.00-1.15V. A striking feature of the data for these compounds is that the first oxidation occurs at an unusually low potential (0.06-0.16V). A possible reason for this behaviour is that the oxidation of the entire delocalised system is observed, involving significant interaction between the two 1,3-dithiole rings and ferrocene. By comparison, compound **193** does not display its first oxidation wave at such a low value, but it does, however, undergo three separate reversible oxidations within a narrow range (0.29-0.67V). These results suggest that compounds **169-171** behave quite differently, in terms of their electrochemistry, than the π-extended analogue **193**.

Dimer **173** displays four redox waves between 0.14V and 0.83V. The first value is also quite low and may be due to the high electron-rich state of the molecule as a whole. Remarkably, the fourth oxidation (probably corresponding to ferrocene → ferricinium), occurs at a similar value to $E_2^{1/2}$ for compounds **163** and **165**; due to the close proximity of charges in the tetra-cationic state of **173**, $E_4^{1/2}$ was expected to be much higher.

The [3]-dendralenes **176a-176c** display two initial single-electron reversible waves,[119] which correspond to the electrochemical behaviour of simple vinylogous TTF systems (*e.g.* **19**, **21**, **23** and **24**, Chapter 1). The third oxidation of these species, however, occurs at a much higher potential (*ca.* 1.2V), and is consistent with

values for isolated 1,3-dithiole-2-ylidene systems. The latter oxidation, therefore, is assigned to the orthogonal dithiole ring of [3]-dendralenes **176a-176c** (see Figure 3.3).

COMPOUND	DITHIOLE: FERROCENE RATIO	$E_1^{1/2}$/V	$E_2^{1/2}$/V	$E_3^{1/2}$/V	$E_4^{1/2}$/V
146	0:2	0.34	0.55	---	---
164	1:1	0.33	0.77	---	---
166	1:1	0.42	0.85	---	---
169	2:1	0.16	0.47	1.00[b]	---
170	2:1	0.06	0.51	1.05[b]	---
171	2:1	0.10	0.56	1.15[b]	---
173	2:2	0.14	0.35	0.70	0.83
176a	3:0	0.08	0.33	1.25	---
176b	3:0	0.36	0.49	1.20	---
176c	3:0	0.25	0.47	1.24	---
177a	4:0	0.26	0.37	0.69[a]	---
177b	4:0	0.23	0.39	0.81[a]	---
180	2:0	0.61[b]	0.81[b]	---	---
181	2:1	0.35	0.48	0.65	---
182	2:1	0.35	0.50	0.65	---
185	1:1	0.33	0.49	---	---
186	1:1	0.38	0.86[b]	---	---
189	1:2	0.26	0.40	0.55	---
191	2:2	0.37[a]	0.61	0.76	---
193	2:1	0.29	0.55	0.67	---

Table 3.1: Cyclic voltammetric data; Pt working electrode, Pt gauze counter electrode, Ag/AgCl reference electrode, 0.2 mol dm^{-3} $^nBu_4N^+PF_6^-$, 10^{-4} mol dm^{-3} compound in dry dichloromethane, under nitrogen or argon at 20°C, with iR compensation. All waves represent a reversible, one electron process except where indicated. [a] Single two electron wave. [b] Irreversible wave.

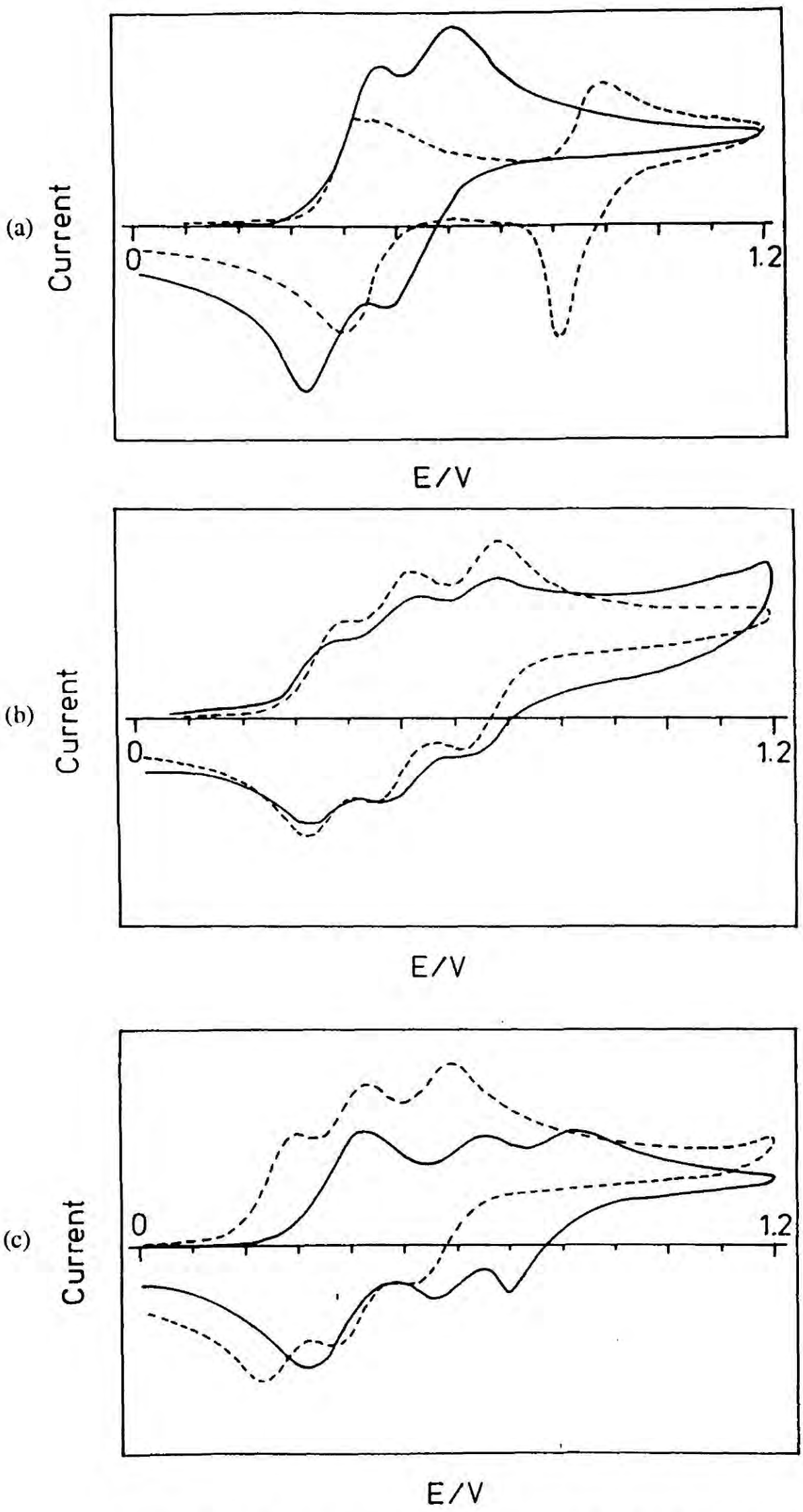


Figure 3.8: Cyclic voltammograms of compounds (a) **166** [----] and **185** [——]; (b) **181** [----] and **182** [——] (c) **189** [----] and **191** [——].

The [4]-dendralenes **177a** and **177b** exhibit similar $E_1^{1/2}$ and $E_2^{1/2}$ values,[119] but the third oxidation waves represent a reversible two-electron process at much lower values (*ca.* 0.7-0.8V), than those corresponding to the final waves for compounds **176a-176c**. The coalescence of the third and fourth oxidation waves is most unusual with this family of compounds and must be a particular feature of the extensively conjugated [4]-dendralene π-system.

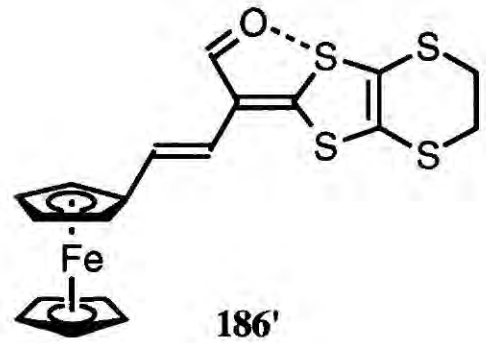
The analogous 2:1 dithiole-ferrocene [3]-dendralenes **181** and **182** display identical electrochemical behaviour to each other. The first two oxidation waves are similar to the methylthio substituted [3]-dendralene **176b**, and can, therefore, be assigned to the two 1,3-dithiole units. The third oxidation waves both occur at 0.65V, and are attributed to the formation of the ferricinium cation. These results indicate a planar configuration between the two dithiole rings, with the pendant ferrocenylethene moiety in orthogonal position. This arrangement represents a deviation from other structures of this family of compounds, where planarity predominates between ferrocene and a single 1,3-dithiole species. Unfortunately, crystallographic proof of structures **181** or **182** could not be obtained.

The first two redox values of [3]-dendralene **189** were expected to be similar to those of compound **185**. In fact, $E_1^{1/2}$ and $E_2^{1/2}$ for the former were found to be lower by 0.07V and 0.09V, respectively. The third oxidation wave is assigned to the orthogonal ferrocene unit, and is at a lower potential than that of the ferrocene units in **181** and **182** by 0.1V - this is possibly due to the extra spacer length between the redox centres of **189**, and, hence, a decrease in Coulombic repulsion.

The 2:2 dithiole-ferrocene [4]-dendralene **191** is rather different from the tetrakis(1,3-dithiole)-[4]-dendralenes **177a** and **177b** in its redox behaviour. Compound **191** displays a reversible two-electron oxidation wave at 0.37V, followed by two single-electron waves at 0.61V and 0.76V. From the X-ray crystallographic structure of **191**, we know that planarity arises once again between one cyclopentadienyl and one dithiole ring. Primary oxidation of dendralene **191** must take place simultaneously at both 1,3-dithiole sites - an unusual feature which is rarely seen in a pair of dithiole species which are separated by only two sp^2 carbon atoms. The third and fourth waves are responsible for the oxidation of the two ferrocenes, and take place independently at 0.61V and 0.76V; both these values are exactly 0.21V higher than the corresponding final two waves of compound **189** - this increase probably results from the extra Coulombic repulsion arising from one additional 1,3-dithiole unit.

Once again, some of the conclusions made in this section are speculative, relying heavily upon deductions from molecular structure and inter-relating CV data. Due to the complicated nature of dendralene systems, most model compounds were of

no benefit for the assignment of redox peaks. Aldehydes **180** and **186**, in particular gave confusing results: irreversible oxidation waves were recorded for the dithiole units of these compounds, and are possibly due to the formation of stable alkoxide radicals. Furthermore, a very low oxidation wave for ferrocene was noted in compound **186** (0.38V); the ferrocene unit, therefore, is a better donor than the dithiole-ylidene, since the latter will be deactivated by the electron withdrawing effect of the aldehyde group. It is also possible that the existence of conformation **186'** with a close intramolecular O---S contact will modify the electrochemical behaviour. Consequently, the first oxidation of **186** can be likened to that of *trans*-1,2-diferrocenylethene **146** which displays an initial redox potential at 0.34V.



186'

In summary, we have prepared a series of 1,3-dithiole-ferrocene compounds with fascinating and variable redox properties. The formation of the ferrocene-containing [3]- and [4]-dendralenes, in particular, has established a group of compounds with high donor ability - electrochemical multi-stage redox reactions can be performed on these systems to attain tri- and tetra-cation species in the region of 0.26-0.76V.

CHAPTER 4

[4+2] CYCLOADDITION REACTIONS OF VINYLTETRATHIAFULVALENE DERIVATIVES

4.1 INTRODUCTION

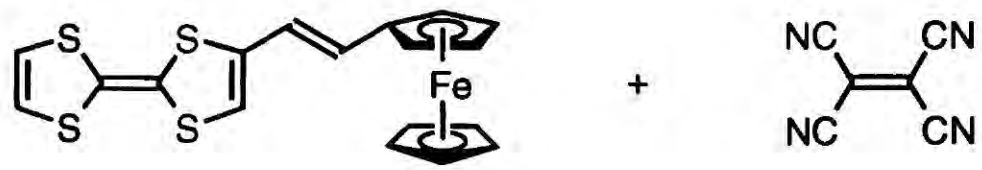
During our attempts to form charge transfer (CT) salts of vinyl-TTF species **137** with TCNQ and TCNE, initial analyses suggested that the materials obtained were not CT complexes but, instead, compounds that were formed by covalent interaction between the donor and the acceptor. Identification of these products has provided a series of compounds representing a novel reaction scheme for TTF derivatives.

4.2 TCNE ADDUCT 194: CHARACTERISATION AND X-RAY STRUCTURE

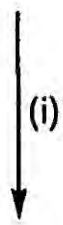
Mixing equimolar amounts of *trans*-1-ferrocenyl-2-(4-tetrathiafulvalenyl)ethene **137** and tetracyanoethylene (TCNE) **30** in acetonitrile, under reflux, produced a very dark and instantaneous colour change of the solution which is characteristic of a TTF CT complex being formed. Unexpectedly, the mixture quickly turned orange, and after several hours a crystalline solid was deposited. Elemental analysis of this compound indicated a 1:1 adduct, but from IR and NMR data it was clear that the product was not a CT complex. Furthermore, the mass spectrum of the product gave a peak at 543 mass units (DCI), suggesting that a covalent compound had been isolated (RMM **137** + RMM **30** = 542). X-Ray crystallographic analysis showed the product to be the novel Diels-Alder adduct **194** (Scheme 4.1).

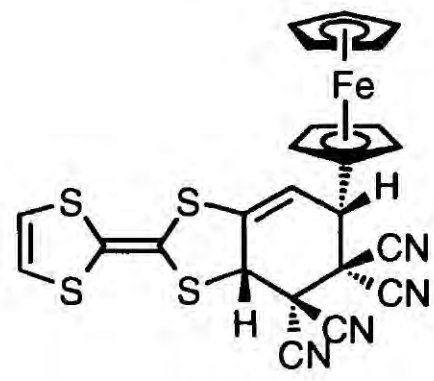
Compound **194** crystallises as a 1:1 acetonitrile solvate (Figures 4.1a and 4.1b). A remarkable feature of the structure of **194** is that the π-bonding of TTF has been disrupted. Thus while ring A preserves the usual geometry of TTF, with a slight folding of 5.3Å along the S(3)---S(4) line, ring B contains an sp^3 carbon atom, C(14), and adopts a nonsymmetric half-chair conformation. The fused six-membered ring adopts a twisted sofa conformation, with C(12) and C(13) deviating by 0.16 and

-0.61Å from the C(14)-C(15)-C(16)-C(11) plane. The crystal structure revealed the stereochemistry shown in Figures 4.1a and 4.1b.



137 **13**





194

Scheme 4.1: (i) MeCN, reflux 5mins.

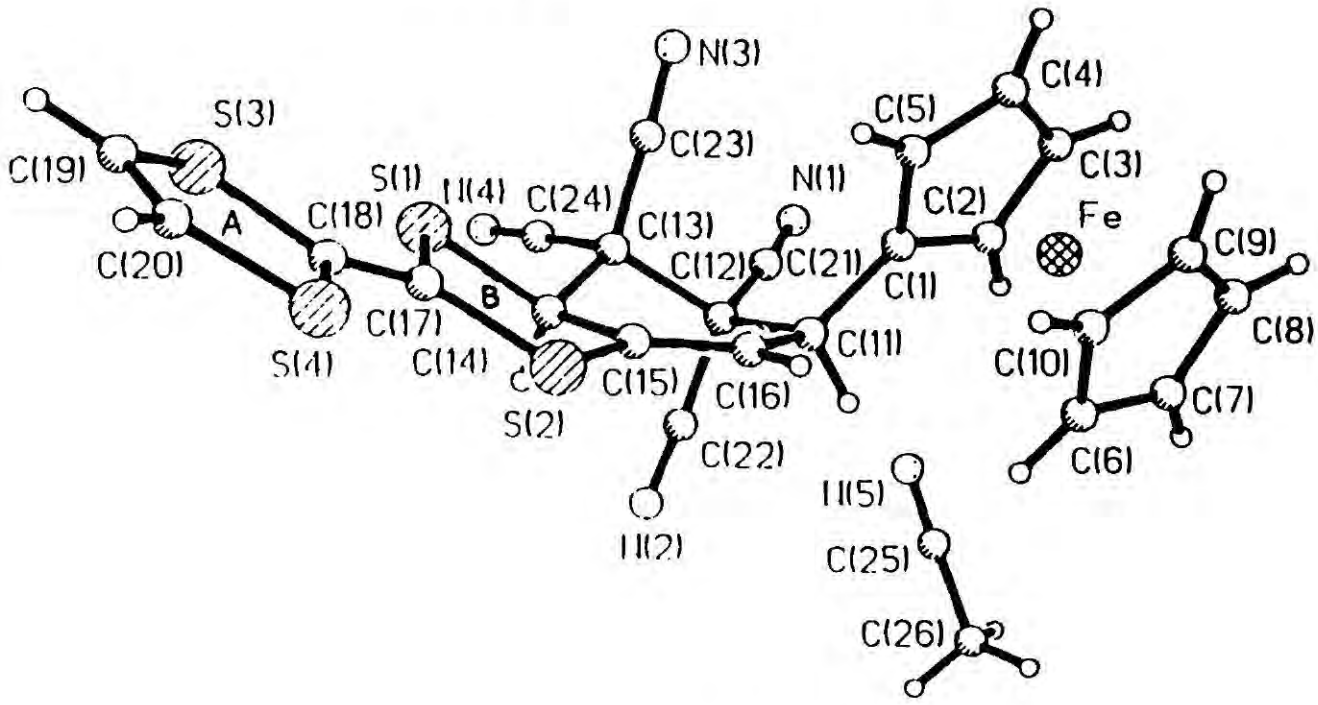


Figure 4.1a: X-ray molecular structure of adduct **194**:acetonitrile solvate with crystallographic numbering scheme.

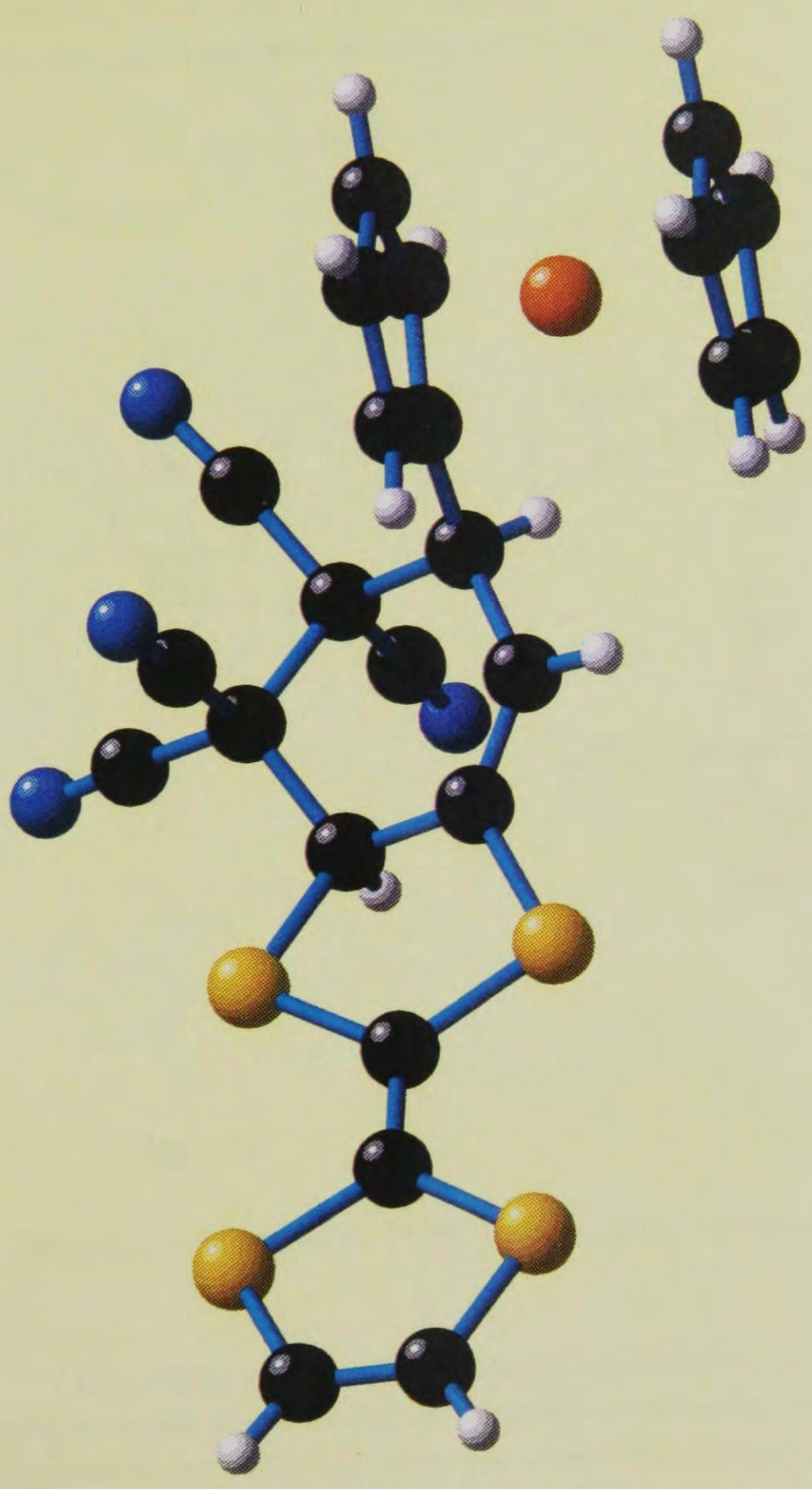
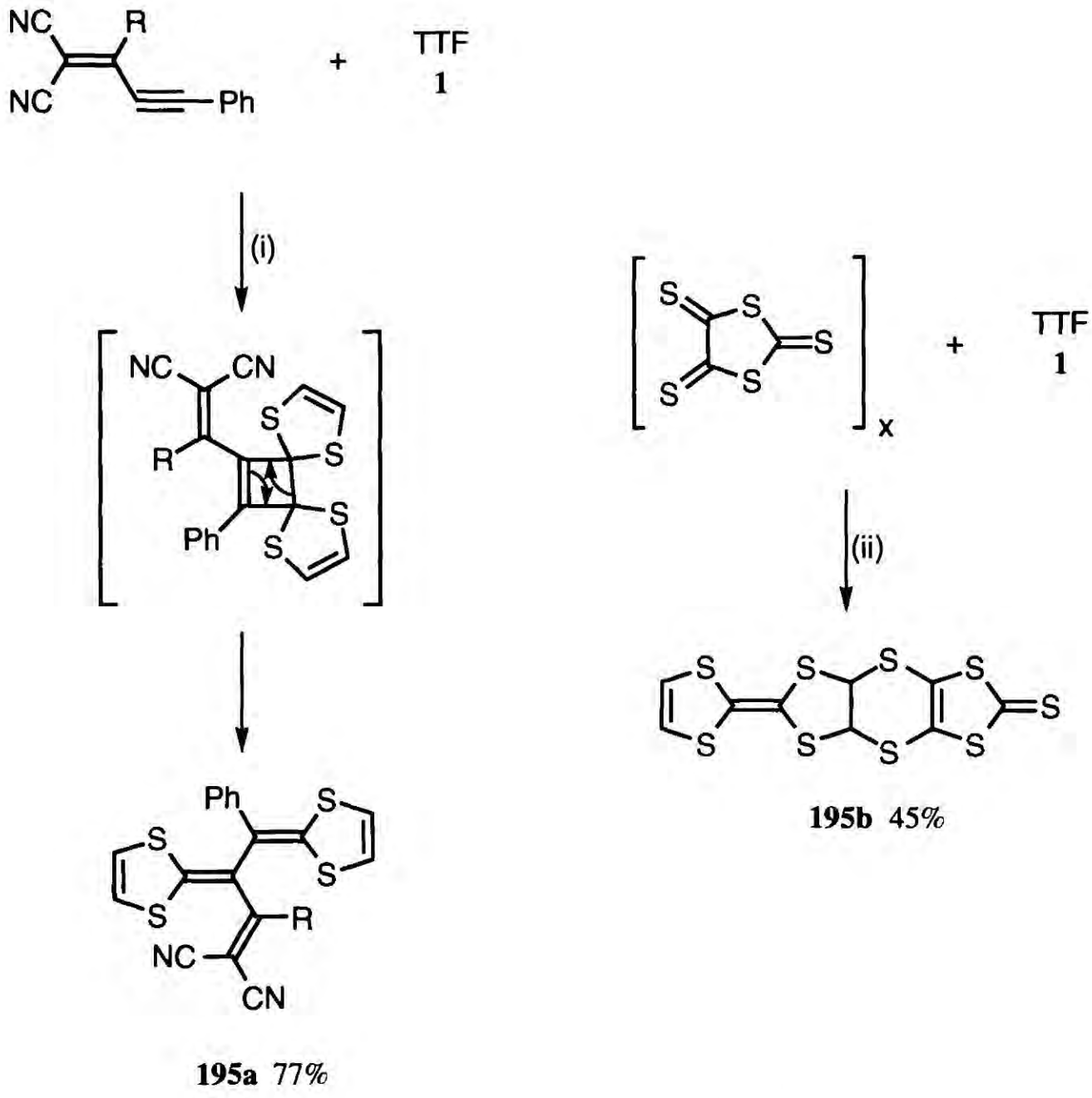


Figure 4.1b: X-Ray molecular structure of **194**:acetonitrile solvate.

This reaction provides the first example of a [4+2] Diels-Alder cycloaddition to a TTF derivative in which the TTF moiety acts as a diene. There are, however, two recent examples where TTF acts as a 2π electron dienophile: cycloaddition can take place at the central C=C bond of TTF,[122] and also at the peripheral C=C bond[123] affording adducts **196a** and **196b**, respectively (Scheme 4.2).

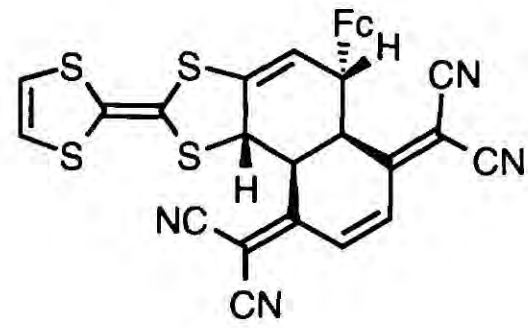


Scheme 4.2: (i) toluene, reflux, 2d; (ii) thiophene, reflux, 4h; then 20°C, 12h.

A similar result to Scheme 4.1 was also observed with **137** and TCNQ, under identical conditions. Elemental analysis of the pale yellow product indicated a 1:1 adduct, however, the ^{1}H NMR spectrum gave broad peaks characteristic of a radical species; the mass spectrum also failed to show an adduct peak, although the possibility of a retro-Diels-Alder reaction occurring under mass spectroscopic conditions cannot be

discounted. The failure to provide conclusive proof for either structures **196a** or **196b** was rather disappointing, since this would be a rare example of a [4+2] TCNQ adduct.

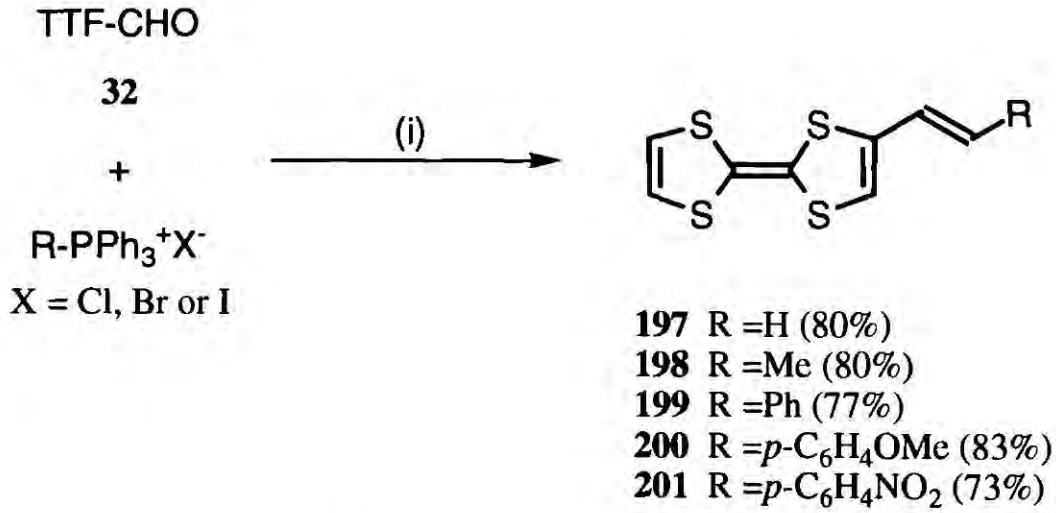
196a



196b

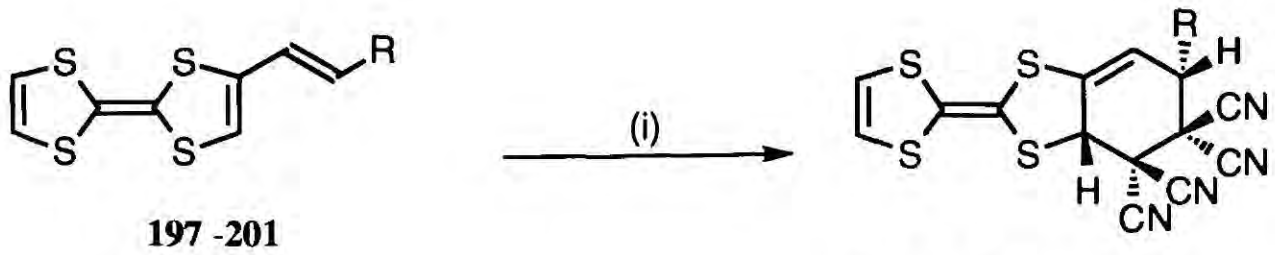
4.3 OTHER VINYL-TTF ADDUCTS

To explore the generality of the reaction in Scheme 4.1, a modest range of vinyl-TTF derivatives was prepared from TTF-carboxaldehyde **32** and a selection of Wittig salts (Scheme 4.3).



Scheme 4.3: (i) ^{n}BuLi, THF, -78°C, 15mins.

Compounds **197-201** were reacted with TCNE to afford the [4+2] adducts **202-206** (Scheme 4.4). Predictably, the reactions proceed more readily when substituent R is electron releasing (*i.e.* **137**, **200**).

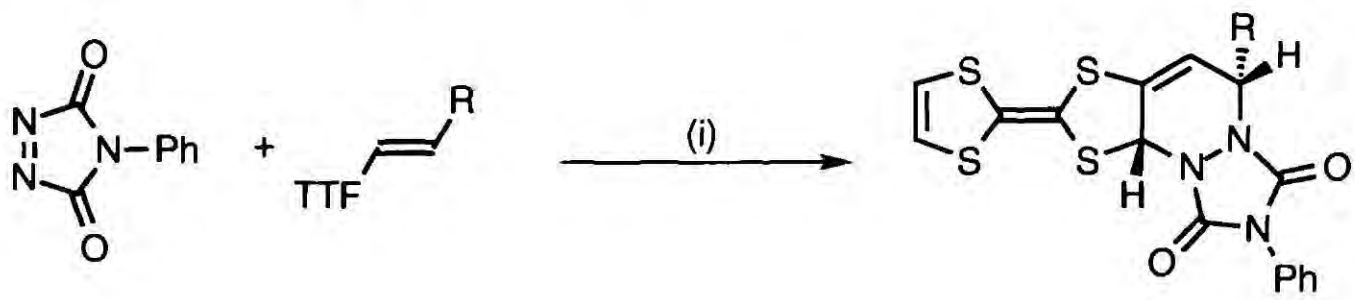


197 -201

194 R =Fc (77%)
202 R =H (70%)
203 R =Me (56%)
204 R =Ph (59%)
205 R =*p*-C_6H_4OMe (75%)
206 R =*p*-$C_6H_4NO_2$ (42%)

Scheme 4.4: (i) TCNE, toluene, reflux, 16h.

The dienophile *N*-phenyl-1,2,4-triazoline-3,5-dione reacted readily with the vinyl-TTF compounds **137** and **197-200** (Scheme 4.5).

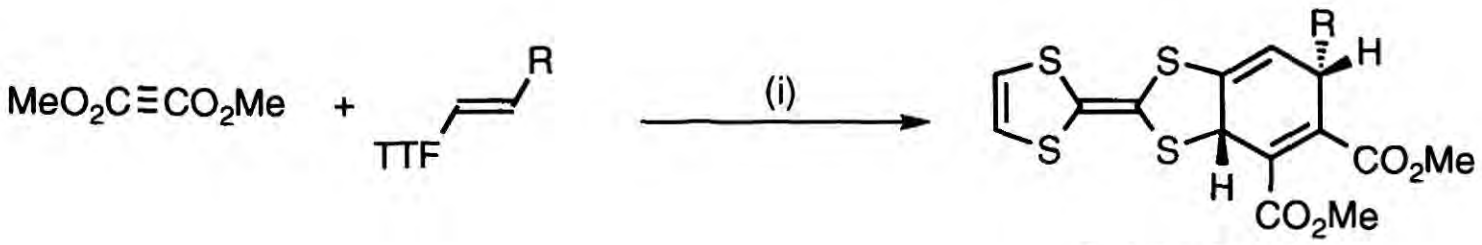


207 R =H
208 R =Me
209 R =Ph
210 R =*p*-C_6H_4OMe (61%)
211 R =Fc (33%)

Scheme 4.5: (i) toluene, reflux, 4h.

Unfortunately, a number of products were formed in each reaction (TLC evidence). Mass spectroscopic data gave the correct masses for 1:1 adducts **207-211**, but only species **210** and **211** (61% and 33% yield, respectively) were obtained pure. Similar results were obtained using dimethylacetylenedicarboxylate as the dienophile (Scheme 4.6). Early TLC observations indicated the formation of the DMAD adducts **212-216**, which decomposed as the reaction time increased. The only product obtained pure was compound **212** which was isolated as a red solid in 46% yield.

Even this compound, however, eventually decomposed over several days, at 20°C. Mass spectroscopy of the crude product mixtures gave peaks corresponding to compounds **213-216**, together with additional peaks several hundred mass units higher.



212 R =H (46%)
213 R =Me
214 R =Ph
215 R =*p*-C_6H_4OMe
216 R =Fc

Scheme 4.6: (i) toluene, reflux, 16h.

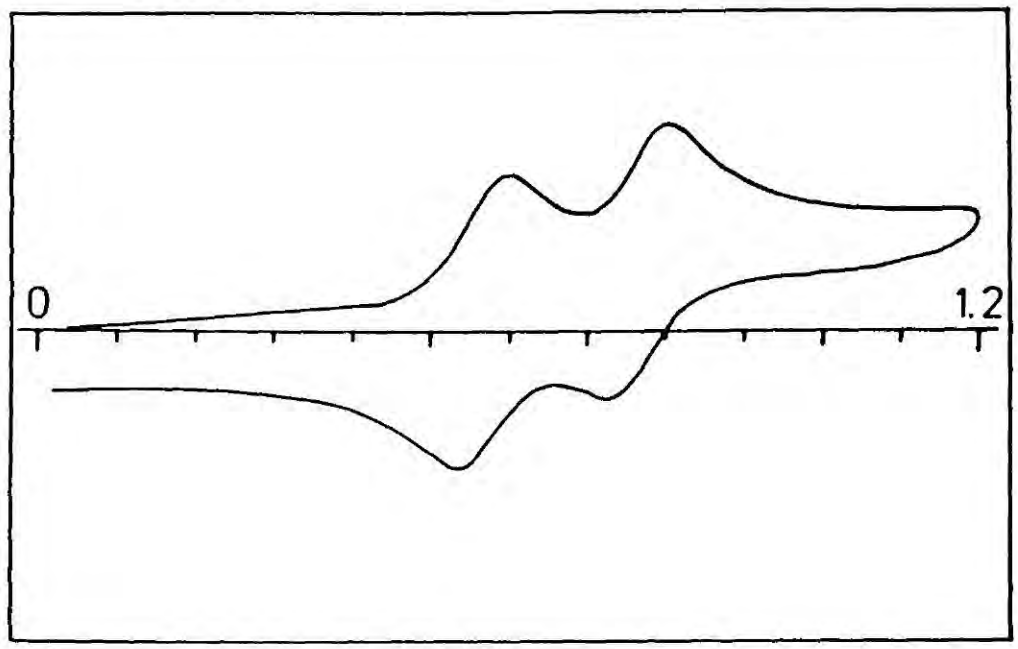
4.3 CV DATA AND DISCUSSION

The electrochemical properties of the vinyl-TTF species and their adducts, were examined by cyclic voltammetry; the CV data are presented in Table 4.1, with selected voltammograms shown in Figure 4.2. Compounds **196-200** gave standard voltammograms for simple TTF derivatives, with redox potentials slightly higher than TTF itself. Ferrocene species **194** displays two single-electron reversible waves: the first at 0.57V is due to the ferrocene component, whilst the second at 0.77V is typical of an isolated 1,3-dithiole-2-ylidene system.

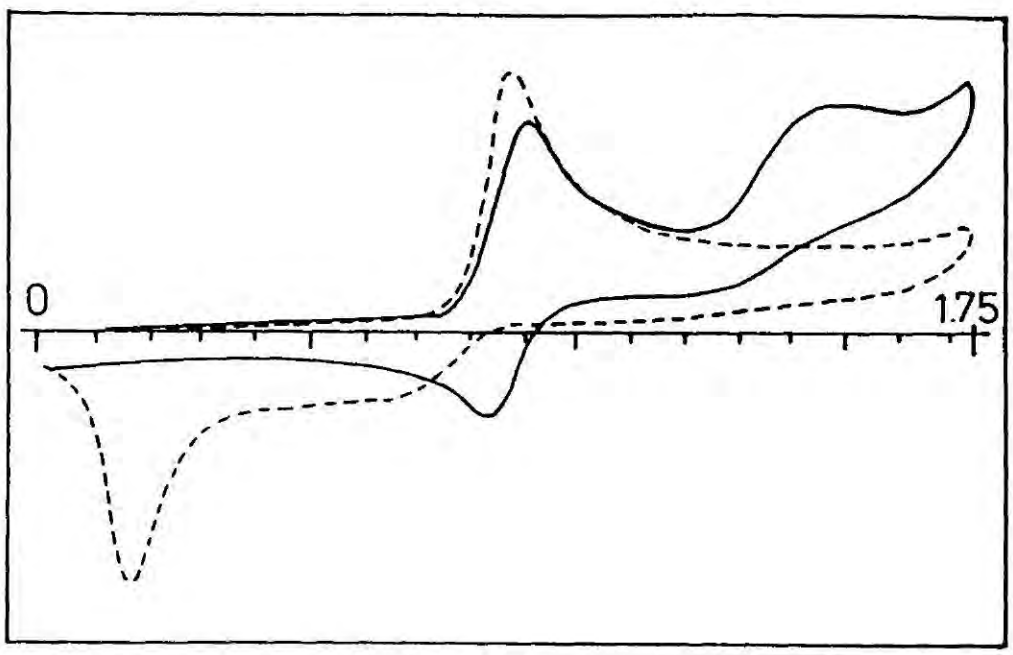
Molecule	TTF-CH=CH-R	Dienophile	$E_1^{1/2}$	$E_2^{1/2}$
197	H	---	0.41[74b]	0.77[74b]
198	Me	---	0.38	0.83
199	Ph	---	0.40	0.90
200	*p*-C_6H_4OMe	---	0.39	0.85
201	*p*-$C_6H_4NO_2$	---	0.43	0.80
194	Fc	TCNE	0.57	0.77
202	H	TCNE	0.52	1.08
203	Me	TCNE	0.52	---
204	Ph	TCNE	0.88	1.45[a]
205	*p*-C_6H_4OMe	TCNE	0.87	1.37[a]
210	*p*-C_6H_4OMe	NPTAD	0.68	1.06
211	Fc	NPTAD	0.47	1.11[a]
212	H	DMAD	0.61	1.19[a]

Table 4.1: Cyclic voltammetric data; Pt working electrode, Pt gauze counter electrode, Ag/AgCl reference electrode, 0.2 mol dm^{-3} $^nBu_4N^+PF_6^-$, 10^{-4} mol dm^{-3} compound in dry dichloromethane, under nitrogen or argon at 20°C, with iR compensation. All waves represent a reversible, one electron process except where indicated: [a] irreversible wave.

(a)



(b)



(c)

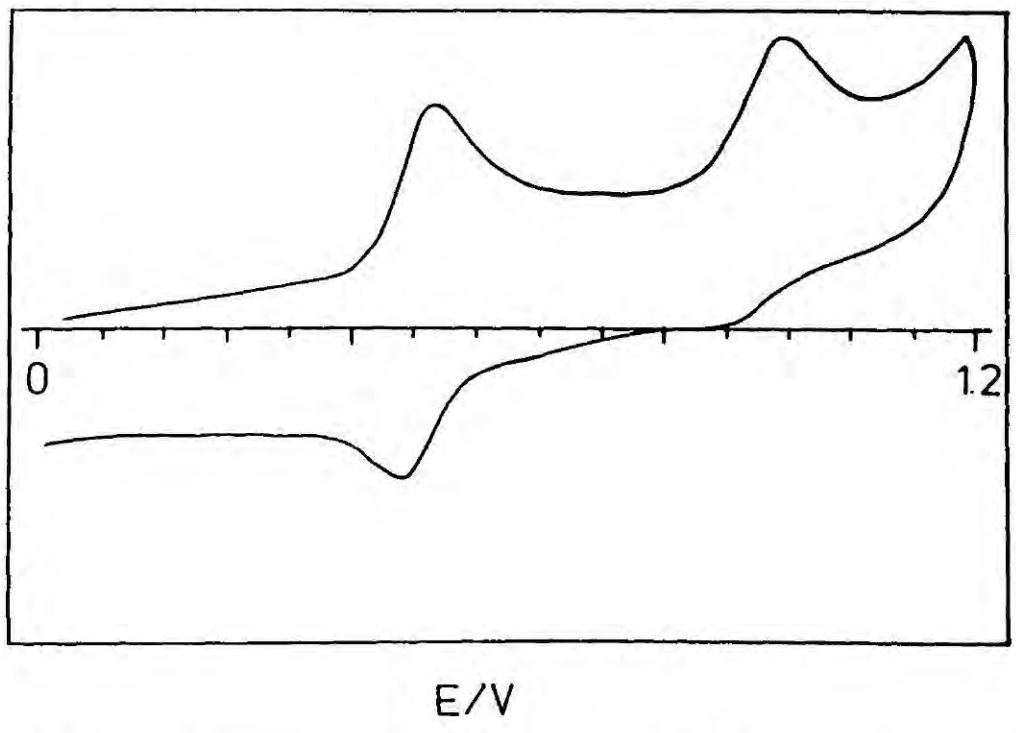


Figure 4.2: Cyclic voltammograms of compounds (a) **194** [——]; (b) **203** [----] and **204** [——]; (c) **202** [----].

Adducts **204**, **205**, **211** and **212** give one single-electron reversible wave, followed by a second irreversible oxidation peak. The latter is postulated to arise from a product formed by chemical reaction of the cation radical. Compound **202**, however, displays one extra peak (at *ca.* 0.1V), compared to **204**, **205** and **212**. This occurrence results in $E_1^{1/2}$ and $E_2^{1/2}$ values of 0.52V and 1.08V, respectively, although the E_{ox}-E_{red} are extremely large (0.82V for the first wave, and 0.59V for the second). Such high values are not typical of standard redox species, therefore, some doubt arises whether these peaks are actually related. A similar result is also seen with adduct **203**, which displays only one single-electron reversible wave at 0.52V (E_{ox}-E_{red} = 0.75V). In summary, we have presented a collection of CV data which are in some cases predictable, and in others inexplicable. We are able to conclude from these results, however, that the π-delocalisation within the TTF moieties of the [4+2] adducts has been disturbed to the extent that the unique electrochemical properties of the donor have been essentially destroyed.

CHAPTER 5

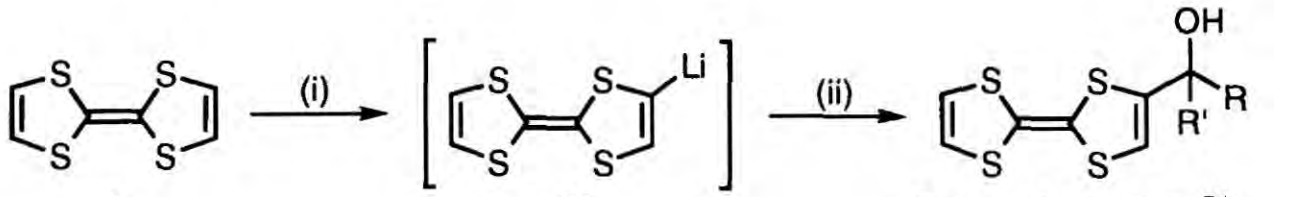
NUCLEOPHILIC ADDITION OF TETRATHIAFULVALENYLLITHIUM TO ALDEHYDES AND KETONES

5.1 INTRODUCTION

Green[74c] first demonstrated that TTF organolithium species **31** was a suitable reagent for nucleophilic addition to a carbonyl functionality yielding TTF-CH_2OH **37** (34%), from the reaction with formaldehyde. Remarkably, extension to other aldehydes and ketones had not been reported. In this chapter, we present a series of TTF derivatives prepared from the reaction of TTFLi **31** with a range of aldehydes and ketones. Results show that these TTF-anion reactions can proceed in excellent yield, to give highly functionalised redox active materials.

5.2 THE EFFICIENT SYNTHESIS OF HYDROXYMETHYL-TTF DERIVATIVES

The first new molecules to be synthesised in this family were compounds **217-220** (Scheme 5.1), which were isolated in good yield.



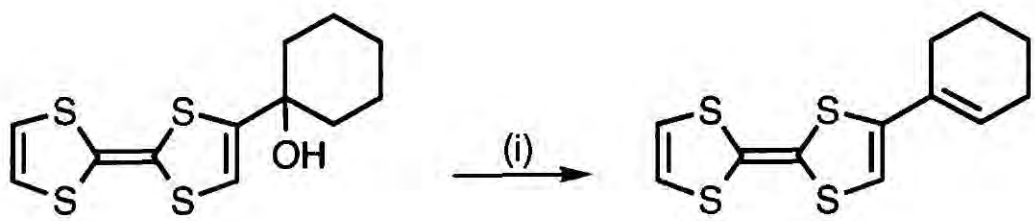
1 **31**

37 R = R' = H (34%)[74c]
217 R = Me, R' = H (60%)
218 R = Ph, R' = H (54%)
219 R = R' = Me (72%)
220 R = R' = Ph (86%)

Scheme 5.1: (i) LDA, Et_2O, -78°C, 1h;
(ii) RC(O)R', -78°C, 1h, then slowly to 20°C, H_2O.

These initial results established that ketones give a slightly better yield than aldehydes. This is probably due to the stability of the resulting compounds, since the secondary alcohols **217** and **218** are less stable than the tertiary compounds **219** and **220**.

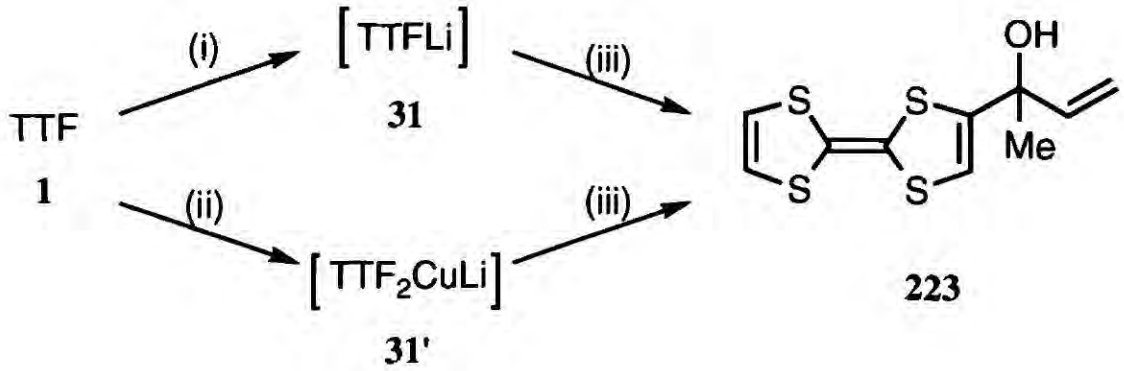
One decomposition pathway of the TTF alcohols involved the elimination of water. Compound **221**, prepared from TTFLi **31** and cyclohexanone (44% yield, Scheme 5.2), slowly dehydrated under ambient conditions (^{1}H NMR spectroscopic evidence - the process is efficiently catalysed with the addition of HCl.Et_2O), to the cyclohexene derivative **222**.



221 **222**

Scheme 5.2: (i) HCl.Et_2O, DCM, 1h.

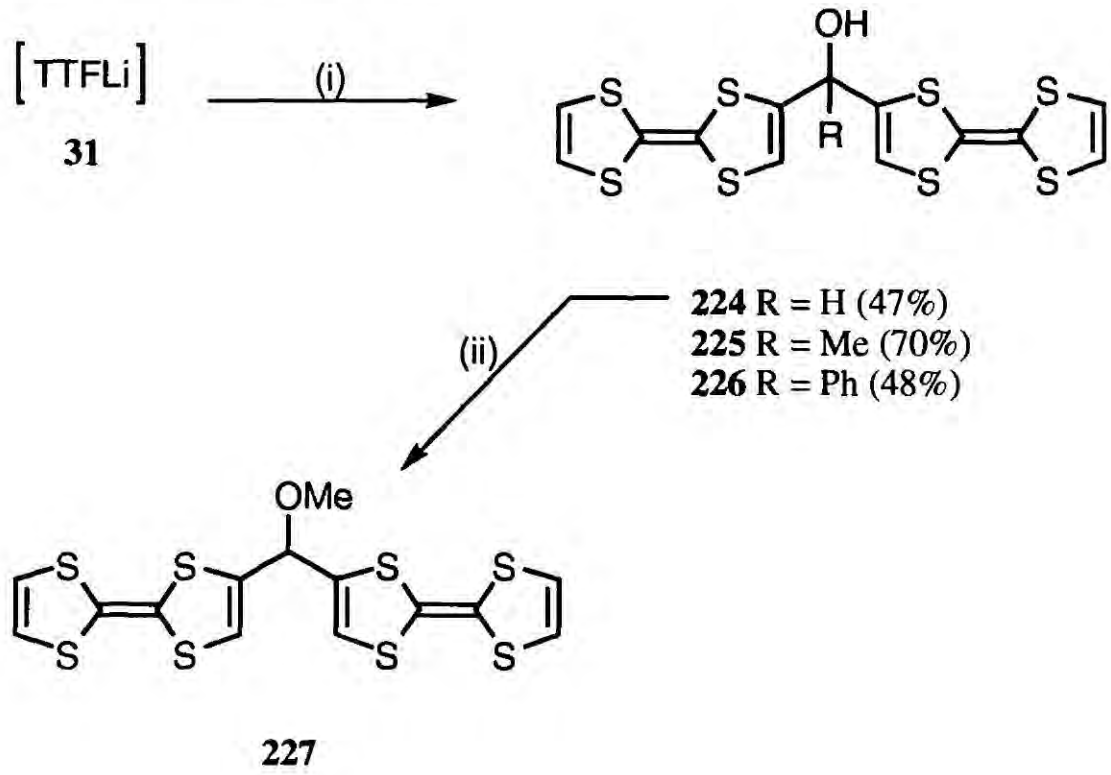
We have also studied the feasibility for the TTF anion to perform 1,4-Michael addition reactions. TTFLi **31** and the cuprate complex, TTF_2CuLi **31'** (which we assume was formed from the addition of cuprous chloride to **31**), were reacted with methylvinylketone (Scheme 5.3); the only compound isolated in both cases was, however, the 1,2-addition product **223** (66% yield).



223

Scheme 5.3: (i) LDA, Et_2O, -78°C; (ii) LDA, Et_2O, -78°C, CuCl;
(iii) CH_2=CHC(O)Me, H_2O.

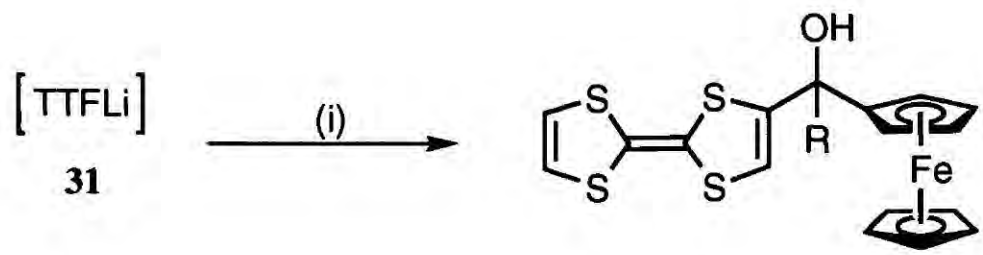
TTFLi **31** reacted with carboxaldehyde **32**, acetyl-TTF and benzoyl-TTF (the latter two prepared from the reaction of **31** with acetyl chloride and benzoyl chloride, respectively), to produce the bis-TTF compounds **224-226**. Although several close-linked bis-TTF compounds (containing chalcogen, alkyl, aryl, silyl, phosphorus and mercuric spacer groups), have been synthesised in recent years,[124-136] none has hitherto been reported which bears functional groups which can be used in further syntheses. Methylation of **224**, for instance, can be carried out in 75% yield to give the methyl ether **227** (Scheme 5.4).



227

Scheme 5.4: (i) TTFC(O)R; (ii) NaH, THF, 20°C, MeI.

Functionalised mixed redox-active systems have also been prepared by reacting TTFLi **31** with ferrocene carboxaldehyde, acetylferrocene and benzoylferrocene, to give compounds **228-230** (Scheme 5.5).



228 R = H (47%)
229 R = Me (90%)
230 R = Ph (63%)

Scheme 5.5: (i) FcC(O)R.

In the structure of compound **229**, deduced by X-ray crystallography, the asymmetric unit (Figure 5.1), comprises two molecules linked by an OH---O bond (O---O distance 3.075Å). In molecule A, the hydroxy H atom is directed towards the ferrocenyl moiety and probably forms an O-H---π bond with the unsubstituted Cp ring. There is also the possibility that the hydroxy H atom may be involved in an O-H---Fe bond: both types of hydrogen bonding have been extensively studied and identified by Epstein *et al.*, using IR spectroscopic techniques, with similar ferrocenylcarbinol compounds of general formula FcCH(R)OH.[137-141] In molecule B, whose OH group is engaged in an intermolecular H-bond, the unsubstituted ring is rotationally disordered. In both molecules, the ferrocene unit is almost perpendicular to the TTF ring; stacks are formed parallel to the [1 1 0] direction, with the ferrocene unit of each molecule sandwiched between the TTF moieties of the adjacent molecules, and *vice versa* (Figure 5.2).

The successful syntheses of the TTF alcohols provided us with a possible route towards a directly attached TTF-ferrocene derivative. Buchmeiser and Schottenberger[142] have prepared the dimetallocene **232** in 21% yield, from ferrocenyl alcohol **231** (Scheme 5.6).

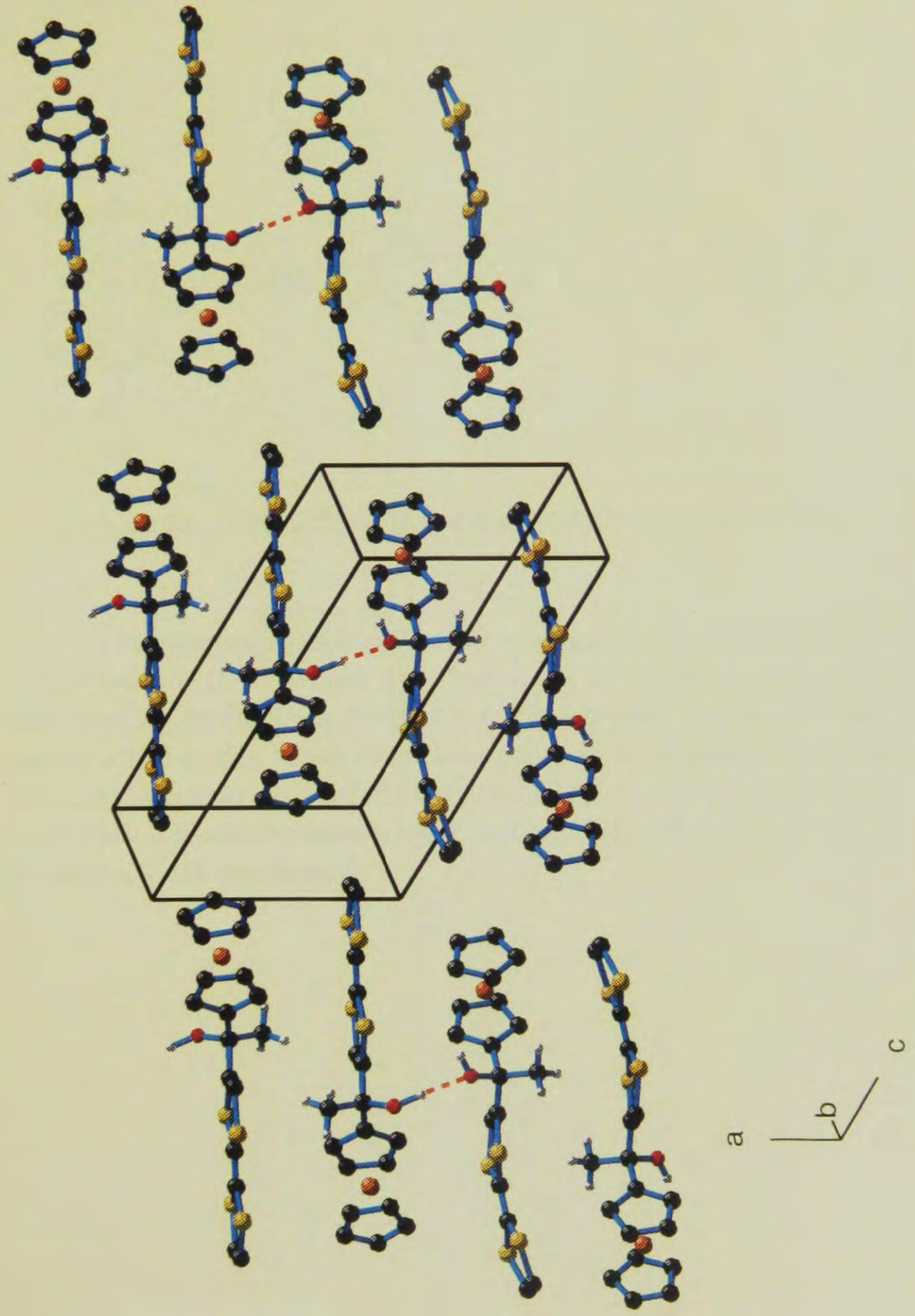
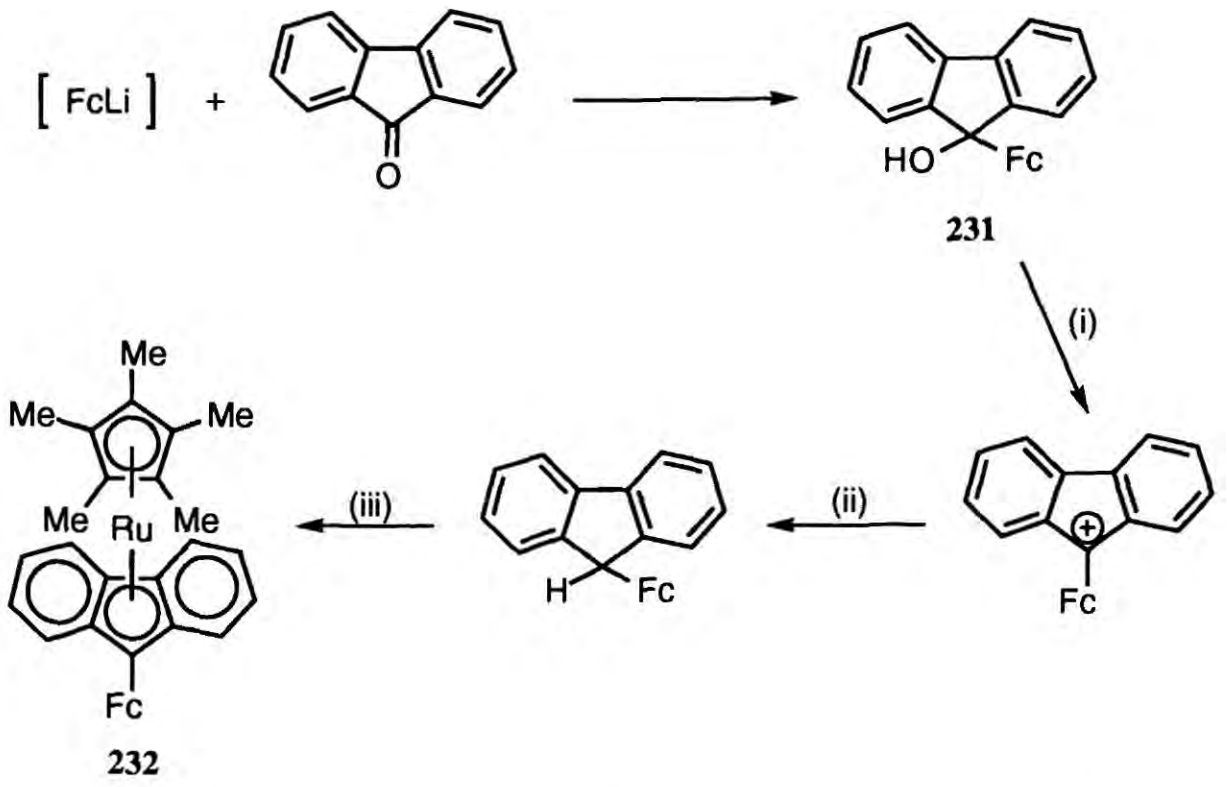
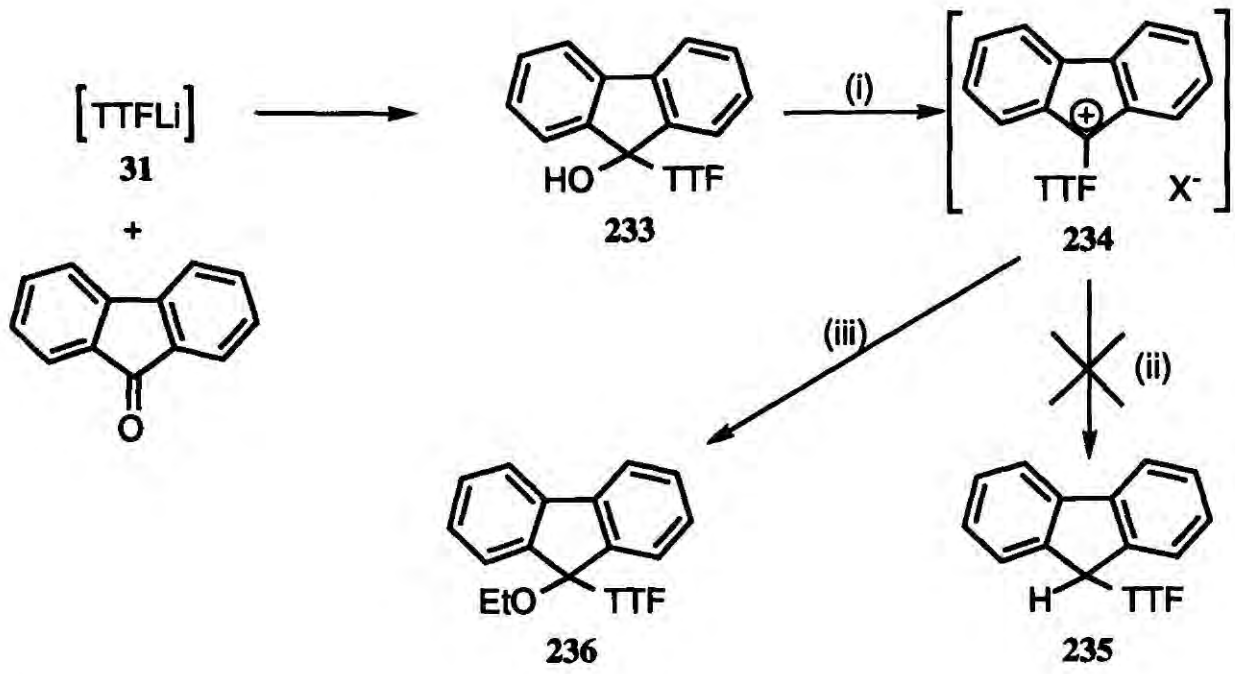


Figure 5.1: X-Ray crystallographic packing diagram of **229**.



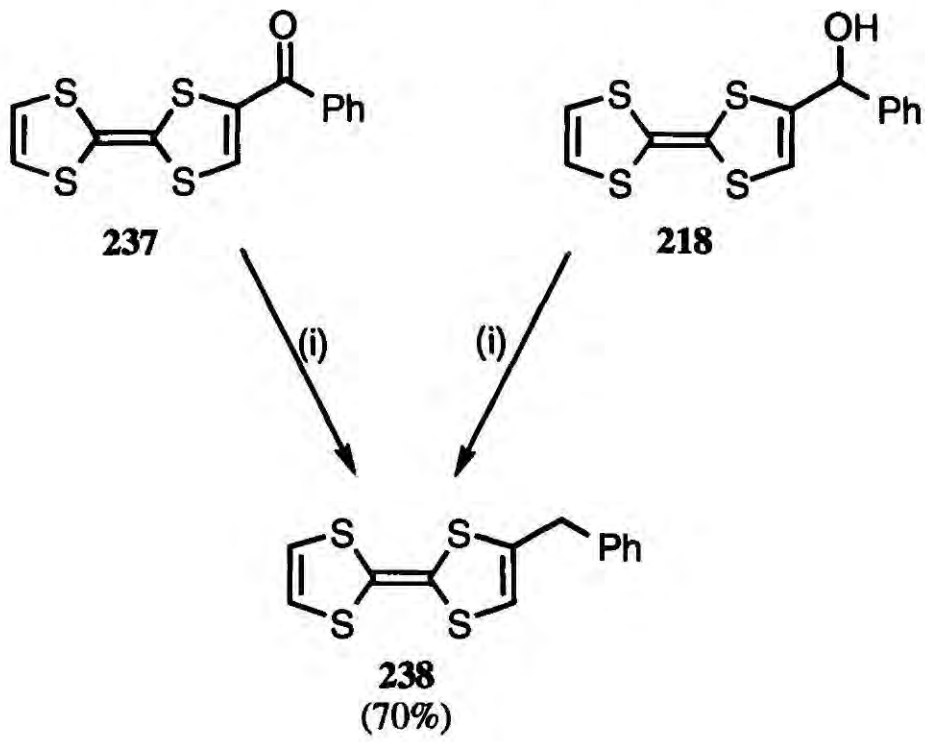
Scheme 5.6: (i) HBF_4, Et_2O; (ii) Na/NH_3 then H_2O; (iii) BuLi, Cp^*Ru^+.

In the same way, TTF derivative **233** was prepared from the reaction of **31** with fluorenone (77%, Scheme 5.7). Protonation of the hydroxy group, and subsequent loss of water, was attempted with tetrafluoroboric acid and also with a solution of HCl etherate. In both cases a black precipitate was obtained which refused to undergo hydride reduction to **235**. Nonetheless evidence for the formation of TTF-cation **234** was provided by the isolation of ethyl ether **236** (33% yield), derived from the reaction of **234** with ethoxide.



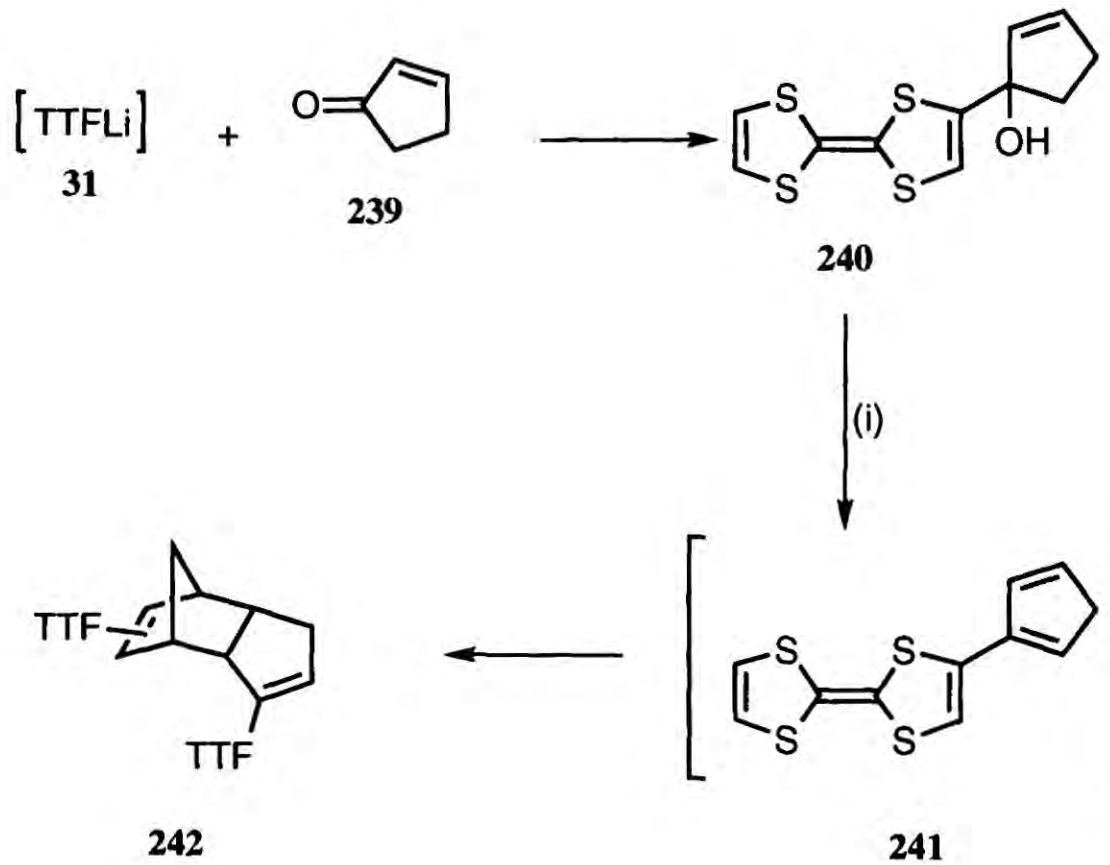
Scheme 5.7: (i) HBF_4 or $HCl.Et_2O$, Et_2O, 0.5h; (ii) $NaBH_4$, MeCN, ^iPrOH; (iii) Na, EtOH.

Another approach towards compound **235** involved the direct reduction of alcohol **233**, using lithium aluminium hydride and aluminium chloride. Indeed, both benzoyl-TTF **237** and alcohol **218** can be reduced to benzyl-TTF **238** with the same reagents (Scheme 5.8). Reduction of **233** by $LiAlH_4/AlCl_3$, however, produced a number of inseparable products; consequently, the use of fluorenyl species for the direct attachment of TTF to a ferrocene derivative was finally abandoned.



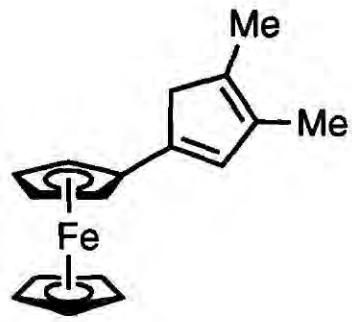
Scheme 5.8: (i) $LiAlH_4/AlCl_3$, Et_2O, 20°C.

Because the TTF cations **234** were causing us many problems, our next attempts at synthesising directly-linked TTF-ferrocene compounds utilised the reliable dehydration process (*e.g.* **221**→**222**) discussed earlier. Cyclopentene alcohol **240** was prepared in 60% yield from the reaction of TTFLi **31** with 2-cyclopenten-1-one **239** (Scheme 5.9). As expected, the 1,4-Michael product was not observed. Acid catalysed dehydration of **240** gave an orange oil in 90% yield; the molecule was assigned structure **242** although the mass spectrum was consistent with monomer species **241**. The ^{1}H NMR spectrum of the product displayed a complex pattern of TTF protons, indicative of dimerisation between two cyclopentadienyl units of **241**.



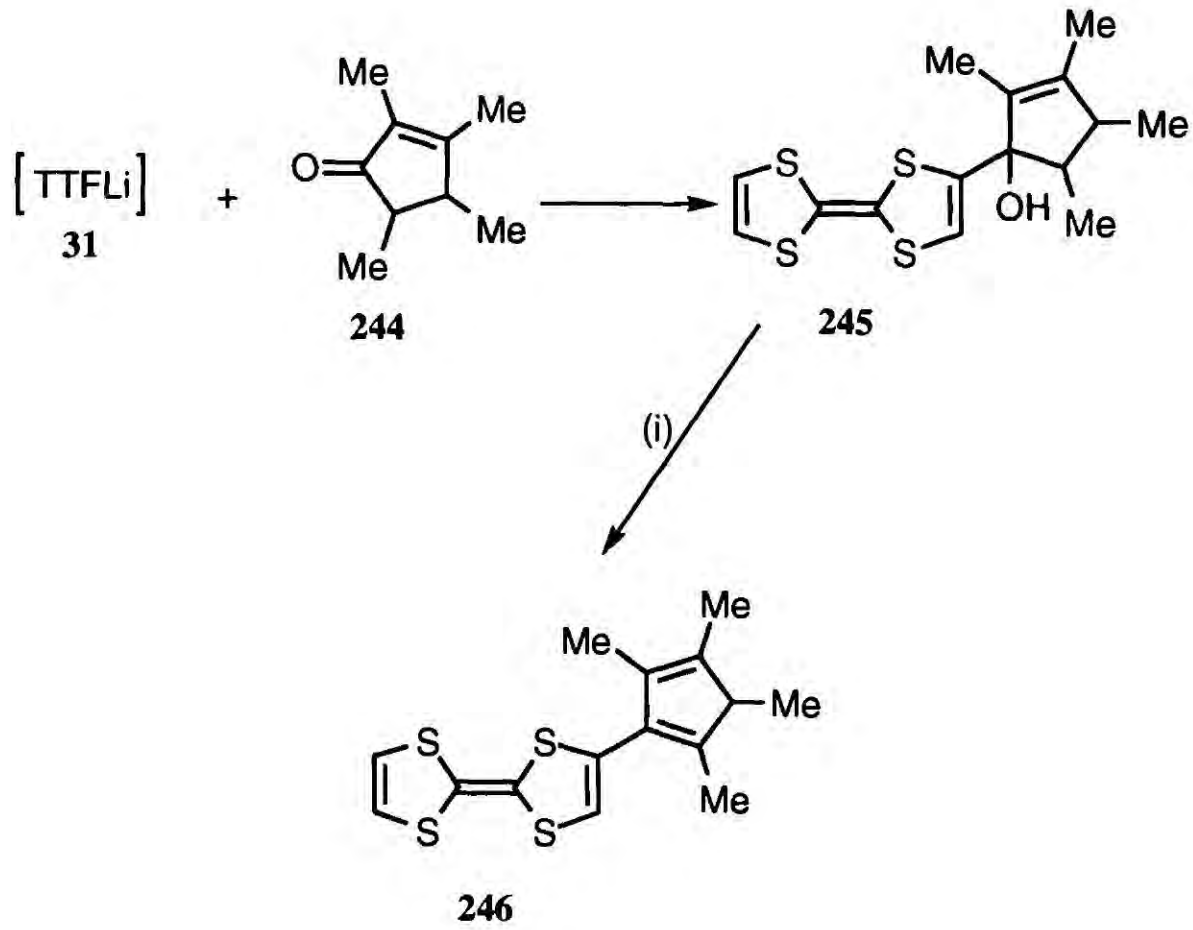
Scheme 5.9: (i) HCl.Et_2O, Et_2O, 20°C, 0.5h.

A similar problem was reported by Rieker *et al.*,[143] who stated that cyclopentadienylferrocene rapidly dimerises even at 0°C. By substituting two of the hydrogen atoms with methyl groups, Plenio[144] found that compound **243** was much more stable, and could be handled at room temperature over several hours.



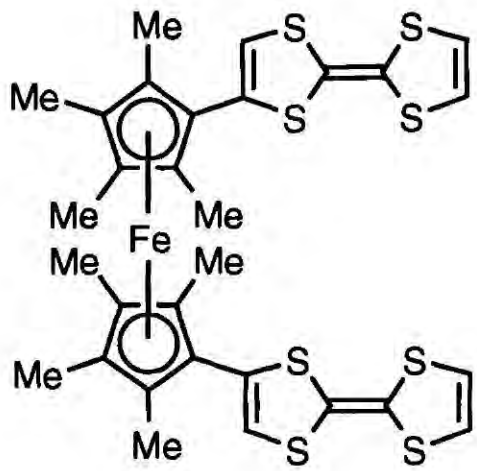
243

We, therefore, prepared TTF derivative **246**, which was stable at room temperature for several weeks. The reaction of TTFLi **31** with 2,3,4,5-tetramethyl-2-cyclopentenone **244** (Scheme 5.9) gave alcohol **245** in 73% yield (Scheme 5.10), protonation of which, followed by elimination of water, produced **246** in 87% yield.



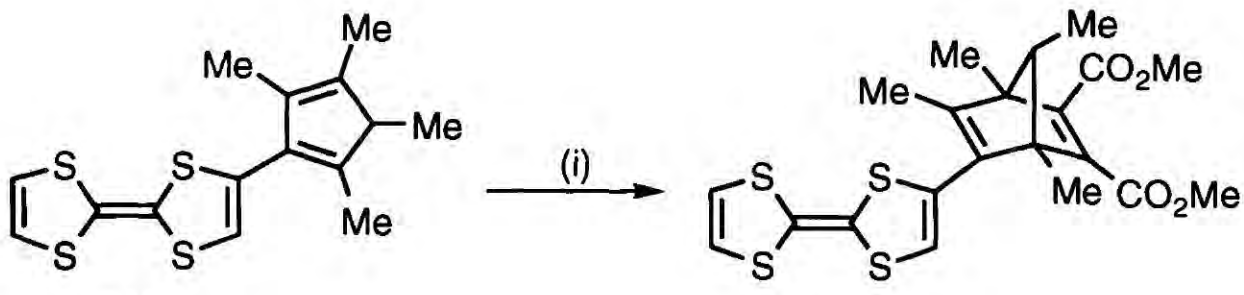
Scheme 5.10: (i) HCl.Et_2O, Et_2O, 20°C, 1h.

Deprotonation of **246**, followed by complexation with Fe^{2+}, was attempted using a range of bases and iron salts. Unfortunately, TTF-ferrocene derivative **247** was not detected from any of the methods used; **246** was recovered unchanged.



247

To probe whether or not dimerisation had taken place with the TTF-cyclopentadienyl derivatives, compounds **242** and **246** were treated, in turn, with dimethyl acetylenedicarboxylate. Only the starting material **242** was recovered after a reaction time of 4 hours in the first instance, whereas the [4+2] adduct **248** was isolated in 89% yield from the reaction with tetramethylcyclopentadienyl-TTF **246** (Scheme 5.11). It is also interesting to note that Diels-Alder [4+2] cycloaddition to **246** did not take place across the vinyl-TTF portion of the molecule.



246 **248**

Scheme 5.11: (i) DMAD, PhMe, 50°C, 4h.

5.3 CV DATA AND DISCUSSION

The CV data of a selection of TTF compounds presented in this chapter are collated in Table 5.1, with sample voltammograms shown in Figure 5.2. Two reversible single-electron oxidation waves are seen for each molecule at redox values similar to those of TTF (with the exception of **238** whose two redox values are both higher by *ca.* 0.3V), with small deviations either side of $E_1^{1/2}$ and $E_2^{1/2}$. Donors **224-226** in each case display a small shoulder at $E_1^{1/2}$ - the second TTF unit is oxidised at a slightly higher potential due to Coulombic repulsion; the second oxidation of each TTF unit, however, occurs simultaneously. Compounds **228-230** display an additional third wave corresponding to the oxidation of the ferrocene unit, 0.47V-0.52V. Finally, the similarity of the voltammogram of compound **248** with TTF itself provides further evidence that the molecule is derived from a [4+2] cycloaddition reaction involving the cyclopentadiene unit, rather than the vinyl-TTF portion (*c.f.* the voltammograms of various adducts, Figure 4.2).

Molecule	R and R' in TTFCR(OH)R' where applicable	$E_1^{1/2}$/V	$E_2^{1/2}$/V	$E_3^{1/2}$/V
218	H, Ph	0.31	0.70	---
219	Me, Me	0.24	0.63	---
220	Ph, Ph	0.35	0.76	---
221	'Cyclohexyl'	0.27	0.68	---
222	see page 96	0.30	0.70	---
224	H, TTF	0.36	0.76	---
225	Me, TTF	0.32	0.74	---
226	Ph, TTF	0.36	0.75	---
227	see page 97	0.43	0.85	---
228	H, Fc	0.28	0.47	0.72
229	Me, Fc	0.29	0.51	0.75
230	Ph, Fc	0.29	0.52	0.75
233	'Fluorenyl'	0.38	0.79	---
238	see page 101	0.60	1.06	---
245	see page 103	0.37	0.74	---
248	see page 104	0.38	0.78	---

Table 5.1: Cyclic voltammetric data; Pt working electrode, Pt gauze counter electrode, Ag/AgCl reference electrode, 0.2 mol dm^{-3} $^nBu_4N^+PF_6^-$, 10^{-4} mol dm^{-3} compound in dry acetonitrile, under nitrogen or argon at 20°C, with iR compensation. All waves represent a reversible, one electron process.

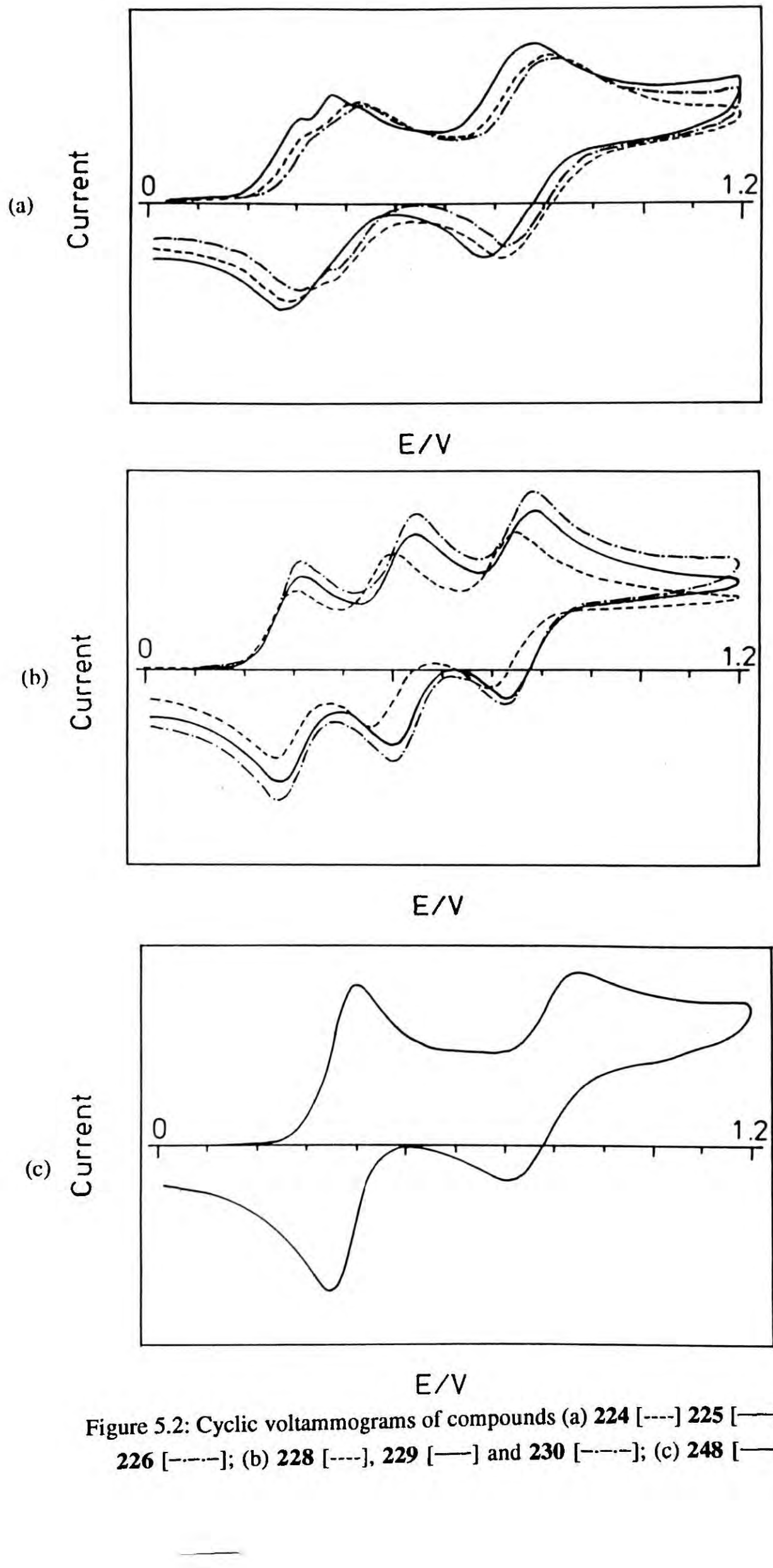
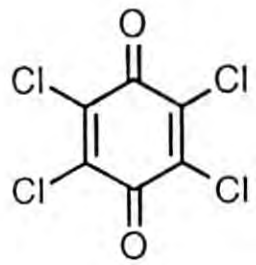


Figure 5.2: Cyclic voltammograms of compounds (a) **224** [----] **225** [——] and **226** [–·–·–]; (b) **228** [----], **229** [——] and **230** [–·–·–]; (c) **248** [——].

5.4 CONDUCTING AND MAGNETIC PROPERTIES OF CHARGE TRANSFER SALT 250

Donor **229** formed a charge transfer complex with chloranil **249** to form a salt **250**, of 2:1 stoichiometry (**229**:**249**). The resulting powder gave a room temperature compressed pellet conductivity of $\sigma_{rt} = 4 \times 10^{-4} Scm^{-1}$.



249

Variable temperature magnetic susceptibility data have been obtained for **250**, and are plotted against temperature as direct (Figure 5.3a) and inverse (Figure 5.3b) functions. The complex shows Curie-Weiss behaviour between *ca.*90-40K; below 40K the material exhibits some form of ferromagnetic ordering. Further detailed investigations into the magnetic behaviour of **250** and other complexes of **229** are currently being made.

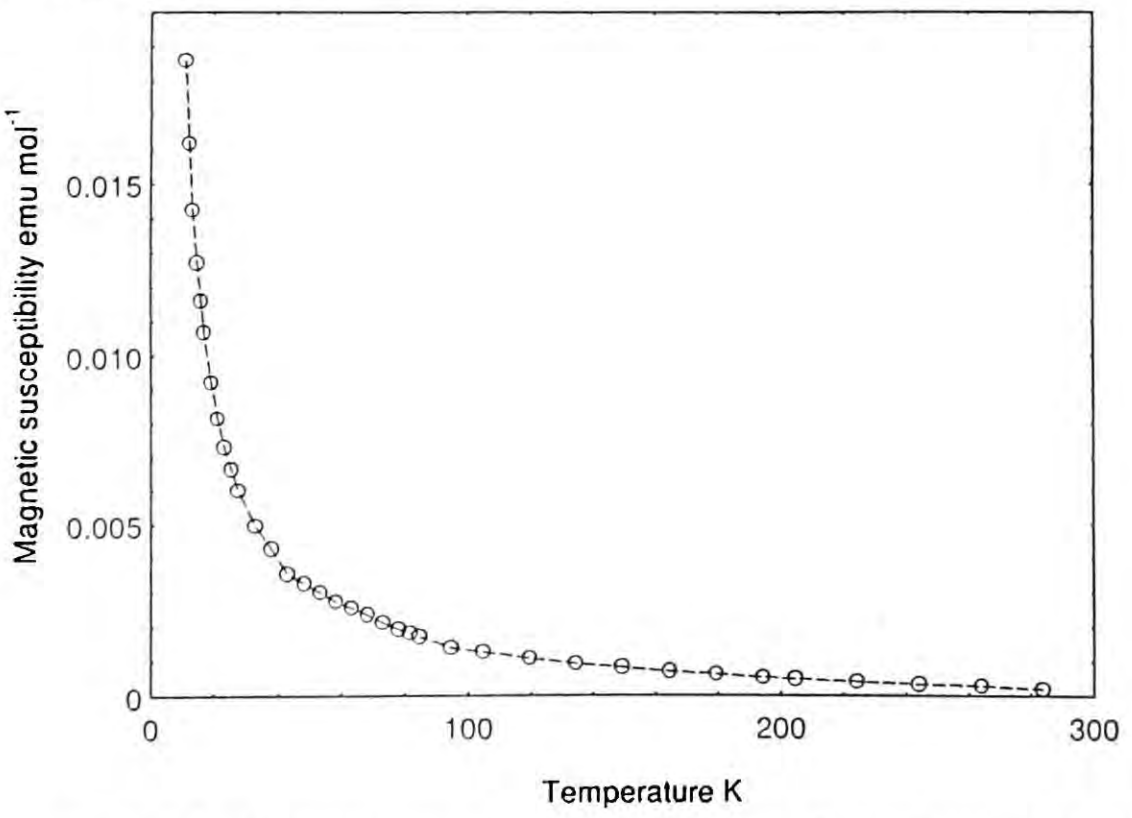


Figure 5.3a: Variable magnetic susceptibility data of complex **250** *vs* temperature.

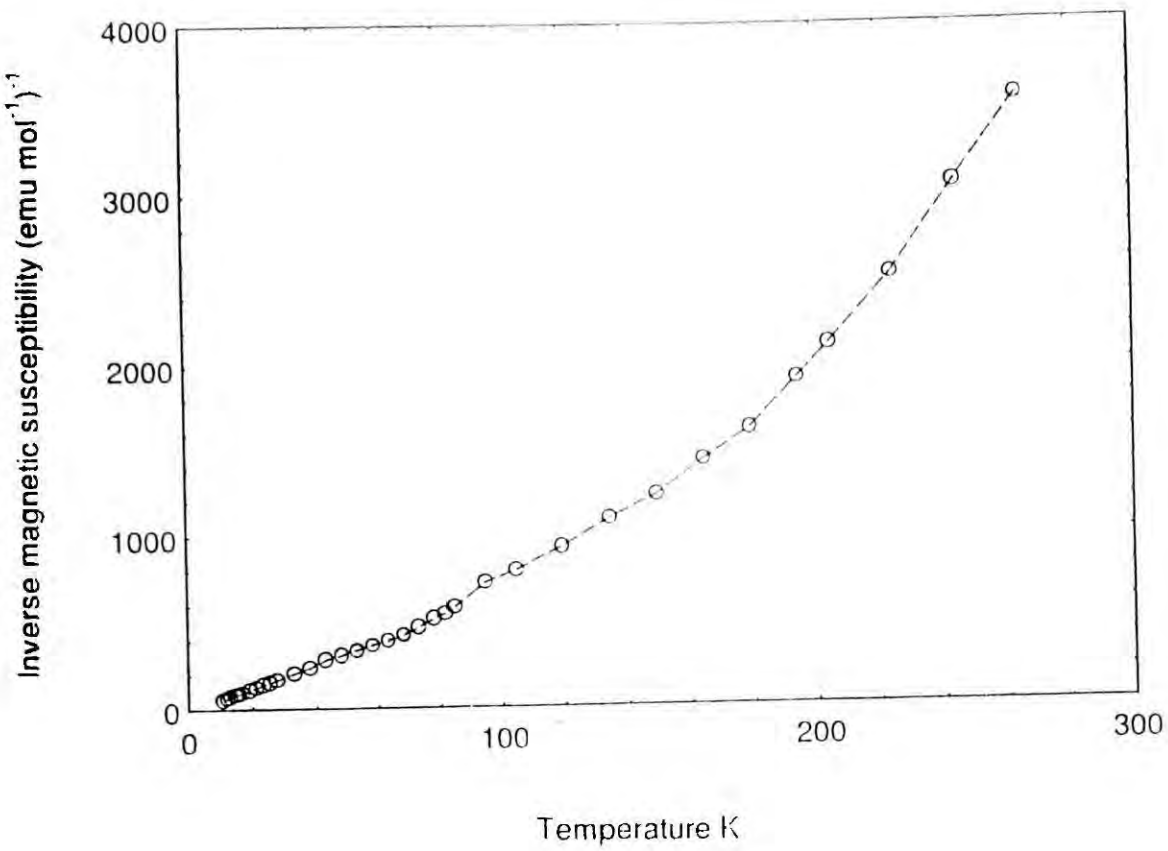


Figure 5.3b: Inverse variable magnetic susceptibility data of complex **250** *vs* temperature.

CHAPTER 6

EXPERIMENTAL SECTION

6.1 GENERAL METHODS

Melting points were recorded on a Kofler hot-stage microscope apparatus and are uncorrected.

Infra-red spectra were recorded on Perkin-Elmer 377, 547, 577 and 1720 FT-IR spectrophotometers; samples were embedded in KBr discs, Nujol mulls or analysed neat between KBr plates, as indicated.

^{1}H NMR spectra were recorded on Bruker AC 250, Varian Gemini 200 and XL 200 instruments. ^{13}C NMR spectra were recorded on a Varian Unity 500 spectrometer. Chemical shifts are quoted in ppm, relative to tetramethylsilane (TMS) as internal reference (0 ppm).

Mass spectra were obtained on VG 7070E and Varian MAT 311A instruments, with ionisation modes as indicated; ammonia was used as the impingent gas for chemical ionisation mode.

Elemental analyses were performed on a Carlo-Erba Strumentazione.

UV spectra were recorded on a Unicam UV2-100 spectrometer.

CV spectra were recorded using a BAS 100 electrochemical analyser. The experiments were performed in a one-compartment cell with platinum working and counter electrodes and a silver/silver chloride reference electrode. Further experimental detail is given in the corresponding CV section of each relevant chapter.

The conductivity measurement presented in section 5.4 was performed on a powdered sample and was obtained using the two-probe technique; the sample was manually compressed between two steel probes and the sample resistance measured with a Fluke 8000A Digital Multimeter.

Bulk magnetic susceptibility data were obtained using a Faraday balance.

Column chromatography was carried out using Merck silica gel (70-230 mesh) or Merck alumina (activity II to III, 70-230 mesh), the latter neutralised by pre-soaking in ethyl acetate for 24 h.

All reactions were carried out under a nitrogen atmosphere, the inert gas firstly being dried by passing through a column of phosphorus pentoxide. Solvents were dried over and distilled from the following reagents, under a dry nitrogen atmosphere: diethyl ether and THF (sodium metal); toluene (lithium aluminium hydride);

chlorocarbons (phosphorus pentoxide); acetonitrile (calcium hydride); acetone (potassium carbonate); methanol (magnesium methoxide) and ethanol (magnesium ethoxide).

LDA and BuLi were used as solutions in hexanes. All other reagents were reagent grade and used as supplied, unless otherwise stated.

6.2 EXPERIMENTAL TO CHAPTER 2

4-[2-(N-Phenylcarbamoyloxy)ethylsulfanyl]tetrathiafulvalene **86**

To a solution of **51**[82] (50mg, 0.18mmol) in dichloromethane (30ml) was added phenylisocyanate (0.018ml, 0.17mmol), followed by triethylamine (0.25ml, excess). The reaction was stirred at 20°C for 24h. Water was added, and the organic layer separated, dried ($MgSO_4$), filtered and evaporated under reduced pressure. The residue was chromatographed on a neutral alumina column, with cyclohexane-dichloromethane (3:1 v/v) as eluent to afford product **86**, which was crystallised from methanol-ether, as a yellow solid (40mg, 56% yield); m.p. 86-88°C (Found: C, 45.1; H, 3.3; N, 3.9. $C_{15}H_{13}NO_2S_5$ requires C, 45.0; H, 3.5; N, 3.8%); *m/z* (DCI) 400 (M^++1), HRMS found 398.9786, $C_{15}H_{13}NO_2S_5$ requires 398.9550; δ_H ($CDCl_3$) 7.5-7.1 (5H, m) 6.43 (1H, s), 6.32 (2H, s), 4.38 (1H, s), 4.24 (2H, m) and 3.03 (2H, t, *J* 6.0 Hz); υ_{max} (Nujol)/cm^{-1} 3345, 2930, 1708, 1531, 1449 and 1232.

4-{2-[N-(2-Chloroethyl)carbamoyloxy]ethylsulfanyl}tetrathiafulvalene **87**

To a solution of **51**[82] (80mg, 0.29mmol) in dichloromethane (30ml) was added chloroethylisocyanate (0.025ml, 0.29mmol), followed by triethylamine (0.25ml, excess). The reaction to stirred at 20°C for 24h. Aqueous work-up and chromatography, as described for **86** afforded product **87**, which was crystallised from methanol-ether, as a yellow solid (70mg, 63% yield); m.p. 74-77°C (Found: C, 34.5; H, 2.6; N, 3.8. $C_{15}H_{12}ClNO_2S_5$ requires C, 34.3; H, 2.6; N, 3.6%); *m/z* (DCI) 388, 386 (M^++1), HRMS found 384.8992, $C_{15}H_{12}ClNO_2S_5$ requires 384.9160; δ_H ($CDCl_3$) 6.43 (1H, s), 6.32 (2H, s), 5.13 (1H, s), 4.27 (2H, t, *J* 6.1 Hz), 3.59 (2H, m), 3.52 (2H, t, *J* 5.2 Hz) and 2.98 (2H, t, *J* 6.2 Hz); υ_{max} (Nujol)/cm^{-1} 3140, 2962, 1700, 1519,1462 and 1258.

4,5-(Ethylenedisulfanyl)tetrathiafulvalene **88**

To an ethereal slurry of anion **31** [obtained from tetrathiafulvalene **1** (250mg, 1.23mmol) and LDA (0.85ml, 1.5M, 1.28mmol)] at -78°C was added elemental sulfur (60mg, 1.84mmol); the mixture was stirred at this temperature for 7h, before the

addition of 1,2-dibromoethane (0.1ml, 1.23mmol). After a further 16h water was added, and the organic layer separated, dried ($MgSO_4$) and evaporated under reduced pressure. Column chromatography on silica gel using cyclohexane-toluene (3:1 v/v) as eluent afforded **88** as an orange solid, recrystallised from dichloromethane-hexane (95mg, 26%); m.p. 199°C (lit.[96] 200°C) (Found: C, 32.4; H, 2.1. $C_8H_6S_6$ requires C, 32.7; H, 2.0%).

4,5-(Ethylenediseleno)tetrathiafulvalene **89**

To an ethereal slurry of anion **31** [obtained from tetrathiafulvalene **1** (250mg, 1.23mmol) and LDA (0.85ml, 1.5M, 1.28mmol)] at -78°C was added elemental selenium (145mg, 1.84mmol); the mixture was stirred at this temperature for 7h, before the addition of 1,2-dibromoethane (0.1ml, 1.23mmol). After a further 16h water was added, and the organic layer separated, dried ($MgSO_4$) and evaporated under reduced pressure. Column chromatography on silica gel using dichloromethane-hexane (1:1 v/v) as eluent afforded **89** an orange-brown solid, which was recrystallised from dichloromethane-hexane (83mg, 18%); m.p. 194-197°C (lit.[145] 195°C) (Found: C, 33.3; H, 2.7. $C_8H_6S_4Se_2$ requires C, 33.3; H, 2.8%).

4,5-Bis(2-hydroxyethylsulfanyl)tetrathiafulvalene **90**

To an ethereal slurry of anion **31** [obtained from tetrathiafulvalene **1** (250mg, 1.23mmol) and LDA (0.85ml, 1.5M, 1.28mmol)] at -78°C was added elemental sulfur (120mg, 3.75mmol); the mixture was stirred at this temperature for 7h, before the addition of 2-bromoethanol (1.0ml, 15mmol). After a further 16h water was added, and the organic layer separated, dried ($MgSO_4$) and evaporated under reduced pressure. Column chromatography on silica gel using dichloromethane-ethyl acetate (1:1 v/v) as eluent afforded firstly **51**[82] (110mg, 32%) followed by product **90**, which was crystallised from methanol as a yellow-orange solid (87mg, 20%); m.p. 98-101°C (Found: C, 33.7; H, 3.4. $C_{10}H_{12}O_2S_6$ requires C, 33.7; H, 3.4%); *m/z* (DCI) 357 (M^++1), HRMS found 355.9091, $C_{10}H_{12}O_2S_6$ requires 355.9162; δ_H ($CDCl_3$) 6.34 (2H, s), 3.75 (4H, q, *J* 4.5 Hz), 3.01 (4H, t, *J* 3.0 Hz), and 2.90 (2H, t, *J* 6.1 Hz); δ_C ($CDCl_3$) 128.2, 118.9, 116.9, 104.5, 59.8, and 39.2; υ_{max} (KBr)/cm^{-1} 3277, 2921, 2860, 1287, 1068 and 642.

4-Hexylselenotetrathiafulvalene **93** and 4,5-Bis(hexylseleno)tetrathiafulvalene **94**

To an ethereal slurry of anion **31** [obtained from tetrathiafulvalene **1** (180mg, 0.88mmol) and LDA (0.60ml, 1.5M, 0.90mmol)] at -78°C was added elemental ground selenium (200mg, 2.53mmol); the mixture was stirred at this temperature for 7h, before the addition of tosyl hexane (0.25ml, 1.25mmol). After a further 16h water was added, and the organic layer separated, dried ($MgSO_4$) and evaporated under

reduced pressure. Column chromatography on silica gel using cyclohexane-toluene (3:1 v/v) as eluent afforded a brown oil **93** (40mg, 13% yield) as well as a small amount of **94** (10mg, 2%), also as a brown oil; *m/z* (DCI) (369, 267, 103) and (533, 281, 103) (M^++1), respectively.

4,5-Bis(2-acetyloxyethylsulfanyl)-1,3-dithiole-2-thione **96**

To a solution of **74**[83] (500mg, 1.75mmol) in dichloromethane (30ml) was added acetyl chloride (0.25ml, 3.52mmol), followed by triethylamine (0.5ml). The reaction was stirred at 20°C for 24h. The mixture was washed with water and the organic layer separated, dried ($MgSO_4$), and evaporated under reduced pressure. Column chromatography on neutral alumina using dichloromethane as the eluent afforded **96** as a brown oil (590mg, 91% yield); *m/z* (DCI) 371 (M^++1); δ_H ($CDCl_3$) 4.29 (2H, t, *J* 6.3 Hz), 3.13 (2H, t, *J* 6.4 Hz), and 2.09 (3H, s); υ_{max} (KBr)/cm^{-1} 2930, 1740, 1385, 1228, 1063 and 1030.

4,5-Bis(2-benzoyloxyethylsulfanyl)-1,2-dithiole-2-thione **99**

To a solution of **74**[83] (1.1g, 3.85mmol) in dichloromethane (40ml) was added benzoyl chloride (1ml, 8.61mmol), followed by triethylamine (1ml). The reaction was allowed to stir at 20°C for 24h. Aqueous work-up and chromatography as described for **96** yielded an orange solid, which was recrystallised from dichloromethane-hexane to give **99** (1.18g, 62% yield); m.p. 85-87°C (Found: C, 51.4; H, 3.8. $C_{21}H_{18}O_4S_5$ requires C, 51.0; H, 3.7%); *m/z* (DCI) 495 (M^++1); δ_H ($CDCl_3$) 8.18-7.30 (10H, m), 4.52 (4H, t, *J* 6.2 Hz) and 3.23 (4H, t, *J* 6.2 Hz); υ_{max} (KBr)/cm^{-1} 1722, 1272, 1112, 1098, 1061 and 709.

4,5-Bis(2-benzoyloxyethylsulfanyl)-1,3-dithiole-2-one **100**

To a solution of **99** (750mg, 1.52mmol) in chloroform-acetic acid (3:1 v/v; 80ml), was added mercuric acetate (800mg, 2.51mmol), and the reaction was stirred at 20°C for 2h. The reaction mixture was washed sequentially with water (3 x 30ml), and sodium bicarbonate solution (to neutrality), and then dried ($MgSO_4$). The solvent was evaporated under reduced pressure, to give crude **100** as a pale yellow semi-solid inseparable from unreacted **99** (TLC evidence) (560mg, 76% combined yield); *m/z* (DCI) 479 (M^++1); υ_{max} (KBr)/cm^{-1} 1715, 1664, 1272, 1111, 882 and 711.

4,5-Bis(methylsulfanyl)-4',5'-bis(2-hydroxyethylsulfanyl)tetrathiafulvalene **102**

To a solution of sodium ethoxide [generated from sodium metal (0.01, 4.3mmol)] in ethanol, at -10°C, was added **103** (100mg, 0.15mmol). After stirring for 4h at 20°C water was added, the product extracted into dichloromethane, and the organic layer separated and dried ($MgSO_4$). Column chromatography using silica gel

and ethyl acetate-dichloromethane (1:1 v/v) as the eluting solvent gave **102** as a yellow solid, which was recrystallised from dichloromethane-hexane (60mg, 88% yield); m.p. 111-112°C (Found: C, 32.1; H, 3.5. $C_{12}H_{16}O_2S_8$ requires C, 32.1; H, 3.6%); *m/z* (DCI) 448 (M^++1); δ_H ($CDCl_3$) 3.77 (4H, t, *J* 5.3 Hz), 3.03 (4H, t, *J* 5.4 Hz), 2.45 (3H, s) and 1.62 (2H, s); υ_{max} (KBr)/cm^{-1} 3320, 2916, 1064, 1047, 890 and 770.

4,5-Bis(Methylsulfanyl)-4',5'-bis(2-benzoyloxyethylsulfanyl)tetrathiafulvalene **103**

To a mixture of **100** (contaminated with **99**) (500mg, 1.05mmol) and **95b** (240mg, 1.06mmol), was added of freshly distilled triethylphosphite (3ml). The reaction was stirred under reflux for 4h. The resulting mixture was placed on a neutral alumina column, whuch was flushed with hexane to remove the triethylphosphite. Finally, using dichloromethane as the eluting solvent, **103** was obtained as an orange-brown oil (100mg, 15% yield based on pure **100**); *m/z* (DCI) 657 (M^++1), HRMS found 655.9534, $C_{26}H_{24}O_4S_8$ requires 655.9441; δ_H ($CDCl_3$) 8.03-7.38 (10H, m), 4.49 (4H, t, *J* 6.2 Hz), 3.17 (4H, t, *J* 6.2 Hz), and 2.43 (6H, s); υ_{max}(neat)/cm^{-1} 2921, 1719, 1451, 1269, 1111 and 709.

4,5-Bis[2-(*tert*-butyldiphenylsiloxy)ethylsulfanyl]-1,3-dithiole-2-thione **104**

To a solution of **74**[83] (5.38g, 18.8mmol) in dimethylformamide (60ml), was added ^{t}butyldiphenylsilyl chloride (6.2g, 22.5mmol) followed by imidazole (2.6g, 38.2mmol). The reaction was stirred at 20°C for 16 h, after which water was added and the product extracted into dichloromethane. After drying the organic layer ($MgSO_4$), column chromatography using silica gel and dichloromethane as the eluting solvent gave **104** as an orange oil (13.20g, 92% yield); δ_H ($CDCl_3$) 7.67-7.38 (20H, m), 3.80 (4H, t), 2.93 (4H, t) and 1.07 (18H, m).

4,5-Bis[2-(*tert*-butyldiphenylsiloxy)ethylsulfanyl]-1,3-dithiole-2-one **105**

To a solution of **104** (13.20g, 17.3mmol) in chloroform-acetic acid (3:1 v/v; 250ml), was added mercuric acetate (9.60g, 30.1mmol), and the reaction was stirred at 20°C for 16h. The reaction mixture was washed with water (3 x 30ml), sodium bicarbonate solution (to neutrality), and finally dried ($MgSO_4$). The solvent was evaporated under reduced pressure, to give **105** as an orange oil inseparable from unreacted **104** (TLC evidence) (10.9g, 84% combined yield); δ_H ($CDCl_3$) 7.67-7.38 (20H, m), 3.80 (4H, t), 2.93 (4H, t) and 1.07 (18H, m); υ_{max} (KBr)/cm^{-1} 2920, 2848, 1670, 1430, 1124 and 701.

4,5-Bis[2-(*tert*-butyldiphenylsiloxy)ethylsulfanyl]tetrathiafulvalene **106** and 4,5-Bis(2-hydroxyethylsulfanyl)tetrathiafulvalene **90**

To a mixture of **105** (10.90g, 14.61mmol) and vinylenetrithiocarbonate **95a** (1.96g, 14.63mmol), was added freshly distilled triethylphosphite (10ml, excess). The reaction was stirred at 60°C for 16h. The resulting mixture was placed on a silica column, and flushed with hexane to remove the triethylphosphite, then, using dichloromethane-cyclohexane (1:1 v/v) as the eluting solvent, an orange brown solid was obtained which was primarily **106** that was inseparable from a minor amount of other coupling products (TLC evidence) and residual triethylphosphite (1.20g combined yield). After addition of tetrabutylammonium fluoride (20ml, 1.0M, 20.0mmol.) to a solution of this mixture in THF (40ml), the reaction was stirred at 20°C for 16h; water was then added and the product extracted into dichloromethane. The organic layer was separated, dried ($MgSO_4$) and evaporated under reduced pressure. Column chromatography using silica gel and, initially, dichloromethane, then dichloromethane-ethyl acetate (1:1 v/v) as the eluting solvent afforded a yellow-orange solid (2.01g, 39% yield) possessing identical melting point and NMR spectra to compound **90**, previously prepared directly from TTF.

1{[2,2'-Bi (1,3-dithiolylidene)-4-yl]carbonyl}ferrocene **120**

To an ethereal slurry of anion **31** [obtained from tetrathiafulvalene **1** (250mg, 1.23mmol) and LDA (0.85ml, 1.5M, 1.28mmol)] in ether (30ml) at -78°C was added ferrocenecarbonyl chloride **118**[102] (400mg, 1.61mmol) and the reaction was warmed to 20°C and stirred at this temperature for 4h. The mixture was washed with water and the organic layer separated, dried ($MgSO_4$), and evaporated under reduced pressure. Column chromatography on silica gel using hexane-toluene (3:1 v/v) as eluent afforded **120** as a purple solid, which was recystallised from dichloromethane-hexane (50mg, 10% yield); m.p. 181-184°C (Found: C, 49.0; H, 2.9. $C_{17}H_{12}FeOS_4$ requires C, 49.0; H, 2.9%); *m/z* (DCI) 417 (M^++1); δ_H ($CDCl_3$) 7.45 (1H, s), 6.34 (2H, m), 4.87 (2H, m), 4.57 (2H, m) and 4.24 (5H, s); υ_{max} (KBr)/cm^{-1} 1593, 1451, 1301, 1137, 772 and 644.

1{[2,2'-Bi (1,3-dithiolylidene)-4-yl]sulfanylcarbonyl}ferrocene **121**

To a suspension of **52**[82] (200mg, 0.59mmol) in ethanol (30ml) at -10°C was added sodium ethoxide in ethanol (from sodium metal, 13mg, 0.57mmol), and the mixture was stirred at -10°C for 30min. Compound **118**[102] (300mg, 1.21mmol), was then added and the temperature maintained at -10°C for a further 30min. The reaction was evaporated under reduced pressure, and the residue taken up into dichloromethane. Water was added, the organic layer separated, dried ($MgSO_4$), and evaporated. Purification using column chromatography on silica gel with cyclohexane-

dichloromethane (3:1 v/v) as the eluting solvent, afforded **121** as an orange solid which was recrystallised from dichloromethane-hexane (70mg, 27% yield); m.p. 159-161°C (Found: C, 45.4; H, 2.7. $C_{17}H_{12}FeOS_5$ requires C, 45.5; H, 2.7%); *m/z* (DCI) 449 (M^++1); δ_H ($CDCl_3$) 6.54 (1H, s), 6.32 (2H, m), 4.85 (2H, m), 4.56 (2H, m) and 4.28 (5H, s); υ_{max} (KBr)/cm^{-1} 1731, 1676, 1242, 1048, 806 and 659.

1-{2-[2,2'-Bi (1,3-dithiolylidene)-4-yl]sulfanylethyloxycarbonyl}ferrocene **122**

To a solution of **51**[82] (200mg, 0.71mmol) in dichloromethane (30ml) was added ferrocenecarbonyl chloride **118**[102] (300mg, 1.21mmol), followed by triethylamine (0.5ml). The reaction was stirred at 20°C for 24h. After evaporating the solvent under reduced pressure, purification using column chromatography on neutral alumina and dichloromethane as the eluent afforded **122** as an orange solid, which was recrystallised from dichloromethane-hexane (280mg, 80% yield); m.p. 87-89°C (Found: C, 46.5; H, 3.3. $C_{19}H_{16}FeO_2S_5$ requires C, 46.3; H, 3.3%); *m/z* (DCI) 493 (M^++1); δ_H ($CDCl_3$) 6.47 (1H, s), 6.31 (2H, s), 4.79 (2H, t, *J* 2.0 Hz), 4.39 (4H, m), 4.21 (5H, s) and 3.06 (2H, t, *J* 6.2 Hz); υ_{max} (KBr)/cm^{-1} 1697, 1449, 1263, 1121, 761 and 652.

4,5-{Bis{2-[1-cyclopentadienyl(cyclopentadienyl)iron]carbonyloxy}ethylsulfanyl)}tetrathiafulvalene **123**

To a solution of **90** (180mg, 0.51mmol) in dichloromethane (20ml) was added ferrocenecarbonyl chloride **118**[102] (400mg, 1.61mmol), followed by triethylamine (0.5ml). The reaction was stirred at 20°C for 24h. Work-up and purification as for **122** afforded **123** as an orange oil (260mg, 59% yield); *m/z* (DCI) 781 (M^++1), HRMS found 779.9015, $C_{32}H_{28}Fe_2O_4S_6$ requires 779.9011; δ_H ($CDCl_3$) 6.34 (2H, s), 4.81 (4H, m), 4.39 (8H, m), 4.22 (10H, s) and 3.16 (4H, t, *J* 6.3 Hz); δ_C ($CDCl_3$) 172.0, 128.6, 119.5, 117.4, 105.2, 72.0, 70.8, 70.4, 63.3, 62.3, and 35.5; υ_{max} (KBr)/cm^{-1} 1715, 1460, 1384, 1275, 1133 and 822.

4,5-{Bis{2-[1-cyclopentadienyl(cyclopentadienyl)iron]carbonyloxy}ethylthio)}-1,3-dithiole-2-thione **124**

To a solution of **74**[83] (300mg, 1.05mmol) in dichloromethane (50ml) was added ferrocenecarbonyl chloride **118**[102] (700mg, 2.82mmol), followed by triethylamine (0.5ml). The reaction was stirred at 20°C for 24h. Work-up and purification as for **122** afforded **124** as an orange oil (480mg, 64% yield); *m/z* (DCI) 711 (M^++1); δ_H ($CDCl_3$) , 4.83 (2H, m), 4.45 (4H, m), 4.24 (5H, s) and 3.24 (2H, t); υ_{max} (KBr)/cm^{-1} 2926, 1713, 1462, 1272, 1134 and 1067.

1,1'-Bis{2-[2,2'-bi(1,3-dithiolylidene)-4-yl]sulfanylethyloxycarbonyl}ferrocene **128**

To a solution of **51**[82] (500mg, 1.79mmol) in dichloromethane (30ml) was added compound **119**[103] (250mg, 0.80mmol), followed by triethylamine (0.5ml). The reaction was allowed to stir at 20°C for 24h. Work-up and purification as for **122** afforded **128** as an orange solid, which was recrystallised from dichloromethane-hexane (80mg, 11% yield); m.p. 81-83°C (Found: C, 42.3; H, 2.8. $C_{28}H_{22}FeO_4S_{10}$ requires C, 42.1; H, 2.8%); *m/z* (DCI) 799 (M^++1); δ_H (d_6 acetone) 6.82 (2H, s), 6.65 (4H, s), 4.84 (4H, m), 4.52 (4H, m), 4.46 (4H, t, *J* 6.2 Hz) and 3.23 (4H, t, *J* 6.3 Hz); υ_{max} (KBr)/cm^{-1} 1714, 1463, 1277, 1137, 795 and 772.

1,1'-Bis{[2,2'-bi(1,3-dithiolylidene)-4-yl]methyloxycarbonyl}ferrocene **129**

To a solution of **37**[76] (500mg, 2.13mmol) in dichloromethane (50ml) was added compound **119**[103] (310mg, 1.00mmol) followed by triethylamine (1ml), and the reaction stirred at 20°C for 16h. After evaporating the solvent under reduced pressure, purification using column chromatography with silica gel and dichloromethane-hexane (2:1 v/v) as the eluent afforded **129** as an orange-red solid, which was recrystallised from dichloromethane-hexane (457mg, 65%); m.p. 182-184°C (Found: C, 44.4; H, 2.7. $C_{26}H_{18}FeO_4S_8$ requires C, 44.2; H, 2.6%); *m/z* (DCI) 707 (M^++1); δ_H ($CDCl_3$) 6.43 (2H, s), 6.30 (4H, s), 4.96 (4H, m), 4.87 (4H, m) and 4.48 (4H, m); υ_{max} (KBr)/cm^{-1} 3050, 1705, 1458, 1269, 1123 and 653.

1-{2-[2,2'-Bi (1,3-dithiolylidene)-4-yl]sulfanylethyloxycarbonylmethyl}ferrocene **132**

To a solution of **51**[82] (200mg, 0.71mmol) in dichloromethane (20ml) was added **131** (300mg, 1.14mmol), followed by triethylamine (0.5ml). The reaction was allowed to stir at 20°C for 16h. Work-up and purification as for **122** afforded **132** as an orange-brown oil (30mg, 8% yield); *m/z* (DCI) 507 (M^++1); δ_H ($CDCl_3$) 6.43 (1H, s), 6.32 (2H, s), 4.32-4.10 (11H, m), 3.37 (2H, s) and 2.99 (2H, t, *J* 6.3 Hz).

4,4'(5')-diformyltetrathiafulvalene **136**

To a solution of TTF **1** (600mg, 2.94mmol) in ether (50ml) was added LDA (7.9ml, 1.5M, 11.85mmol) at -78°C. After 2h of stirring at this temperature, *N*-methylformanilide (0.90ml, 7.29mmol) was added, and the reaction was stirred for a further 1h, at -78°C, before warming to room temperature. Water was added to the reaction mixture, followed by conc. HCl (5 drops), and the mixture was filtered through a sintered glass funnel. The precipitate was washed with dichloromethane (5 x 30ml), and finally dried under reduced pressure to give **136** as a dark purple solid needing no further purification (300mg, 40% yield); m.p. >250°C (Found: C, 37.2; H, 1.8. $C_{28}H_{22}FeO_4S_{10}$ requires C, 36.9; H, 1.6%); *m/z* (DCI) 261 (M^++1); δ_H (d_6

DMSO) 9.54 (2H, s), 8.28 (1H, s), and 8.27 (1H, s); υ_{max} (KBr)/cm^{-1} 1641, 1527, 1232, 1140, 840 and 642.

trans-1-{2-[2,2'-bi(1,3-dithiolylidene)-4-yl]vinyl}ferrocene **137**

To a solution of **134**[104] (3.5g, 5.96mmol) in THF (50ml) at -78°C, was added butyllithium (3.7ml, 1.6M, 6.00mmol). After 15min., **32** (1g, 4.31mmol) was added and the reaction left to warm to room temperature for 24h. The mixture was evaporated under reduced pressure, and the residue extracted into dichloromethane. Water was added, the organic layer separated, dried ($MgSO_4$), and evaporated. Purification using column chromatography on silica gel with cyclohexane-dichloromethane (3:1 v/v) as the eluent, afforded a mixture of *cis* and *trans* isomers of **137** (1.28g, 72% yield). The *trans* isomer was isolated pure by fractional recrystallisation from toluene as a purple solid (1.03g, 58% yield); m.p. 186-187°C (Found: C, 52.4; H, 3.5. $C_{18}H_{14}FeS_4$ requires C, 52.2; H, 3.4%); *m/z* (DCI) 415 (M^++1); δ_H (d_6 acetone) 6.77 and 6.69 (1H, d, *J* 15.8 Hz), 6.65 (2H, s), 6.58 (1H, s), 6.29 and 6.21 (1H, d, *J* 15.5 Hz), 4.52 (2H, m), 4.32 (2H, m), and 4.14 (5H, s).

4,4'(5')-Bis{2-[1-cyclopentadienyl(cyclopentadienyl)iron]vinyl}tetrathiafulvalene **138**

To a solution of **134**[104] (2.0g, 3.41mmol) in THF (60ml), at 20°C, was added butyllithium (2.2m 1.6M, 3.52mmol), and the ylide was left to form for 30min. After this time **136** (300mg, 1.15mmol) was added, and the reaction temperature was raised to 20°C, remaining so for 16h. The reaction mixture was evaporated under reduced pressure, and the residue extracted into dichloromethane. Water was added, the organic layer separated, dried ($MgSO_4$), and evaporated. Purification using column chromatography on silica gel with hexane-dichloromethane (3:1 v/v) as the eluent, afforded **138** as a dark orange oil (220mg, 30% yield); *m/z* (DCI) 625 (M^++1), HRMS found 623.9441, $C_{30}H_{24}Fe_2S_4$ requires 623.9460; δ_H (d_6 acetone) 6.80-6.02 (6H, m), 4.51 (4H, m), 4.31 (4H, m) and 4.15 (10H, m). The isomers could not be separated by chromatography or recrystallisation.

1,1'-Bis(*N,N,N*-trimethylaminomethyl)ferrocene diiodide **139**

To a solution of **110** (0.90g, 3.00mmol) in acetonitrile (10ml) was slowly added methyliodide [4.5ml, 72.3mmol, in MeCN (10ml)], at 0°C. The reaction was stirred at 0°C for a further 6h. The crude solution was then cooled to -5°C before pouring into ether (100ml). The suspension was filtered, and the precipitate washed sequentially with ice-cold acetonitrile (20ml), and ether (3 x 30ml), to afford salt **139** as a yellow solid (1.10g, 63% yield); (Found: C, 37.4; H, 5.3; N, 4.7. $C_{18}H_{30}FeI_2N_2$ requires C, 37.0; H, 5.1; N, 4.8%).

1,1'-Bis[(triphenylphosphonium)methyl]ferrocene dibromide **143**

A solution of **141** (1.72g, 6.99mmol) in ether (150ml) was cooled to 0°C; phosphorus tribromide (1.10ml, 11.57mmol) was slowly added, and the reaction warmed to room temperature with stirring for 6h. Triphenylphosphine (6.00g, 22.90mmol) was then added and the mixture stirred for a further 16h. The suspension was filtered and the preciptate washed with ether (10 x 50ml) to afford **143** as a yellow solid (3.50g, 56% yield); (Found: C, 64.1; H, 4.8. $C_{48}H_{42}Br_2FeP_2$ requires C, 64.3; H, 4.7%).

1,1'-Bis{2-[2,2'-bi(1,3-dithiolylidene)-4-yl]vinyl}ferrocene **145**

To a suspension of **143** (250mg, 0.28mmol) in THF (50ml) was added butyllithium (0.35ml, 1.6M, 0.56mmol) at 20°C. The ylide was left to form for 30min whence **32** (150mg, 0.65mmol) was added, and the reaction was then stirred for 16h at 20°C. The mixture was evaporated under reduced pressure, and the residue taken up into dichloromethane. Water was added, the organic layer separated, dried ($MgSO_4$), and evaporated. Column chromatography using neutral alumina and toluene as the eluent afforded an orange oil constituting a mixture of three isomers of **145** as seen by ^1H NMR (75mg, 42% yield); *m/z* (EI) 642, HRMS found 641.8536, $C_{26}H_{18}FeS_8$ requires 641.8524; δ_H ($CDCl_3$) 6.49-5.92 (10H, m) and 4.44-4.23 (8H, m).

trans, trans-1,1'-Bis{2-[(1,3-dithiole-2-thione)-4-yl]vinyl}ferrocene **150**

To a suspension of **149**[110] (500mg, 1.02mmol) in THF (60ml) was added ^{n}BuLi (0.75ml, 1.6M, 1.20mmol), at -78°C, and the reaction stirred at this temperature for 2h. 1,1'-Ferrocenedicarboxaldehyde **148**[109] (100mg, 0.41mmol) was added and the mixture warmed to room temperature with stirring for a further 16h. The reaction was evaporated under reduced pressure, and the residue taken up into dichloromethane. Water was added, the organic layer separated, dried ($MgSO_4$), and evaporated. Column chromatography using neutral alumina and dichloromethane-hexane (1:1 v/v) as the eluent afforded **150** as an orange solid, which was recrystallised from dichloromethane-hexane (140mg, 67% yield); m.p. 147-150°C; *m/z* (DCI) 503 (M^++1), HRMS found 501.9077, $C_{20}H_{14}FeS_6$ requires 501.8769; δ_H ($CDCl_3$) 6.89 (2H, s), 6.42 and 6.36 (2H, d, *J* 11.5 Hz), 6.14 and 6.09 (2H, d, *J* 11.6 Hz) and 4.32 (8H, s).

6.3 EXPERIMENTAL TO CHAPTER 3

6.3.1 GENERAL PROCEDURE FOR COMPOUNDS 164-166 AND 169-172

To a stirred solution of the corresponding species **159** in THF (100ml), at -78°C, was added butyllithium and the reaction allowed to stir at this temperature for 15min. The corresponding ferrocenyl aldehyde or ketone was added, and the reaction warmed to room temperature with stirring for a further 16h. Water was added and the product extracted into dichloromethane. The organic layer was separated, dried ($MgSO_4$) and evaporated. Column chromatography using silica gel and dichloromethane-hexane (1:1 v/v) as the eluting solvent afforded the desired product. Recrystallisations were performed using dichloromethane-hexane.

1-[(1,3-Dithiole-2-ylidene)methyl]ferrocene **164**

Using general procedure 6.3.1 with **160** (1.00g, 4.72mmol), ^{n}BuLi (3.25ml, 1.6M, 5.20mmol) and **112** (1.00g, 4.67mmol) an orange solid was obtained (1.15g, 81% yield); m.p. 81-82°C (Found: C, 55.7; H, 4.1. $C_{14}H_{12}FeS_2$ requires C, 56.0; H, 4.0%); *m/z* (DCI) 301 (M^++1); δ_H ($CDCl_3$) 6.25 (2H, s), 6.16 (1H, s), 4.39 (2H, m), 4.22 (2H, m) and 4.18 (5H, s).

1-[(4,5-Dimethyl-1,3-dithiole-2-ylidene)methyl]ferrocene **165**

Using general procedure 6.3.1 with **161** (1.00g, 4.17mmol), ^{n}BuLi (2.87ml, 1.6M, 4.59mmol) and **112** (0.89g, 4.16mmol) an orange solid was obtained (1.07g, 78% yield); m.p. 109-111°C (Found: C, 58.7; H, 5.0. $C_{16}H_{16}FeS_2$ requires C, 58.5; H, 4.9%); *m/z* (DCI) 329 (M^++1); δ_H ($CDCl_3$) 6.01 (1H, s), 4.35 (2H, m), 4.18 (2H, m), 4.15 (5H, s), 1.96 (3H, s) and 1.91 (3H, s).

1-[(4,5-Dimethylsulfanyl-1,3-dithiole-2-ylidene)methyl]ferrocene **166**

Using general procedure 6.3.1 with **162** (1.00g, 3.29mmol), ^{n}BuLi (2.26ml, 1.6M, 3.62mmol) and **112** (0.70g, 3.28mmol) a yellow-orange oil was obtained (0.84g, 65% yield); (Found: C, 49.5; H, 4.4. $C_{16}H_{16}FeS_4$ requires C, 49.0; H, 4.1%); *m/z* (DCI) 393 (M^++1); δ_H ($CDCl_3$) 6.10 (1H, s), 4.34 (2H, m), 4.22 (2H, m), 4.16 (5H, s), 2.44 (3H, s) and 2.42 (3H, s).

Dimethyl 1-[(1,3-dithiole-2-ylidene)methyl]ferrocene-4,5-dicarboxylate **167**

To a solution of **163** (1.00g, 1.97mmol) and **112** (0.42g, 1.97mmol) in THF (100ml) was added triethylamine (1ml) at 20°C, and the reaction stirred for 16h. After aqueous washing and extraction into dichloromethane, the organic layer was separated, dried ($MgSO_4$) and evaporated. Column chromatography using silica gel and

dried ($MgSO_4$) and evaporated. Column chromatography using silica gel and dichloromethane as the eluent afforded **167** as an orange solid, which was recrystallised from dichloromethane (0.72g, 88% yield); m.p. 94-96°C (Found: C, 52.0; H, 4.0. $C_{18}H_{18}FeO_4S_2$ requires C, 51.9; H, 3.9%); *m/z* (DCI) 417 (M^++1); δ_H ($CDCl_3$) 6.09 (1H, s), 4.34 (2H, m), 4.24 (2H, m), 4.17 (5H, s) and 3.86 (6H, s); υ_{max} (KBr)/cm^{-1} 1733, 1721, 1591, 1436, 1253 and 1018.

1,1'-Bis{dimethyl[(1,3-dithiole-2-ylidene)methyl]-4,5-dicarboxylate}ferrocene **168**

To a solution of **148** (240mg, 0.99mmol) and **163** (1.00g, 1.97mmol) in THF (100ml) at 20°C was added triethylamine (1ml, excess), and the reaction stirred for 16h. The mixture was evaporated under reduced pressure. Column chromatography using silica gel and dichloromethane as the eluent afforded **168** as an orange solid, which was recrystallised from dichloromethane (442mg, 69% yield); m.p. 177-179°C (Found: C, 48.5; H, 3.4. $C_{26}H_{22}FeO_8S_4$ requires C, 48.3; H, 3.4%); *m/z* (DCI) 646 (M^++1); δ_H ($CDCl_3$) 5.92 (2H, s), 4.32 (4H, s), 4.23 (4H, s), 3.84 (6H, s) and 3.83 (6H, s); υ_{max} (KBr)/cm^{-1} 1735, 1707, 1592, 1428, 1265 and 1029.

1,1'-Bis[(4,5-dimethyl-1,3-dithiole-2-ylidene)methyl]ferrocene **169**

Using general procedure 6.3.1 with **161** (1.00g, 4.17mmol), ^nBuLi (2.87ml, 1.6M, 4.59mmol) and **148** (485mg, 2.00mmol) an orange solid was obtained (622mg, 66% yield); m.p. 161-162°C (Found: C, 56.4; H, 4.8. $C_{22}H_{22}FeS_4$ requires C, 56.2; H, 4.7%); *m/z* (DCI) 471 (M^++1); δ_H ($CDCl_3$) 5.91 (2H, s), 4.30 (4H, m), 4.16 (4H, m), 1.95 (6H, s) and 1.90 (6H, s).

1,1'-Bis[1-(4,5-dimethyl-1,3-dithiole-2-ylidene)ethyl]ferrocene **170**

Using general procedure 6.3.1 with **161** (1.00g, 4.17mmol), ^nBuLi (2.87ml, 1.6M, 4.59mmol) and **108** (540mg, 2.00mmol) an orange solid was obtained (707mg, 71% yield); m.p. 160-161°C (Found: C, 57.8; H, 5.3. $C_{24}H_{26}FeS_4$ requires C, 57.7; H, 5.4%); *m/z* (DCI) 499 (M^++1); δ_H ($CDCl_3$) 4.43 (4H, m), 4.21 (4H, m), 1.99 (6H, s) and 1.94 (12H, s).

1,1'-Bis[1-(1,3-dithiole-2-ylidene)ethyl]ferrocene **171**

Using general procedure 6.3.1 with **160** (1.00g, 4.72mmol), ^nBuLi (3.25ml, 1.6M, 5.20mmol) and **108** (590mg, 2.19mmol) an orange solid was obtained (675mg, 70% yield); m.p. 109°C (Found: C, 55.3; H, 4.1. $C_{20}H_{18}FeS_4$ requires C, 55.3; H, 4.1%); *m/z* (DCI) 443 (M^++1); δ_H ($CDCl_3$) 6.27 (4H, s), 4.43 (4H, m), 4.22 (4H, m) and 2.01 (6H, s).

1,1'-Bis[1-(4,5-dimethylsulfanyl-1,3-dithiole-2-ylidene)ethyl]ferrocene **172**

Using general procedure 6.3.1 with **162** (1.00g, 3.29mmol), ^{n}BuLi (2.26ml, 1.6M, 3.62mmol) and **108** (405mg, 1.50mmol) an orange-red oil was obtained (545mg, 58% yield); (Found: C, 45.5; H, 4.6. $C_{24}H_{26}FeS_4$ requires C, 46.0; H, 4.2%); *m/z* (DCI) 627 (M^++1); δ_H ($CDCl_3$) 4.37 (4H, m), 4.20 (4H, m), 2.38 (12H, m) and 1.95 (6H, s).

1,1'-Bis[1,2-bis(4,5-dimethyl-1,3-dithiole-2-ylidene)ethane-1,2-diyl]diferrocene **173**

To a solution of **165** (100mg, 0.30mmol) in ether (50ml) was added HCl.Et_2O (0.30ml, 1.0M, 0.30mmol) and the reaction stirred for 24h. Separation of the product by preparative TLC using hexane-dichloromethane (5:1 v/v) as the eluent afforded **173** as an orange solid, which was recrystallised from dichloromethane-hexane (60mg, 60% yield); m.p. >250°C (Found: C, 58.8; H, 4.7. $C_{32}H_{30}Fe_2S_4$ requires C, 58.7; H, 4.6%); *m/z* (DCI) 655 (M^++1); δ_H ($CDCl_3$) 4.47 (2H, m), 4.38 (2H, m), 4.23 (10H, s), 4.14 (4H, m), 2.02 (6H, s) and 1.94 (6H, s).

1,1'-Bis[1,2-bis(1,3-dithiole-2-ylidene)ethane-1,2-diyl]diferrocene **174**

To a solution of **164** (100mg, 0.33mmol) in ether (50ml) was added HCl.Et_2O (0.33ml, 1.0M, 0.33mmol) and the reaction stirred for 24h. Purification as described for **173** afforded **174** as an orange solid, which was recrystallised from dichloromethane-hexane (50mg, 50% yield); m.p. >250°C (Found: C, 56.1; H, 3.8. $C_{28}H_{22}Fe_2S_4$ requires C, 56.2; H, 3.7%); *m/z* (DCI) 599 (M^++1); δ_H ($CDCl_3$) 6.40 (4H, m) 4.48 (2H, m), 4.38 (2H, m), 4.23 (10H, s) and 4.17 (4H, m).

1-[3,4-Bis(4,5-dimethylsulfanyl-1,3-dithiole-2-ylidene)but-1-enyl]ferrocene **181**

To a solution of **134**[104] (600mg, 1.02mmol) in THF (60ml) was added butyllithium (0.7ml, 1.6M, 1.12mmol) and the ylide left to form for 15min. After this time **180**[120] (170mg, 0.38mmol) was added, and the mixture stirred at 20°C for 16h, then evaporated under reduced pressure, and the residue extracted into dichloromethane. Water was added, the organic layer separated, dried ($MgSO_4$), and evaporated. Purification by column chromatography using neutral alumina with hexane-dichloromethane (3:1 v/v) as the eluent, afforded **181** as a red solid, which was recrystallised from dichloromethane-hexane (1.30g, 54% yield); m.p. 54-56°C (Found: C, 46.5; H, 4.1. $C_{24}H_{24}FeS_8$ requires C, 46.2; H, 3.9%); *m/z* (EI) 624; HRMS found 623.9157, $C_{24}H_{24}FeS_8$ requires 623.8993; δ_H ($CDCl_3$) 6.19 (2H, s), 5.89 (1H, s), 4.43 (2H, m), 4.30 (2H, m), 4.17 (5H, s), and 2.46-2.38 (12H, m); λ_{max} (DCM)/nm 261 (ε/dm^3 mol^{-1} cm^{-1} 17 200), 288 (38 500) and 374 (32 300).

1-[3,4-Bis(5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4-dithiin-2-ylidene)but-1-enyl]-ferrocene **182**

To a solution of **187** (1.00g, 3.03mmol) in THF (100ml) was added butyllithium (1.9ml, 1.6M, 3.04mmol), at -78°C, and the reaction was stirred at this temperature for 15min. After this time **186** (1.00g, 2.25mmol) was added, the reaction was warmed slowly to room temperature with stirring for a further 16h. The reaction mixture was evaporated under reduced pressure, and extracted into dichloromethane. Water was added, the organic layer separated, dried ($MgSO_4$), and evaporated. Column chromatography using silica gel and dichloromethane-hexane (1:1 v/v) as the eluent afforded **182** as an orange solid, which was recrystallised from dichloromethane-hexane (1.16g, 83% yield); m.p. 187-189°C (Found: C, 46.1 H, 3.2. $C_{24}H_{20}FeS_8$ requires C, 46.4; H, 3.3%); *m/z* (DCI) 621 (M^++1); δ_H ($CDCl_3$) 6.20 (2H, s), 5.97 (1H, s), 4.41 (2H, m), 4.28 (2H, m), 4.16 (5H, s) and 3.31 (8H, m); λ_{max} (DCM)/nm 229 (ε/dm^3 mol^{-1} cm^{-1} 59 200), 291 (36 500) and 384 (22 000).

1-[3-(5,6-Dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-ylidene)diallyl]ferrocene **185**

To a solution of **134**[104] (4.00g, 6.81mmol) in THF (100ml) was added butyllithium (4.3ml, 1.6M, 6.88mmol) and the ylide was left to form for 15min. After this time **184**[121] (1.40g, 5.98mmol) was added, and the reaction was stirred at 20°C for 24h. The reaction mixture was evaporated under reduced pressure, and the residue extracted into dichloromethane. Water was added, the organic layer separated, dried ($MgSO_4$), and evaporated. Purification using column chromatography on silica gel with hexane-dichloromethane (3:1 v/v) as the eluent, afforded **185** as a dark red solid, which was recrystallised from dichloromethane-hexane (1.60g, 64% yield); m.p. 148-150°C (Found: C, 52.3; H, 3.9. $C_{18}H_{16}FeS_4$ requires C, 51.9; H, 3.9%); *m/z* (DCI) 417 (M^++1); δ_H ($CDCl_3$) 6.53-5.66 (3H, m), 4.27 (2H, m), 4.18 (2H, m), 4.03 (5H, s), and 3.22 (4H, s); δ_C (d_6 acetone) 129.8, 127.1, 123.4, 117.4, 111.3, 84.0, 70.0, 69.9, 67.5, and 30.0; λ_{max} (DCM)/nm 261 (ε/dm^3 mol^{-1} cm^{-1} 15 000), 288 (12 500) and 374 (20 100).

1-[4-oxo-3-(5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-ylidene)but-1-enyl]-ferrocene **186**

To anhydrous dimethylformamide (15ml, excess) cooled to 0°C, oxalyl chloride (0.6ml, 6.87mmol) was added slowly dropwise and the mixture stirred for 5min at 0°C, and then warmed to 20°C, remaining so for a further 30min. After this time **185** (1.4g, 3.37mmol) was added and the mixture stirred at 20°C for 16h. The reaction was quenched at 0°C with aqueous sodium hydroxide (50ml, 1M), and then with water (200ml). Dichloromethane was added (75ml), and the organic layer separated, dried ($MgSO_4$), and evaporated under reduced pressure. Column chromatography using

silica gel and dichloromethane as the eluent afforded **186** as a bright red solid, which was recrystallised from dichloromethane-hexane (1.1g, 74% yield); m.p. 169-172°C (Found: C, 51.3; H, 3.8. $C_{19}H_{16}FeOS_4$ requires C, 51.4; H, 3.6%); *m/z* (DCI) 445 (M^++1); δ_H ($CDCl_3$) 9.63 (1H, s), 6.70 (1H, d, *J* 16.1 Hz), 6.48 (1H, d, *J* 16.1 Hz), 4.44 (2H, m), 4.30 (2H, m), 4.14 (5H, s), and 3.39 (4H, s); υ_{max} (KBr)/cm^{-1} 1616, 1471, 1425, 1282, 1033 and 832.

1,1'-Bis[3-(5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-ylidene)penta-1,4-diene-1,5-diyl]diferrocene **189**

To a suspension of **134**[104] (1.00g, 1.70mmol) in THF (60ml), at room temperature, was added butyllithium (1.1ml, 1.6M, 1.76mmol), and the reaction stirred for 15min before **186** (500mg, 1.13mmol) was added and the reaction stirred for 16h. The reaction mixture was evaporated under reduced pressure, and extracted into dichloromethane. Water was added, the organic layer separated, dried ($MgSO_4$), and evaporated. Column chromatography using silica gel and toluene as the eluent afforded **189** as an orange solid, which was recrystallised from dichloromethane-hexane (510mg, 72% yield); m.p. 189°C (dec.) (Found: C, 57.5 H, 4.4. $C_{30}H_{26}Fe_2S_4$ requires C, 57.5; H, 4.2%); *m/z* (DCI) 627 (M^++1); δ_H ($CDCl_3$) 6.37 (4H, s), 4.44 (4H, m), 4.31 (4H, m), 4.18 (10H, s), and 3.35 (4H, s); λ_{max} (DCM)/nm 270sh, 288 (ε/dm^3 mol^{-1} cm^{-1} 35 100) and 394 (23 800).

1-[5-Oxo-3,4-bis(5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-ylidene)pent-1-enyl]ferrocene **190**

Anhydrous dimethylformamide (10ml, excess) was cooled to 0°C, and oxalyl chloride (0.2ml, 2.29mmol) added slowly dropwise; the mixture was stirred for 5min at 0°C, and then warmed to 20°C, stirring for a further 30min. After this time **134** (500mg, 0.81mmol) was added and the mixture was stirred at 20°C for 3h. The reaction was quenched at 0°C with aqueous sodium hydroxide (50ml, 1M), and finally with water (200ml). Dichloromethane was added (75ml), and the organic layer separated, dried ($MgSO_4$), and evaporated under reduced pressure. Column chromatography using silica gel and dichloromethane as the eluent afforded **190** as a red solid, which was recrystallised from dichloromethane-hexane (370mg, 71% yield); m.p. 175°C(dec.); δ_H ($CDCl_3$) 9.14 (1H, s), 6.32 (1H, m), 6.89 (1H, m), 4.35 (2H, m), 4.27 (2H, m), 4.10 (5H, s), and 3.31 (8H, m); υ_{max} (KBr)/cm^{-1} 1610, 1410, 1261, 1103, 1024 and 802.

trans-1,1'-Bis[3,4-bis(5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-ylidene)hexa-1,5-diene-1,6-diyl]diferrocene **191**

To a suspension of **134**[104] (1.00g, 1.70mmol) in THF (60ml), at room temperature, was added butyllithium (1.1ml, 1.6M, 1.76mmol), and the reaction stirred for 15min. After this time, **190** (300mg, 0.46mmol) was added and the reaction stirred at 20°C for 16h. The reaction mixture was evaporated under reduced pressure, and extracted into dichloromethane. Water was added, the organic layer separated, dried ($MgSO_4$), and evaporated. Column chromatography using silica gel and toluene as the eluent afforded **191** as a red solid which was recrystallised from dichloromethane (250mg, 65% yield); m.p. 182°C (dec.) (Found: C, 52.3 H, 3.7. $C_{36}H_{30}Fe_2S_8$ requires C, 52.0; H, 3.6%); *m/z* (DCI) 831 (M^++1); δ_H ($CDCl_3$) 6.30 and 6.23 (2H, d, *J* 15.2 Hz), 6.00 and 5.92 (2H, d, *J* 15.5 Hz), 4.39 (4H, m), 4.24 (4H, m), 4.11 (10H, s), and 3.31 (8H, s); λ_{max} (DCM)/nm 290 (ε/dm^3 mol^{-1} cm^{-1} 73 700) and 384 (74 200).

1,1'-Bis[3-(5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-ylidene)diallyl]ferrocene **193**

To a suspension of **143** (2.00g, 2.23mmol) in THF (200ml), at -78°C, was added butyllithium (3.0ml, 1.6M, 4.80mmol) and the reaction stirred for 30min. After this time **184**[121] (1.00g, 4.27mmol) was added. The reaction was warmed slowly to room temperature, with stirring for a further 16h. The reaction mixture was evaporated under reduced pressure, and extracted into dichloromethane. Water was added, the organic layer separated, dried ($MgSO_4$) and evaporated. Column chromatography using silica gel and hexane-dichloromethane (3:1 v/v) as the eluent afforded **193** as an orange solid which was a mixture of isomers (480mg, 33% yield); m.p. 173-176°C (Found: C, 47.9 H, 3.6. $C_{26}H_{22}FeS_8$ requires C, 48.3; H, 3.4%); *m/z* (DCI) 647 (M^++1); δ_H ($CDCl_3$) 6.14-5.80 (6H, m), 4.25 (4H, m), 4.20 (4H, m) and 3.31 (8H, s). The isomers could not be separated by either chromatography or recrystallisation.

6.4 EXPERIMENTAL TO CHAPTER 4

2-(1,3-Dithiole-2-ylidene)-6-[1-cyclopentadienyl(cyclopentadienyl)iron]-3a,4,5,6-tetrahydro-1,3-benzodithiole-4,4,5,5-tetracarbonitrile **194**

A solution of **137** (50mg, 0.12mmol) in acetonitrile (3ml) was heated until a dark but clear solution was obtained. Similarly, a solution of tetracyanoethylene **13** (15mg, 0.12mmol) in acetonitrile (5ml) was heated until all the solid had dissolved. The two solutions were combined, at 60°C, and refluxed for 5min. The solution was

cooled to 20°C and after 16h the product was filtered and washed with ice-cold acetonitrile. Yellow crystals of **194**.MeCN were harvested for X-ray analysis, together with **194** as a yellow powder (45mg, 68% combined yield). Data for **194**: m.p. >250°C (Found: C, 53.1; H, 2.6; N, 11.1. $C_{24}H_{14}FeN_4S_4$ requires C, 53.1; H, 2.6; N, 10.3%); *m/z* (DCI) 543 (M^++1); δ_H (CD_2Cl_2) 6.54 (1H, m), 6.46 (2H, dd, *J* 14.1 Hz), 5.00 (1H, m), 4.68 (1H, m), 4.46 (2H, t, *J* 1.3 Hz), 4.35 (2H, t, *J* 1.4 Hz), and 4.27 (5H, s); υ_{max} (KBr)/cm^{-1} 3059, 2923, 2364, 2198, 1590 and 1437.

6.4.1 GENERAL PROCEDURE FOR COMPOUNDS 198-201

To a suspension of the respective Wittig salt in THF (60ml) was added butyllithium at -78°C, the reaction stirred at this temperature for 15min whence **32** was added and the reaction temperature raised to 20°C, with stirring for a further 16h. The reaction mixture was evaporated under reduced pressure, and the residue extracted into dichloromethane. Water was added, the organic layer separated, dried ($MgSO_4$), and evaporated once more. Purification by column chromatography using silica gel and toluene as the eluent afforded the desired product, which was recrystallised from dichloromethane-hexane where applicable.

1-[2,2'-Bi(1,3-dithiolylidene)-4-yl]propylene **198**

Using general procedure 6.4.1, ethyltriphenylphosphonium bromide (1.0g, 2.70mmol), butyllithium (1.7ml, 1.6M, 2.72mmol) and **32** (500mg, 2.16mmol) afforded **198** as a dark orange oil 1:4 *cis*:*trans* (420mg, 80% yield); *m/z* (DCI) 245 (M^++1), HRMS found 243.9428, $C_9H_8S_4$ requires 243.9509; δ_H ($CDCl_3$) 6.58 (2H, s), 6.45 (1H, s), 6.35 (1H, d, *J* 15.4 Hz), 5.60 (1H, m), 1.81 (3H, dd, *J* 6.7 Hz).

1-[2,2'-Bi(1,3-dithiolylidene)-4-yl]-2-phenylethylene **199**

Using general procedure 6.4.1, benzyltriphenylphosphonium chloride (2.0g, 5.14mmol), butyllithium (3.3ml [1.6M], 5.28mmol) and **32** (1.0g, 4.31mmol) afforded **199** as a purple solid (1.02g, 77% yield); m.p. 124-126°C (Found: C, 54.8; H, 3.2. $C_{14}H_{10}S_4$ requires C, 54.9; H, 3.3%); *m/z* (DCI) 307 (M^++1); δ_H (d_6 acetone) 7.76-7.31 (5H, m), 7.24 and 7.16 (1H, d, *J* 15.9 Hz), 6.81 (1H, s), 6.66 (2H, s), and 6.51 and 6.43 (1H, d, *J* 15.6 Hz).

1-[2,2'-Bi(1,3-dithiolylidene)-4-yl]-2-(*p*-methoxyphenyl)ethylene **200**

Using general procedure 6.4.1, *p*-methoxybenzyltriphenylphosphonium chloride (1.0g, 2.39mmol), butyllithium (1.5ml, 1.6M, 2.40mmol) and **32** (500mg, 2.16mmol) afforded **200** as a dark orange solid (600mg, 83% yield); m.p. 164-167°C (Found: C, 53.5; H, 3.4. $C_{15}H_{12}OS_4$ requires C, 53.5; H, 3.6%); *m/z* (DCI) 337

(M^++1); δ_H ($CDCl_3$) 7.34 (2H, d, *J* 8.6 Hz), 6.87 (2H, d, *J* 8.7 Hz), 6.75 (1H, d, *J* 15.7 Hz), 6.35 (4H, m), and 3.82 (3H, s); δ_H (d_6 DMSO) 7.46 (2H, d, *J* 8.7 Hz), 7.09 and 7.01 (1H, d, *J* 16.1 Hz), 6.90 (2H, d, *J* 8.8 Hz), 6.81 (1H, s), 6.73 (2H, s), 6.37 and 6.29 (1H, d, *J* 16.0 Hz) and 3.74 (3H, s).

1-[2,2'-Bi(1,3-dithiolylidene)-4-yl]-2-(*p*-nitrophenyl)ethylene **201**

Using general procedure 6.4.1, *p*-nitrobenzyltriphenylphosphonium chloride (1.5g, 3.46mmol), butyllithium (2.2ml, 1.6M, 3.52mmol) and **32** (500mg, 2.16mmol) afforded **201** as a dark purple solid (550mg, 73% yield); m.p. >250°C (Found: C, 48.1; H, 2.7; N, 3.8. $C_{14}H_9NO_2S_4$ requires C, 47.8; H, 2.6; N, 4.0%); *m/z* (DCI) 352 (M^++1); δ_H ($CDCl_3$) 8.21 (2H, d, *J* 9.0 Hz), 7.53 (2H, d, *J* 8.5 Hz), 7.07 and 6.99 (1H, d, *J* 15.8 Hz), 6.57 (1H, s), 6.45 and 6.37 (1H, d, *J* 16.6 Hz) and 6.37 (2H, s); δ_H (d_6 DMSO) 8.21 (2H, d, *J* 8.3 Hz), 7.81 (2H, d, *J* 8.7 Hz), 7.54 and 7.46 (1H, d, *J* 16.2 Hz), 7.14 (1H, s), 6.78 (2H, s), 6.59 and 6.51 (1H, d, *J* 16.0 Hz); υ_{max} (KBr)/cm^{-1} 1586, 1504, 1338, 1108, 937 and 658.

6.4.2 GENERAL PROCEDURE FOR COMPOUNDS 202-206

To a solution of the respective vinyl-TTF derivative in toluene (10ml) was added tetracyanoethylene **13**. The mixture was refluxed for 16h. After evaporating the mixture under reduced pressure, column chromatography using silica gel and toluene as the eluting solvent afforded the desired product which was recrystallised from dichloromethane.

2-(1,3-Dithiole-2-ylidene)-3a,4,5,6-tetrahydro-1,3-benzodithiole-4,4,5,5-tetra-carbonitrile **202**

Using general procedure 6.4.2, vinyltetrathiafulvalene **197** (200mg, 0.87mmol) and tetracyanoethylene **13** (250mg, 1.95mmol) afforded **202** as a yellow solid (220mg, 70% yield); m.p. 190-192°C (Found: C, 46.9; H, 1.7. N, 14.8; $C_{14}H_6N_4S_4$ requires C, 46.9; H, 1.7; N, 15.6%); *m/z* (DCI) 359 (M^++1), HRMS found 357.9253, $C_{14}H_6N_4S_4$ requires 357.9475; δ_H ($CDCl_3$) 6.39 (2H, dd, *J* 16.8 Hz), 5.86 (1H, m), 4.89 (1H, m), and 3.86(1H, m); υ_{max}(KBr)/cm^{-1} 3073, 2906, 2254, 1436, 800 and 640.

2-(1,3-Dithiole-2-ylidene)-6-methyl-3a,4,5,6-tetrahydro-1,3-benzodithiole-4,4,5,5-tetracarbonitrile **203**

Using general procedure 6.4.2, **198** (200mg, 0.82mmol) and tetracyanoethylene **13** (110mg, 0.86mmol) afforded **203** as an orange/brown solid (170mg, 56% yield); m.p. 192-194°C; *m/z* (DCI) 373 (M^++1), HRMS found

371.9605, $C_{15}H_8N_4S_4$ requires 371.9632; δ_H ($CDCl_3$) 6.40 (2H, dd, *J* 15.3 Hz), 5.90 (1H, m), 4.90 (1H, m), 3.43 (1H, m), and 1.75 (3H, d, *J* 7.6 Hz); υ_{max} (KBr)/cm^{-1} 3080, 2914, 2251, 1548, 802 and 655.

2-(1,3-Dithiole-2-ylidene)-6-phenyl-3a,4,5,6-tetrahydro-1,3-benzodithiole-4,4,5,5-tetracarbonitrile **204**

Using general procedure 6.4.2, **199** (200mg, 0.65mmol) and tetracyanoethylene **13** (90mg, 0.70mmol) afforded **204** as an orange/brown solid (170mg, 59% yield); m.p. 106-108°C; *m/z* (DCI) 435 (M^++1), HRMS found 433.9779, $C_{20}H_{10}N_4S_4$ requires 433.9788; δ_H ($CDCl_3$) 7.49 (5H, s), 6.42 (2H, dd, *J* 16.6 Hz), 6.14 (1H, m), 4.94 (1H, m), and 4.51 (1H, m); υ_{max} (KBr)/cm^{-1} 3074, 2930, 2253, 1624, 1190 and 1082.

2-(1,3-Dithiole-2-ylidene)-6-(*p*-methoxyphenyl)-3a,4,5,6-tetrahydro-1,3-benzodithiole-4,4,5,5-tetracarbonitrile **205**

Using general procedure 6.4.2, **200** (100mg, 0.30mmol) and tetracyanoethylene **13** (40mg, 0.31mmol) afforded **205** as an orange solid (100mg, 75% yield); m.p. 164-166°C; *m/z* (EI) 464, HRMS found 463.9899, $C_{21}H_{12}N_4OS_4$ requires 463.9894; δ_H ($CDCl_3$) 7.40 (2H, d, *J* 8.7 Hz), 6.97 (2H, d, *J* 8.8 Hz), 6.42 (2H, dd, *J* 16.3 Hz), 6.11 (1H, m), 4.93 (1H, m) and 4.49 (1H, m); υ_{max} (KBr)/cm^{-1} 3054, 2905, 2250, 1608, 1511 and 1261.

2-(1,3-Dithiole-2-ylidene)-6-(*p*-nitrophenyl)-3a,4,5,6-tetrahydro-1,3-benzodithiole-4,4,5,5-tetracarbonitrile **206**

Using general procedure 6.4.2, **201** (130mg, 0.37mmol) and tetracyanoethylene **13** (50mg, 0.39mmol) afforded **206** as a brown solid (75mg, 42% yield); m.p. >250°C; δ_H ($CDCl_3$) 8.34 (2H, d, *J* 8.8 Hz), 7.72 (2H, d, *J* 8.9 Hz), 6.44 (2H, dd, *J* 17.4 Hz), 6.11 (1H, m), 4.97 (1H, m) and 4.63 (1H, m); υ_{max} (KBr)/cm^{-1} 3032, 2916, 2344, 1508, 1340 and 1172.

2-(1,3-Dithiole-2-ylidene)-6-(*p*-methoxyphenyl)-*N*-phenyl-3a,4,5,6-tetrahydro-1,3-dithiolo[2,3-*c*]pyridazine-4,5-dicarboximide **210**

To a solution of **200** (250mg, 0.74mmol) in toluene (10ml) was added 4-phenyl-1,2,4-triazoline-3,5-dione (150mg, 0.86mmol). The mixture was refluxed for 4 hours. Column chromatography using silica gel and toluene as the eluent removed excess starting material. Subsequent use of dichloromethane-acetone (2:1 v/v) as the eluent gave **210** as an orange solid, which was recrystallised from toluene (230mg, 61% yield); m.p. 134-137°C (Found: C, 53.9; H, 3.5; N, 7.9. $C_{23}H_{17}N_3O_3S_4$ requires C, 54.0; H, 3.4; N, 8.2%); *m/z* (DCI) 512 (M^++1); δ_H ($CDCl_3$) 7.40 (4H, m), 6.91

(1H, m), 6.87 (1H, m), 6.36 (2H, dd, *J* 17.3 Hz) and 5.64 (1H, m); υ_{max} (Nujol)/cm^{-1} 1775, 1708, 1599, 1501, 1415 and 1254.

2-(1,3-Dithiole-2-ylidene)-6-[1-cyclopentadienyl(cyclopentadienyl)iron]-*N*-phenyl-3a,4,5,6-tetrahydro-1,3-dithiolo[2,3-*c*]pyridazine-4,5-dicarboximide **211**

To a solution of **137** (100mg, 0.24mmol) in toluene (10ml) was added 4-phenyl-1,2,4-triazoline-3,5-dione (45mg, 0.26mmol). The mixture was refluxed for 4 hours. Purification as described for **210** gave **211** as an orange solid, which was recrystallised from toluene (45mg, 33% yield); m.p. 199-201°C; *m/z* (DCI) 590 (M^++1), HRMS found 588.9494, $C_{26}H_{19}FeN_3O_2S_4$ requires 588.9710; δ_H ($CDCl_3$) 7.52 (5H, m), 6.92 (1H, m), 6.32 (2H, dd, *J* 12.3 Hz), 5.82 (1H, d, *J* 5.9 Hz) and 4.91 (1H, dd, *J* 6.0 Hz); υ_{max} (KBr)/cm^{-1} 3066, 2924, 1772, 1719, 1402 and 1281.

Dimethyl 2-(1,3-dithiole-2-ylidene)-3a,6-dihydro-1,3-benzodithiole-4,5-dicarboxylate **212**

To a solution of **197** (200mg, 0.87mmol) in toluene (15ml) was added dimethylacetylenedicarboxylate (0.1ml, 0.81mmol), and the mixture was refluxed for 16h. The solvent was evaporated under reduced pressure, and the residue chromatographed using neutral alumina and toluene as the eluting solvent. The product was recystallised from methanol to give **212** as a red solid, which was recrystallised from dichloromethane-hexane (1.50g, 46% yield); m.p. 146-149°C (Found: C, 44.7; H, 3.1. $C_{14}H_{12}O_4S_4$ requires C, 45.2; H, 3.3%); *m/z* (DCI) 373 (M^++1); δ_H ($CDCl_3$) 6.31 (2H, dd, *J* 16.9 Hz), 6.12 (1H, d, *J* 2.4 Hz), 4.77-4.63 (1H, m), 3.83 (3H, s), 3.78 (3H, s), 3.28-3.15 (1H, m), 2.82-2.65 (1H, m); υ_{max} (KBr)/cm^{-1} 3060, 2950, 1706, 1541, 1436 and 1286.

6.5 EXPERIMENTAL TO CHAPTER 5

6.5.1 GENERAL PROCEDURE FOR COMPOUNDS 217-221, 223-226, 228-230, 233, 240, AND 245

To a solution of tetrathiafulvalene, in ether (100ml) at -78°C, was added lithium diisopropylamide mono(tetrahydrofuran) (1.05 equiv., 1.5M), and the TTF anion allowed to form over 1.5h. The relevant ketone or aldehyde was then added neat in one portion, and the reaction was stirred at -78°C for a further 1h, before warming slowly to room temperature. Water was added and the organic layer separated, dried ($MgSO_4$), and evaporated under reduced pressure. Column chromatography on silica gel and

hexane-dichloromethane (3:1 v/v) as the eluting solvent, was used to remove residual tetrathiafulvalene. Subsequent use of dichloromethane as the eluent afforded the desired product. All solids were recrystallised from dichloromethane-hexane.

1-[2,2'-Bi(1,3-dithiolylidene)-4-yl]ethanol **217**

Using general procedure 6.5.1, tetrathiafulvalene (600mg, 2.94mmol) and acetaldehyde (0.2ml, 3.58mmol) afforded **217** as an orange oil (440mg, 60% yield); *m/z* (DCI) 249 (M^++1), HRMS found 247.9445, $C_8H_8OS_4$ requires 247.9458; δ_H (d_6-acetone) 6.60 (2H, s), 6.39 (1H, s), 4.67 (1H, d, *J* 6.5 Hz), 2.92 (1H, s), and 1.38 (3H, d, *J* 7.0 Hz); υ_{max} (Nujol)/cm^{-1} 3358, 1715, 1681, 1134, 796 and 733.

[2,2'-Bi(1,3-dithiolylidene)-4-yl]phenylmethanol **218**

Using general procedure 6.5.1, tetrathiafulvalene (600mg, 2.94mmol) and benzylaldehyde (0.4ml, 3.94mmol) afforded **218** as an orange oil (490mg, 54% yield); *m/z* (DCI) 311 (M^++1), HRMS found 309.9588, $C_{13}H_{10}OS_4$ requires 309.9615; δ_H ($CDCl_3$) 7.37 (5H, s), 6.26 (2H, s), 6.09 (1H, s), 5.47 (1H, s), and 3.09 (1H, s); υ_{max} (neat)/cm^{-1} 3384, 3066, 1689, 1452, 1015 and 777.

2-[2,2'-Bi(1,3-dithiolylidene)-4-yl]propan-2-ol **219**

Using general procedure 6.5.1, tetrathiafulvalene (250mg, 1.23mmol) and acetone (0.5ml, 10.90mmol) afforded **219** as a yellow solid (230mg, 72% yield); m.p. 93-94°C (Found: C, 41.1; H, 3.9. $C_9H_{10}OS_4$ requires C, 41.2; H, 3.8%); *m/z* (DCI) 263 (M^++1); δ_H ($CDCl_3$) 6.31 (2H, s), 6.13 (1H, s), 3.22 (1H, s), and 1.53 (6H, s); υ_{max} (KBr)/cm^{-1} 3295, 2978, 1156, 936, 794 and 758.

[2,2'-Bi(1,3-dithiolylidene)-4-yl]diphenylmethanol **220**

Using general procedure 6.5.1, tetrathiafulvalene (600mg, 2.94mmol) and benzophenone (700mg, 3.85mmol) afforded **220** as an orange oil (980mg, 86% yield); *m/z* (EI) 386, HRMS found 385.9928, $C_{19}H_{14}OS_4$ requires 385.9928; δ_H ($CDCl_3$) 7.85-7.28 (10H, m), 6.26 (2H, s), 5.86 (1H, s),and 3.24 (1H, s); υ_{max} (neat)/cm^{-1} 3448, 3062, 1654, 1446, 1279 and 700.

1-[2,2'-Bi(1,3-dithiolylidene)-4-yl]cyclohexanol **221**

Using general procedure 6.5.1, tetrathiafulvalene (600mg, 2.94mmol) and cyclohexanone afforded **221** as a yellow solid (390mg, 44% yield); m.p. 92-94°C; *m/z* (DCI) 303 (M^++1), HRMS found 301.9693, $C_{12}H_{14}OS_4$ requires 301.9928; δ_H ($CDCl_3$) 6.40-6.10 (3H, s br), 2.14 (1H, s), and 1.85-1.55 (10H, m); υ_{max} (KBr)/cm^{-1} 3260, 3178, 2931, 2856, 1059 and 650.

1-[2,2'-Bi(1,3-dithiolylidene)-4-yl]cyclohexene **222**

To a solution of **221** (200mg, 0.66mmol) in dichloromethane (30ml) was added slowly $HCl.Et_2O$ (0.3ml, 1.0M, 0.30mmol), and the solution stirred at room temperature for 1h. Column chromatography using silica gel and hexane-dichloromethane (1:1 v/v) as the eluent afforded **222** as a yellow solid, which was recrystallised from dichloromethane-hexane (160mg, 85% yield); m.p. 115-117°C (Found: C, 50.6; H, 4.3. $C_{12}H_{12}S_4$ requires C, 50.7; H, 4.3%) *m/z* (DCI) 285 (M^++1); δ_H ($CDCl_3$) 6.31 (2H, s), 6.13 (1H, s), 5.78 (1H, m), 2.27-2.18 (4H, m), and 1.69-1.57 (4H, m).

3-[2,2'-Bi(1,3-dithiolylidene)-4-yl]-1-buten-3-ol **223**

Using general procedure 6.5.1, tetrathiafulvalene (500mg, 2.45mmol) and methyl vinyl ketone (0.2ml, 2.45mmol) afforded **223** as a yellow solid (443mg, 66% yield); m.p. 69-71°C (Found: C, 44.0; H, 3.8. $C_{10}H_{10}OS_4$ requires C, 43.8; H, 3.7%); *m/z* (DCI) 275 (M^++1); δ_H ($CDCl_3$) 6.30 (2H, s), 6.16 (1H, s), 6.03 (1H, m), 5.41 (1H, d, *J* 17.1 Hz), 5.22 (1H, d, *J* 10.7 Hz), 2.14 (1H, s) and 1.59 (3H, s); υ_{max} (KBr)/cm^{-1} 3284, 3066, 2978, 924, 792 and 642.

Bis[2,2'-bi(1,3-dithiolylidene)-4-yl]methanol **224**

Using general procedure 6.5.1, tetrathiafulvalene (250mg, 1.23mmol) and tetrathiafulvalenecarboxaldehyde[76] **32** (300mg, 1.29mmol) afforded **224** as a pale orange solid (250mg, 47% yield); m.p. 45-48°C (Found: C, 35.8; H, 1.9. $C_{13}H_8OS_8$ requires C, 35.8; H, 1.9%); *m/z* (DCI) 437 (M^++1); δ_H ($CDCl_3$) 6.40 (1H, d, *J* 1.2 Hz), 6.32 (2H, s), 5.30 (1H, m), and 2.47 (1H, d, *J* 4.2 Hz); υ_{max} (KBr)/cm^{-1} 3420, 3060, 2958, 1636, 1431 and 641.

1,1-Bis[2,2'-bi(1,3-dithiolylidene)-4-yl]ethanol **225**

Using general procedure 6.5.1, tetrathiafulvalene (400mg, 1.96mmol) and acetyltetrathiafulvalene[74c] (250mg, 1.02mmol) afforded **225** as a pale orange solid (320mg, 70% yield); m.p. 128-130°C (Found: C, 37.1; H, 2.2. $C_{14}H_{10}OS_8$ requires C, 37.3; H, 2.2%); *m/z* (DCI) 451 (M^++1); δ_H ($CDCl_3$) 6.33 (6H, s), 2.56 (1H, s), and 1.90 (3H, s); υ_{max} (KBr)/cm^{-1} 3442, 3060, 1654, 820, 786 and 625.

Bis[2,2'-bi(1,3-dithiolylidene)-4-yl]phenylmethanol **226**

Using general procedure 6.5.1, tetrathiafulvalene (250mg, 1.23mmol) and benzoyltetrathiafulvalene[146] (250mg, 0.81mmol) afforded **226** as a pale orange solid (200mg, 48% yield); m.p. 94-96°C (Found: C, 44.6; H, 2.5. $C_{19}H_{12}OS_8$ requires C, 44.5; H, 2.4%); *m/z* (DCI) 513 (M^++1); δ_H ($CDCl_3$) 7.58-7.40 (5H, m), 6.32 (4H, s), 6.24 (2H, s) and 3.04 (1H, s); υ_{max} (KBr)/cm^{-1} 3447, 3063, 1654, 795, 713 and 645.

Bis[2,2'-bi(1,3-dithiolylidene)-4-yl]methylmethoxyether **227**

To a solution of **224** (90mg, 0.21mmol) in THF (20ml) was added sodium hydride (10mg, 60% dispersion in oil, 0.25mmol), and the mixture was stirred for 1h at 20°C. After this time, methyl iodide was added (0.1ml, 1.61mmol), and the solution was stirred for a further 1h at 20°C. The solvent was evaporated under reduced pressure; column chromatography using silica gel and toluene-hexane (1:1 v/v) as the eluting solvent afforded **227** as an orange solid, which was recrystallised from dichloromethane-hexane (70mg, 75% yield); m.p. 151-153°C (Found: C, 37.5; H, 2.3. $C_{14}H_{10}OS_8$ requires C, 37.3; H, 2.2%); *m/z* (DCI) 451 (M^++1); δ_H ($CDCl_3$) 6.36 (2H, d, *J* 1.1 Hz), 6.32 (4H, s), 4.76 (1H, t, *J* 1.1 Hz), and 3.42 (3H, s).

[1-Cyclopentadienyl(cyclopentadienyl)iron][2,2'-bi(1,3-dithiolylidene)-4-yl]-methanol **228**

Using general procedure 6.5.1, tetrathiafulvalene (250mg, 1.23mmol) and ferrocenecarboxaldehyde (400mg, 1.87mmol) afforded **228** as a brown solid (240mg, 47% yield); m.p. 137-139°C (Found: C, 49.0; H, 3.5. $C_{17}H_{14}FeOS_4$ requires C, 48.8; H, 3.4%); *m/z* (DCI) 417 (M^++1); δ_H ($CDCl_3$) 6.30 (2H, s), 6.12 (1H, s), 5.20 (1H, s), 4.32 (2H, m), 4.25 (7H, m), 2.42 (1H, d, *J* 3.8 Hz); υ_{max} (KBr)/cm^{-1} 3550, 3433, 3062, 1090, 641 and 487.

1-[1-Cyclopentadienyl(cyclopentadienyl)iron]-1-[2,2'-bi(1,3-dithiolylidene)-4-yl]ethanol **229**

Using general procedure 6.5.1, tetrathiafulvalene (1.00g, 4.90mmol) and acetylferrocene (1.30g, 5.70mmol) afforded **229** as a yellow solid (1.91g, 90% yield); m.p. 139-141°C (Found: C, 50.2; H, 3.6. $C_{18}H_{16}FeOS_4$ requires C, 50.0; H, 3.7%); *m/z* (EI) 432; δ_H ($CDCl_3$) 6.28 (2H, s), 5.96 (1H, s), 4.33-4.19 (9H, m), 2.70 (1H, s), and 1.80 (3H, s); υ_{max} (KBr)/cm^{-1} 3495, 3074, 2978, 1104, 820 and 642.

[1-Cyclopentadienyl(cyclopentadienyl)iron][2,2'-bi(1,3-dithiolylidene)-4-yl]-phenylmethanol **230**

Using general procedure 6.5.1, tetrathiafulvalene (500mg, 2.45mmol) and benzoylferrocene[147] (500mg, 1.72mmol) afforded **230** as an orange solid (540mg, 63% yield) ; m.p. 66-67°C (Found: C, 55.5; H, 3.7. $C_{23}H_{18}FeOS_4$ requires C, 55.9; H, 3.7%); *m/z* (DCI) 495 (M^++1), HRMS found 493.9560, $C_{23}H_{18}FeOS_4$ requires 493.9590; δ_H ($CDCl_3$) 7.42-7.32 (5H, m), 6.29 (2H, s), 5.82 (1H, s), 4.47 (1H, s), 4.33 (1H, s), 4.25 (6H, s), 3.89 (1H, s) and 3.41 (1H, s); υ_{max} (KBr)/cm^{-1} 3490, 3064, 2922, 729, 644 and 488.

9-Hydroxy-9-[2,2'-bi(1,3-dithiolylidene)-4-yl]fluorene **233**

Using general procedure 6.5.1, tetrathiafulvalene (500mg, 2.45mmol) and 9-fluorenone (500mg, 2.78mmol) afforded **233** as a yellow solid (730mg, 77% yield); m.p. 72-74°C (Found: C, 59.5; H, 3.4. $C_{19}H_{12}OS_4$ requires C, 59.4; H, 3.2%); *m/z* (DCI) 385 (M^++1); δ_H ($CDCl_3$) 7.65-7.25 (8H, m), 6.27 (2H, s), 6.21 (1H, s), and 2.66 (1H, s); υ_{max} (KBr)/cm^{-1} 3416, 3063, 1448, 768, 743 and 731.

(i) 9-[2,2'-Bi(1,3-dithiolylidene)-4-yl]fluorenate chloride **234**.Cl and
(ii) 9-[2,2'-Bi(1,3-dithiolylidene)-4-yl]fluorenate tetrafluoroborate **234**.BF_4

(i) To a solution of **233** (460mg, 1.20mmol) in dichloromethane (10ml) was added HCl.Et_2O (1.2ml, 1.0M, 1.2mmol). The reaction was stirred for 30min at 20°C before adding ether (100ml). A brown/black precipitate presumed to be **234**.chloride salt was filtered from the reaction mixture (450mg).

(ii) To a solution of **223** (200mg, 0.52mmol) in dichloromethane (10ml) was added tetrafluoroboric acid, dropwise at 20°C, until deposition ceased. Ether (100ml) was added to the reaction mixture and a brown/black precipitate presumed to be **234**.tetrafluoroborate salt was obtained by filtration (170mg).

In each case, satisfactory analysis could not be obtained.

9-Ethoxy-9-[2,2'-bi(1,3-dithiolylidene)-4-yl]fluorene **236**

To a suspension of **234** tetrafluoroborate salt (100mg, 0.22mmol) in ethanol (20ml) was added sodium ethoxide in ethanol (2.5ml, 0.1M, 0.25mmol), and the mixture stirred for 15min. The solvent was evaporated under reduced pressure; column chromatography using silica gel and dichloromethane as the eluent afforded **236** as an orange oil (30mg, 33% yield); *m/z* (DCI) 413 (M^++1), HRMS found 412.0160, $C_{21}H_{16}OS_4$ requires 412.0084; δ_H ($CDCl_3$) 7.70-7.28 (8H, m), 6.27 (2H, s), 6.00 (1H, s), 2.99 (2H, q, *J* 7.0 Hz) and 1.09 (3H, t, *J* 7.0 Hz).

4-Benzyltetrathiafulvalene **238**

To a solution of lithium aluminium hydride (70mg, 1.84mmol) in ether (30ml), was added aluminium chloride (220mg, 1.65mmol) at 0°C. After 5min the ice bath was removed and a suspension of benzoyltetrathiafulvalene[146] **237** (500mg, 1.62mmol), in ether (10ml) was slowly added [alternatively, **218** (500mg, 161mmol) can also be used]. The reduction was allowed to proceed over 16h. The ethereal mixture was poured onto ice, separated once the ice had melted, and dried ($MgSO_4$). Column chromatography using silica gel and hexane-dichloromethane (3:1 v/v) as the eluting solvent afforded **238** as a bright yellow oil [320mg, 67% yield (340mg, 72% from **218**)]; (Found: C, 53.0; H, 3.4. $C_{13}H_{10}S_4$ requires C, 53.0; H, 3.4%); *m/z* (DCI) 295

(M^++1); δ_H ($CDCl_3$) 7.43-7.28 (5H, m), 6.71 (1H, s), 6.34 (2H, dd), and 4.20 (2H, s).

1-Hydroxy-1-[2,2'-bi(1,3-dithiolylidene)-4-yl]-2-cyclopentene **240**

Using general procedure 6.5.1, tetrathiafulvalene (500mg, 2.45mmol) and 2-cyclopenten-1-one (0.3ml, 3.58mmol) afforded **240** as an orange solid (420mg, 60% yield); m.p. 63-65°C; *m/z* (DCI) 287 (M^++1); δ_H ($CDCl_3$) 6.31 (2H, s), 6.11 (1H, s), 6.12-6.07 (1H, m), 5.81-5.76 (1H, m), 2.67-2.29 (4H, m), and 2.17-2.01 (1H, m); δ_C ($CDCl_3$) 143.8, 137.0, 134.8, 119.7, 112.8, 40.1, and 31.7; υ_{max} (KBr)/cm^{-1} 3396, 3062, 2933, 1733, 1400 and 1164.

3-[2,2'-Bi(1,3-dithiolylidene)-4-yl]-2,4-cyclopentadiene (Dimer) **242**

To a solution of **240** (500mg, 1.75mmol) in dichloromethane (20ml) was added HCl.Et_2O (1.75ml, 1.0M, 1.75mmol), and the mixture stirred at 20°C for 15 min. Column chromatography using silica gel and dichloromethane as the eluting solvent afforded an orange oil (420mg, 90% yield); *m/z* (DCI) 269 (M^++1) HRMS found 267.9593, $C_{11}H_8S_4$ requires 267.9509; δ_H ($CDCl_3$) 6.70-5.41 (12H, m), 3.25 (2H, m), 3.16 (1H, m) and 3.02 (1H, m).

1-Hydroxy-1-[2,2'-bi(1,3-dithiolylidene)-4-yl]-2,3,4,5-tetramethyl-2-cyclopentene **245**

Using general procedure 6.5.1, tetrathiafulvalene (500mg, 2.45mmol) and 2,3,4,5-tetramethyl-2-cyclopentenone (0.4ml, 2.52mmol) afforded **245** as an orange oil (610mg, 73% yield), which proved to be a mixture of *cis* and *trans* isomers, able to be separated by silica gel column chromatography using dichloromethane-hexane (1:2 v/v); *m/z* (EI) 342; first fraction *trans*: δ_H ($CDCl_3$) 6.31 (2H, s), 6.20 (1H, s), 2.39 (2H, m), 1.70 (3H, s), 1.65 (3H, s), 1.44 (1H, s) and 0.97 (6H, d, *J* 6.9 Hz); second fraction *cis*: 6.30 (2H, s), 6.03 (1H, s), 1.90 (1H, s), 1.66-1.60 (8H, m) and 1.07 (6H, m); υ_{max} (neat)/cm^{-1} 3502, 3067, 2964, 796, 733 and 643.

1-[2,2'-Bi(1,3-dithiolylidene)-4-yl]-2,3,4,5-tetramethyl-2,4-cyclopentadiene **246**

To a solution of **245** (*cis* and *trans* mixture, 200mg, 0.58mmol) in dichloromethane (20ml) was added HCl.Et_2O (0.60ml, 1.0M, 0.60mmol), and the mixture stirred at 20°C for 1h. Column chromatography using silica gel and dichloromethane as the eluent afforded **246** as an orange oil (165mg, 87% yield); *m/z* (EI) 324, HRMS found 324.0119, $C_{15}H_{16}S_4$ requires 324.0135; δ_H ($CDCl_3$) 6.33 (2H, s), 5.89 (1H, q, *J* 7.6 Hz), 2.86 (1H, m), 2.05 (3H, d, *J* 1.7 Hz), 1.87 (3H, s), 1.80 (3H, m) and 1.12 (3H, d, *J* 7.5 Hz).

Dimethyl 5-[2,2'-bi(1,3-dithiolylidene)-4-yl]-1,4,6,7-tetramethylbicyclo[2.2.1]-hepta-2,5-diene-2,3-dicarboxylate **248**

To a solution of **246** (200mg, 0.62mmol) in toluene (30ml) was added dimethyl acetylenedicarboxylate (0.1ml, 0.81mmol). The reaction was stirred at 50°C for 4h. Column chromatography using neutral alumina and dichloromethane-hexane (1:1 v/v) as the eluent afforded **248** as an orange solid, which was recrystallised from dichloromethane-hexane at 0°C (255mg, 89% yield); m.p. 42-44°C (Found: C, 54.0; H, 5.1. $C_{21}H_{22}O_4S_4$ requires C, 54.1; H, 4.8%); *m/z* (DCI) 467 (M^++1); δ_H ($CDCl_3$) 6.30 (2H, s), 6.19 (1H, s), 3.77 (3H, s), 3.75 (3H, s), 2.68 (1H, d, *J* 6.3 Hz), 1.92 (3H, d, *J* 1.4 Hz), 1.67 (3H, d, *J* 1.3 Hz), 1.30 (3H, s) and 0.82 (3H, d, *J* 6.30 Hz); υ_{max} (KBr)/cm^{-1} 3069, 2949, 1716, 1432, 1293 and 1236.

2:1 **229**-chloranil CT complex **250**

A solution of **229** (200mg, 0.46mmol) in acetonitrile (25ml) was refluxed for 5min. Similarly, a solution of chloranil **249** (120mg, 0.48mmol) was refluxed in acetonitrile (25ml) for 5min. The two solvated compounds were added together at refluxing temperature, and the mixture refluxed for a further 5min. After cooling to room temperature, **250** was collected by filtration as a black precipitate, and was then washed with cold acetonitrile (Found: C, 46.0; H, 3.2; S, 23.8. $C_{42}H_{32}Cl_4Fe_2O_4S_8$ requires C, 45.4; H, 2.9; S, 23.1%).

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APPENDIX 1

X-RAY CRYSTALLOGRAPHIC DATA

A.1.1 Crystallographic data for 1,1'-Bis[1-(1,3-dithiole-2-ylidene)-ethyl]ferrocene 171

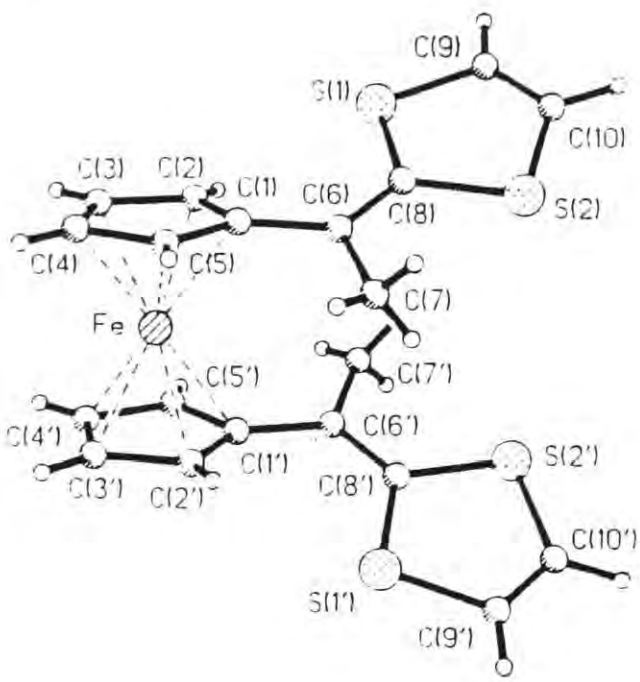

Figure A.1.1: X-Ray molecular structure of compound **171** and crystallographic numbering scheme.

Crystal Data

Empirical Formula	$C_{20}H_{18}FeS_4$
Formula Weight	442.4
Crystal Colour, Habit	red, fragment
Crystal Dimensions (mm)	0.15 x 0.25 x 0.40
Crystal System	Monoclinic
Lattice Parameters	a = 17.847 (2) Å
	b = 10.191 (2) Å
	c = 12.849 (2) Å
	β = 126.01 (1)°
Volume	1890.4 (6) $Å^3$

Space Group	C2/c
Z Value	4
Density (calc.)	1.555 mg/m^3
F_{000}	912
Absorption Coefficient	1.240 mm^{-1}

Intensity Measurements

Radiation	MoKα (λ = 0.71073 Å)
Temperature	296 K
2θ Range	5.5 to 55.0°
No. of Reflections Measured	Total: 2361
	Unique: 2170

Solution and Refinement

Structure solution	Direct Methods
Refinement Method	Full-Matrix Least-Squares
Residuals: R, R_w	0.056, 0.065
Goodness-of-Fit Indicator	1.90

Bond Lengths (Å)

Fe-C(1)	2.073 (5)	Fe-C(2)	2.049 (7)
Fe-C(3)	2.042 (8)	Fe-C(4)	2.049 (5)
Fe-C(5)	2.046 (4)	S(1)-C(8)	1.760 (6)
S(1)-C(9)	1.744 (7)	S(2)-C(8)	1.770 (4)
S(2)-C(10)	1.723 (10)	C(1)-C(2)	1.433 (7)
C(1)-C(5)	1.432 (7)	C(1)-C(6)	1.463 (6)
C(2)-C(3)	1.432 (6)	C(3)-C(4)	1.411 (9)
C(4)-C(5)	1.436 (7)	C(6)-C(7)	1.509 (10)
C(6)-C(8)	1.356 (7)	C(9)-C(10)	1.307 (12)

Bond Angles (°)

C(1)-Fe-C(1A)	108.7 (2)	C(2)-Fe-C(1A)	116.8 (2)
C(3)-Fe-C(1A)	149.2 (2)	C(4)-Fe-C(1A)	169.5 (2)
C(5)-Fe-C(1A)	130.5 (2)	C(2)-Fe-C(2A)	149.5 (3)
C(3)-Fe-C(2A)	168.6 (2)	C(4)-Fe-C(2A)	130.6 (3)
C(5)-Fe-C(2A)	108.5 (2)	C(1)-Fe-C(3A)	149.2 (2)
C(3)-Fe-C(3A)	129.3 (3)	C(4)-Fe-C(3A)	108.0 (2)
C(5)-Fe-C(3A)	116.2 (2)	C(1)-Fe-C(4A)	169.5 (2)
C(2)-Fe-C(4A)	130.6 (3)	C(4)-Fe-C(4A)	116.0 (3)
C(5)-Fe-C(4A)	148.6 (2)	C(1)-Fe-C(5A)	130.5 (2)
C(2)-Fe-C(5A)	108.5 (2)	C(3)-Fe-C(5A)	116.2 (2)
C(5)-Fe-C(5A)	169.2 (3)	C(8)-S(1)-C(9)	95.5 (4)
C(8)-S(2)-C(10)	95.8 (3)	Fe-C(1)-C(2)	68.7 (3)
Fe-C(1)-C(5)	68.6 (3)	C(2)-C(1)-C(5)	107.0 (4)
Fe-C(1)-C(6)	125.9 (4)	C(2)-C(1)-C(6)	128.7 (4)
C(5)-C(1)-C(6)	124.2 (5)	Fe-C(2)-C(1)	70.6 (4)
Fe-C(2)-C(3)	69.3 (4)	C(1)-C(2)-C(3)	108.6 (5)
Fe-C(3)-C(2)	69.8 (4)	Fe-C(3)-C(4)	70.1 (4)
C(2)-C(3)-C(4)	107.8 (5)	Fe-C(4)-C(3)	69.6 (3)
Fe-C(4)-C(5)	69.4 (3)	C(3)-C(4)-C(5)	108.4 (4)
Fe-C(5)-C(1)	70.7 (2)	Fe-C(5)-C(4)	69.6 (2)
C(1)-C(5)-C(4)	108.1 (5)	C(1)-C(6)-C(7)	117.4 (5)
C(1)-C(6)-C(8)	123.5 (5)	C(7)-C(6)-C(8)	119.1 (4)
S(1)-C(8)-S(2)	112.1 (3)	S(1)-C(8)-C(6)	126.5 (4)
S(2)-C(8)-C(6)	121.4 (4)	S(1)-C(9)-C(10)	117.7 (8)
S(2)-C(10)-C(9)	118.1 (6)		

A.1.2 Crystallographic data for 1,1'-Bis[1,2-bis(4,5-dimethyl-1,3-dithiole-2-ylidene)ethane-1,2-diyl]diferrocene 173

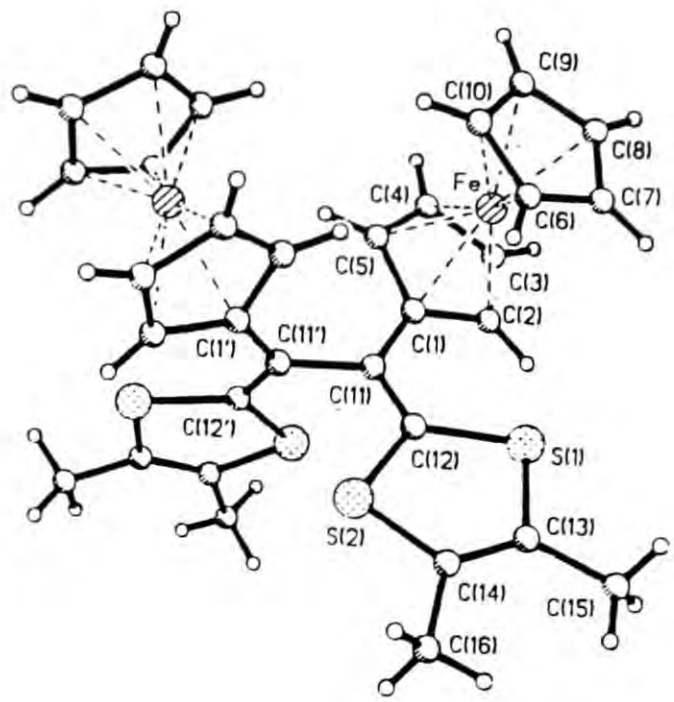

Figure A.1.2: X-Ray molecular structure of compound **173** and crystallographic numbering scheme.

Crystal Data

Empirical Formula	$C_{33}H_{31}Fe_2S_4$
Formula Weight	773.9
Crystal Colour, Habit	orange
Crystal Dimensions (mm)	0.10 x 0.15 x 0.20
Crystal System	Monoclinic
Lattice Parameters	a = 21.977 (1) Å
	b = 8.6364 (3) Å
	c = 18.465 (1) Å
	β = 109.459 (1)°
Volume	3304.33 (1) $Å^3$
Space Group	C2/c
Z Value	4
Density (calc.)	1.556 mg/m^3
F_{000}	1584
Absorption Coefficient	1.397 mm^{-1}

Intensity Measurements

Radiation	MoKα (λ = 0.71073 Å)
Temperature	293 K
2θ Range	3.0 to 60.0°
No. of Reflections Measured	Total: 5216
	Unique: 3862

Solution and Refinement

Structure solution	Direct Methods
Refinement Method	Full-Matrix Least-Squares
Residuals: R, R_w	0.059, 0.060
Goodness-of-Fit Indicator	1.29

Bond Lengths (Å)

Fe-(C)1	2.079 (5)	Fe-C(2)	2.047 (5)
Fe-C(3)	2.038 (5)	Fe-C(4)	2.046 (6)
Fe-C(5)	2.047 (6)	Fe-C(6)	2.042 (6)
Fe-C(7)	2.036 (8)	Fe-C(8)	2.051 (7)
Fe-C(9)	2.056 (6)	Fe-C(10)	2.044 (6)
S(1)-C(12)	1.755 (5)	S(1)-C(13)	1.757 (5)
S(2)-C(12)	1.768 (4)	S(2)-C(14)	1.754 (6)
C(1)-C(2)	1.432 (6)	C(1)-C(5)	1.426 (8)
C(1)-C(11)	1.481 (6)	C(2)-C(3)	1.421 (7)
C(3)-C(4)	1.406 (8)	C(4)-C(5)	1.427 (7)
C(6)-C(7)	1.423 (9)	C(6)-C(10)	1.412 (9)
C(7)-C(8)	1.425 (9)	C(8)-C(9)	1.401 (10)
C(9)-C(10)	1.404 (8)	C(11)-C(12)	1.341 (7)
C(11)-C(11A)	1.501 (10)	C(13)-C(14)	1.333 (8)
C(13)-C(15)	1.502 (10)	C(14)-C(16)	1.508(7)
C(01)-Cl(1A)	1.69 (4)	C(01)-Cl(2A)	1.84 (4)
C(01)-Cl(3A)	1.61 (3)	C(01)-Cl(1B)	1.80 (4)
C(01)-Cl(2B)	1.73 (2)	C(01)-Cl(3B)	1.66 (4)

Bond Angles (°)

C(1)-Fe-C(2)	40.6 (2)	C(1)-Fe-C(3)	68.2 (2)
C(2)-Fe-C(3)	40.7 (2)	C(1)-Fe-C(4)	68.3 (2)
C(2)-Fe-C(4)	68.3 (2)	C(3)-Fe-C(4)	40.3 (2)
C(1)-Fe-C(5)	40.4 (2)	C(2)-Fe-C(5)	68.3 (2)
C(3)-Fe-C(5)	68.2 (2)	C(4)-Fe-C(5)	40.8 (2)
C(1)-Fe-C(6)	107.6 (2)	C(2)-Fe-C(6)	120.3 (2)
C(3)-Fe-C(6)	155.5 (3)	C(4)-Fe-C(6)	162.8 (3)
C(5)-Fe-C(6)	125.4 (2)	C(1)-Fe-C(7)	125.9 (2)
C(2)-Fe-C(7)	107.9 (3)	C(3)-Fe-C(7)	120.6 (2)
C(4)-Fe-C(7)	155.0 (2)	C(5)-FeC(7)	162.8 (2)
C(6)-Fe-C(7)	40.9 (3)	C(1)-Fe-C(8)	163.7 (3)
C(2)-Fe-C(8)	126.6 (2)	C(3)-Fe-C(8)	108.5 (2)
C(4)-Fe-C(8)	120.3 (2)	C(5)-Fe-C(8)	154.8 (3)
C(6)-Fe-C(8)	68.3 (2)	C(7)-Fe-C(8)	40.8 (3)
C(1)-Fe-C(9)	154.8 (2)	C(2)-Fe-C(9)	163.4 (2)
C(3)-Fe-C(9)	126.3 (2)	C(4)-Fe-C(9)	108.3 (3)
C(5)-Fe-C(9)	120.5 (3)	C(6)-Fe-C(9)	67.9 (2)
C(7)-Fe-C(9)	67.9 (3)	C(8)-Fe-C(9)	39.9 (3)
C(1)-Fe-C(10)	120.4 (2)	C(2)-Fe-C(10)	155.1 (2)
C(3)-Fe-C(10)	162.8 (2)	C(4)-Fe-C(10)	125.9 (3)
C(5)-Fe-C(10)	107.9 (2)	C(6)-Fe-C(10)	40.4 (3)
C(7)-Fe-C(10)	68.1 (3)	C(8)-Fe-C(10)	67.5 (2)
C(9)-Fe-C(10)	40.0 (2)	C(12)-S(1)-C(13)	96.9 (3)
C(12)-S(2)-C(14)	96.6 (2)	Fe-C(1)-C(2)	68.5 (3)
Fe-C(1)-C(5)	68.6 (3)	C(2)-C(1)-C(5)	107.0 (4)
Fe-C(1)-C(11)	129.6 (3)	C(2)-C(1)-C(11)	130.3 (5)
C(5)-C(1)-C(11)	122.7 (4)	Fe-C(2)-C(1)	70.9 (3)
Fe-C(2)-C(3)	69.3 (3)	C(1)-C(2)-C(3)	108.1 (5)
Fe-C(3)-C(2)	70.0 (3)	Fe-C(3)-C(4)	70.2 (3)
C(2)-C(3)-C(4)	108.7 (4)	Fe-C(4)-C(3)	69.6 (3)
Fe-C(4)-C(5)	69.6 (3)	C(3)-C(4)-C(5)	107.8 (5)
Fe-C(5)-C(1)	71.0 (3)	Fe-C(5)-C(4)	69.6 (3)
C(1)-C(5)-C(4)	108.5 (5)	Fe-C(6)-C(7)	69.4 (4)
Fe-C(6)-C(10)	69.9 (3)	C(7)-C(6)-C(10)	107.4 (5)
Fe-C(7)-C(6)	69.8 (4)	Fe-C(7)-C(8)	70.2 (4)
C(6)-C(7)-C(8)	107.6 (6)	Fe-C(8)-C(7)	69.0 (4)
Fe-C(8)-C(9)	70.2 (4)	C(7)-C(8)-C(9)	108.0 (5)

Fe-C(9)-C(8)	69.9 (4)	Fe-C(9)-C(10)	69.5 (4)
C(8)-C(9)-C(10)	108.4 (6)	Fe-C(10)-C(6)	69.7 (3)
Fe-C(10)-C(9)	70.4 (3)	C(6)-C(10)-C(9)	108.6 (6)
C(1)-C(11)-C(12)	125.5 (4)	C(1)-C(11)-C(11A)	117.1 (5)
C(12)-C(11)-C(11A)	117.3 (4)	S(1)-C(12)-S(2)	112.3 (3)
S(1)-C(12)-C(11)	126.8 (3)	S(2)-C(12)-C(11)	120.8 (4)
S(1)-C(13)-C(14)	116.8 (5)	S(1)-C(13)-C(15)	116.1 (4)
C(14)-C(13)-C(15)	127.1 (5)	S(2)-C(14)-C(13)	117.1 (4)
S(2)-C(14)-C(16)	116.3 (4)	C(13)-C(14)-C(16)	126.5 (6)
Cl(1A)-C(01)-Cl(2A)	110 (2)	Cl(1A)-C(01)-Cl(3A)	120 (2)
Cl(2A)-C(01)-Cl(3A)	112 (2)	Cl(1B)-C(01)-Cl(2B)	107 (2)
Cl(1B)-C(01)-Cl(3B)	113 (2)	Cl(2B)-C(01)-Cl(3B)	111 (2)

A.1.3 Crystallographic data for 1-[3-(5,6-Dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-ylidene)diallyl]ferrocene 185

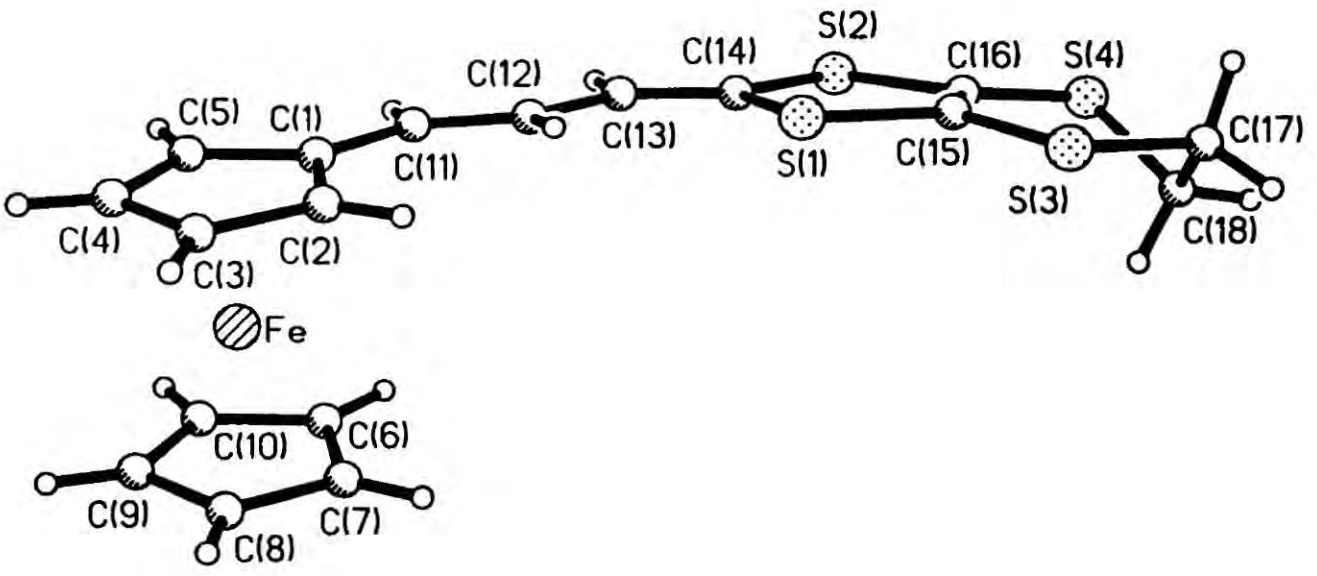

Figure A.1.3: X-Ray molecular structure of compound **185** and crystallographic numbering scheme.

Crystal Data

Empirical Formula	$C_{18}H_{16}FeS_4$
Formula Weight	416.4
Crystal Colour, Habit	brown, plate
Crystal Dimensions (mm)	0.08 x 0.20 x 0.40
Crystal System	Monoclinic
Lattice Parameters	a = 5.985 (2) Å
	b = 12.487 (2) Å
	c = 22.780 (5) Å
	β = 96.57 (3)°
Volume	1691.3 (14) $Å^3$
Space Group	$P2_1/c$
Z Value	4
Density (calc.)	1.635 mg/m^3
F_{000}	856
Absorption Coefficient	1.380 mm^{-1}

Intensity Measurements

Radiation	MoKα (λ = 0.71073 Å)
Temperature	120 K
2θ Range	5.0 to 55.0°
No. of Reflections Measured	Total: 4441
	Unique: 3879

Solution and Refinement

Structure solution	Direct Methods
Refinement Method	Full-Matrix Least-Squares
Residuals: R, R_w	0.043, 0.045
Goodness-of-Fit Indicator	1.16

Bond Lengths (Å)

Fe-(C)1	2.067 (5)	Fe-C(2)	2.047 (5)
Fe-C(3)	2.049 (5)	Fe-C(4)	2.037 (5)
Fe-C(5)	2.038 (5)	Fe-C(6)	2.040 (5)
Fe-C(7)	2.048 (6)	Fe-C(8)	2.057 (5)
Fe-C(9)	2.043 (5)	Fe-C(10)	2.058 (5)

S(1)-C(14)	1.771 (6)	S(1)-C(15)	1.770 (5)
S(2)-C(14)	1.759 (5)	S(2)-C(16)	1.760 (5)
S(3)-C(15)	1.748 (5)	S(3)-C(17)	1.809 (5)
S(4)-C(16)	1.769 (5)	S(4)-C(18)	1.815 (6)
C(1)-C(2)	1.433 (8)	C(1)-C(5)	1.440 (7)
C(1)-C(11)	1.447 (7)	C(2)-C(3)	1.423 (7)
C(3)-C(4)	1.421 (8)	C(4)-C(5)	1.419 (7)
C(6)-C(7)	1.404 (9)	C(6)-C(10)	1.422 (7)
C(7)-C(8)	1.428 (8)	C(8)-C(9)	1.431 (8)
C(9)-C(10)	1.416 (8)	C(11)-C(12)	1.355 (7)
C(12)-C(13)	1.438 (7)	C(13)-C(14)	1.342 (7)
C(15)-C(16)	1.333 (7)	C(17)-C(18)	1.510 (8)

Bond Angles (°)

C(14)-S(1)-C(15)	95.9 (2)	C(14)-S(2)-C(16)	96.1 (2)
C(15)-S(3)-C(17)	101.4 (3)	C(16)-S(4)-C(18)	98.7 (3)
C(2)-C(1)-C(5)	106.7 (4)	C(2)-C(1)-C(11)	128.0 (5)
C(5)-C(1)-C(11)	125.3 (5)	C(1)-C(2)-C(3)	108.7 (5)
C(2)-C(3)-C(4)	107.9 (5)	C(3)-C(4)-C(5)	108.3 (4)
C(1)-C(5)-C(4)	108.4 (5)	C(7)-C(6)-C(10)	109.1 (5)
C(6)-C(7)-C(8)	108.1 (5)	C(7)-C(8)-C(9)	106.9 (5)
C(8)-C(9)-C(10)	108.7 (5)	C(6)-C(10)-C(9)	107.1 (5)
C(1)-C(11)-C(12)	125.1 (5)	C(11)-C(12)-C(13)	125.5 (5)
C(12)-C(13)-C(14)	124.1 (5)	S(1)-C(14)-S(2)	113.4 (3)
S(1)-C(14)-C(13)	122.8 (4)	S(2)-C(14)-C(13)	123.8 (4)
S(1)-C(15)-S(3)	112.5 (3)	S(1)-C(15)-C(16)	116.7 (4)
S(3)-C(15)-C(16)	130.6 (4)	S(2)-C(16)-S(4)	115.2 (3)
S(2)-C(16)-C(15)	117.8 (4)	S(4)-C(16)-C(15)	126.7 (4)
S(3)-C(17)-C(18)	114.7 (4)	S(4)-C(18)-C(17)	112.0 (4)

A.1.4 Crystallographic data for 1,1'-Bis[3-(5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-ylidene)penta-1,4-diene-1,5-diyl]diferrocene 189

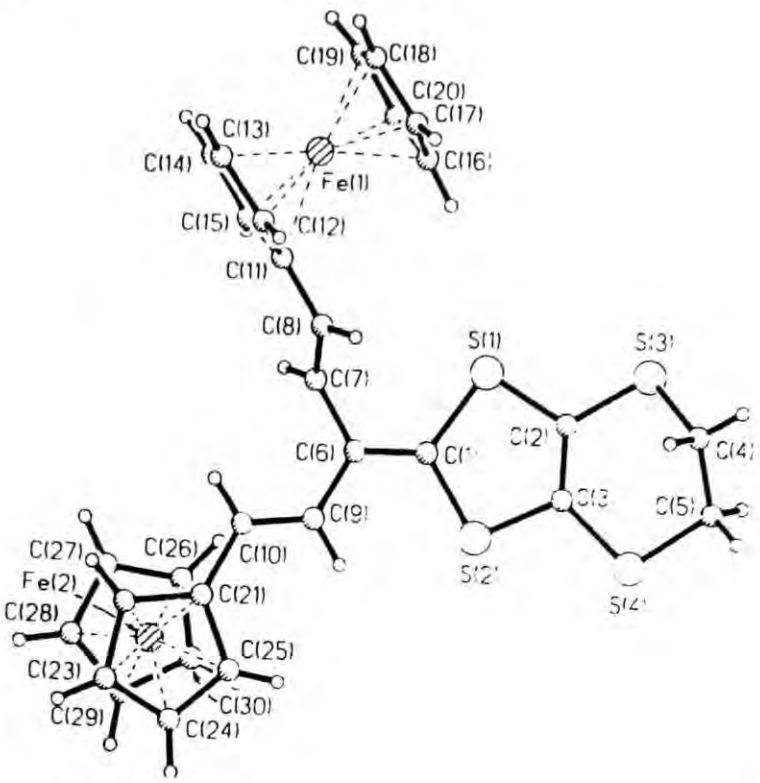

Figure A.1.4: X-Ray molecular structure of compound **189** and crystallographic numbering scheme.

Crystal Data

Empirical Formula	$C_{30}H_{26}Fe_2S_4$
Formula Weight	626.45
Crystal Colour, Habit	orange, needle
Crystal Dimensions (mm)	0.52 x 0.10 x 0.05
Crystal System	Triclinic
Lattice Parameters	a = 7.274 (2) Å
	b = 10.122 (3) Å
	c = 19.168 (5) Å
	α = 77.49 (2)°
	β = 80.94 (2)°
	γ = 71.57 (2)°
Volume	1301.0 (6) $Å^3$
Space Group	P-1 (No. 2)
Z Value	2
Density (calc.)	1.599 mg/m^3
F_{000}	644

Absorption Coefficient	1.456 mm^{-1}

Intensity Measurements

Temperature	150 (2) K
2θ Range	2.58 to 27.50°
No. of Reflections Measured	Total: 6305
	Unique: 5970

Solution and Refinement

Structure solution	Direct Methods
Refinement Method	Full-Matrix Least-Squares
Residuals: R, R_W	0.113, 0.240
Goodness-of-Fit Indicator	1.16

Bond Lengths (Å)

Fe(1)-C(11)	2.04 (2)	Fe(1)-C(12)	2.04 (2)
Fe(1)-C(13)	2.07 (2)	Fe(1)-C(14)	2.04 (2)
Fe(1)-C(15)	2.06 (2)	Fe(1)-C(16)	2.03 (2)
Fe(1)-C(17)	2.08 (2)	Fe(1)-C(18)	2.08 (2)
Fe(1)-C(19)	2.03 (2)	Fe(1)-C(20)	2.05 (2)
Fe(2)-C(21)	2.06 (2)	Fe(2)-C(22)	2.04 (2)
Fe(2)-C(23)	2.06 (2)	Fe(2)-C(24)	2.040 (14)
Fe(2)-C(25)	2.056 (13)	Fe(2)-C(26)	2.063 (14)
Fe(2)-C(27)	2.037 (14)	Fe(2)-C(28)	2.05 (2)
Fe(2)-C(29)	2.05 (2)	Fe(2)-C(30)	2.06 (2)
S(1)-C(2)	1.75 (2)	S(1)-C(1)	1.796 (14)
S(2)-C(1)	1.764 (14)	S(2)-C(3)	1.77 (2)
S(3)-C(2)	1.76 (2)	S(3)-C(4)	1.81 (2)
S(4)-C(3)	1.75 (2)	S(4)-C(5)	1.85 (2)
C(1)-C(6)	1.35 (2)	C(2)-C(3)	1.33 (2)
C(4)-C(5)	1.51 (2)	C(6)-C(9)	1.43 (2)
C(6)-C(7)	1.47 (2)	C(7)-C(8)	1.35 (2)
C(8)-C(11)	1.45 (2)	C(9)-C(10)	1.34 (2)
C(10)-C(21)	1.47 (2)	C(11)-C(12)	1.41 (2)
C(11)-C(15)	1.43 (2)	C(12)-C(13)	1.42 (2)
C(13)-C(14)	1.42 (2)	C(14)-C(15)	1.42 (2)

C(16)-C(20)	1.40 (2)	C(16)-C(17)	1.43 (2)
C(17)-C(18)	1.44 (2)	C(18)-C(19)	1.39 (2)
C(19)-C(20)	1.46 (2)	C(21)-C(22)	1.44 (2)
C(21)-C(25)	1.45 (2)	C(22)-C(23)	1.43 (2)
C(23)-C(24)	1.42 (2)	C(24)-C(25)	1.41 (2)
C(26)-C(30)	1.43 (3)	C(26)-C(27)	1.43 (2)
C(27)-C(28)	1.40 (2)	C(28)-C(29)	1.42 (2)
C(29)-C(30)	1.44 (2)		

Bond Angles (°)

C(2)-S(1)-C(1)	94.9 (7)	C(1)-S(2)-C(3)	95.4 (7)
C(2)-S(3)-C(4)	97.0 (7)	C(3)-S(4)-C(5)	102.6 (7)
C(6)-C(1)-S(2)	122.6 (11)	C(6)-C(1)-S(1)	126.0 (11)
S(2)-C(1)-S(1)	111.3 (8)	C(3)-C(2)-S(1)	118.0 (12)
C(3)-C(2)-S(3)	122.3 (12)	S(1)-C(2)-S(3)	119.2 (8)
C(2)-C(3)-S(4)	130.3 (12)	C(2)-C(3)-S(2)	116.4 (12)
S(4)-C(3)-S(2)	113.1 (9)	C(5)-C(4)-S(3)	111.5 (12)
C(4)-C(5)-S(4)	115.8 (11)	C(1)-C(6)-C(9)	121.4 (13)
C(1)-C(6)-C(7)	121.1 (13)	C(9)-C(6)-C(7)	117.3 (12)
C(8)-C(7)-C(6)	125 (2)	C(7)-C(8)-C(11)	126 (2)
C(10)-C(9)-C(6)	125.9 (13)	C(9)-C(10)-C(21)	123.6 (13)
C(12)-C(11)-C(15)	105.9 (14)	C(12)-C(11)-C(8)	124.8 (14)
C(15)-C(11)-C(8)	129 (2)	C(11)-C(12)-C(13)	111.2 (14)
C(12)-C(13)-C(14)	105.1 (13)	C(15)-C(14)-C(13)	109.8 (14)
C(14)-C(15)-C(11)	108 (2)	C(20)-C(16)-C(17)	110.6 (14)
C(16)-C(17)-C(18)	106 (2)	C(19)-C(18)-C(17)	108.6 (14)
C(18)-C(19)-C(20)	109 (2)	C(16)-C(20)-C(19)	105.8 (14)
C(22)-C(21)-C(25)	106.7 (13)	C(22)-C(21)-C(10)	123.9 (12)
C(25)-C(21)-C(10)	129.4 (13)	C(23)-C(22)-C(21)	108.4 (14)
C(24)-C(23)-C(22)	107.5 (14)	C(25)-C(24)-C(23)	109.3 (13)
C(24)-C(25)-C(21)	108.1 (12)	C(30)-C(26)-C(27)	108 (2)
C(28)-C(27)-C(26)	108 (2)	C(27)-C(28)-C(29)	110 (2)
C(28)-C(29)-C(30)	107 (2)	C(26)-C(30)-C(29)	108 (2)

A.1.5 Crystallographic data for 1,1'-Bis[3,4-bis(5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-ylidene)hexa-1,5-diene-1,6-diyl]diferrocene 191

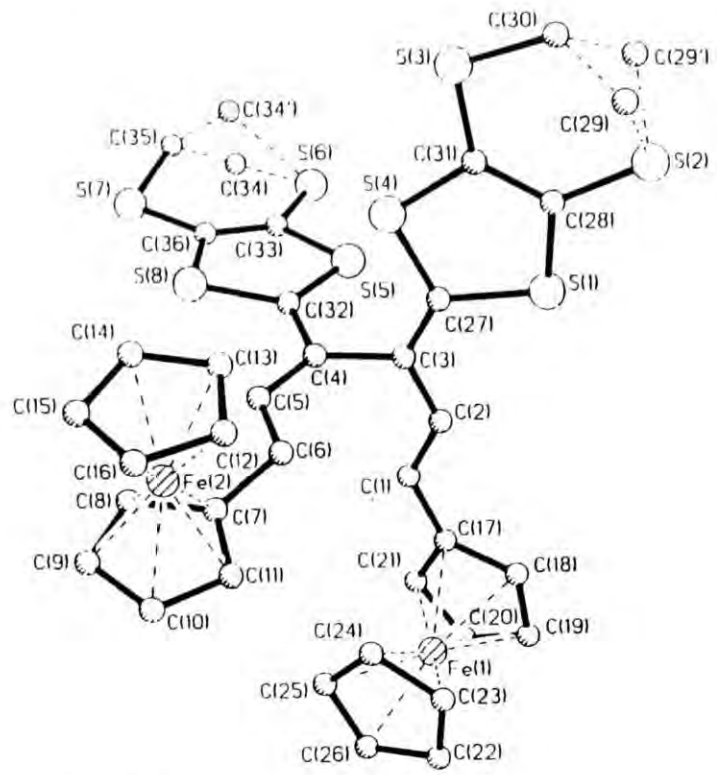

Figure A.1.5: X-Ray molecular structure of compound **191** and crystallographic numbering scheme.

Crystal Data

Empirical Formula	$C_{36}H_{30}Fe_2O_3S_8$
Formula Weight	878.78
Crystal System	Monoclinic
Lattice Parameters	a = 17.844 (4) Å
	b = 11.723 (2) Å
	c = 19.966 (4) Å
	$\alpha = 90°$
	$\beta = 106.55\ (3)°$
	$\gamma = 90°$
Volume	4003.6 (14) $Å^3$
Space Group	$P2_1/n$
Z Value	4
Density (calc.)	1.458 mg/m^3
F_{000}	1800
Absorption Coefficient	1.176 mm^{-1}

Intensity Measurements

Temperature	293 (2) K
2θ Range	2.70 to 22.63°
No. of Reflections Measured	Total: 4962
	Unique: 4776

Solution and Refinement

Structure solution	Direct Methods
Refinement Method	Full-Matrix Least-Squares
Residuals: R, R_w	0.172, 0.425
Goodness-of-Fit Indicator	2.30

Bond Lengths (Å)

Fe(1)-C(18)	1.97(2)	Fe(1)-C(19)	1.99(2)
Fe(1)-C(17)	2.05(2)	Fe(1)-C(23)	2.06(3)
Fe(1)-C(22)	2.06(2)	Fe(1)-C(24)	2.08(2)
Fe(1)-C(20)	2.08(2)	Fe(1)-C(26)	2.08(2)
Fe(1)-C(25)	2.09(2)	Fe(1)-C(21)	2.11(2)
S(1)-C(28)	1.71(3)	S(1)-C(27)	1.82(3)
S(2)-C(29')	1.72(7)	S(2)-C(28)	1.73(3)
S(2)-C(29)	1.91(5)	S(3)-C(31)	1.76(2)
S(3)-C(30)	1.82(3)	S(4)-C(27)	1.69(3)
S(4)-C(31)	1.72(3)	S(5)-C(32)	1.74(3)
S(5)-C(33)	1.78(3)	S(6)-C(33)	1.71(3)
S(6)-C(34)	1.95(5)	S(7)-C(36)	1.69(3)
S(7)-C(35)	1.72(4)	S(8)-C(32)	1.74(3)
S(8)-C(36)	1.79(3)	C(1)-C(2)	1.31(3)
C(1)-C(17)	1.45(3)	C(2)-C(3)	1.51(4)
C(3)-C(27)	1.33(3)	C(3)-C(4)	1.54(4)
C(4)-C(32)	1.35(3)	C(4)-C(5)	1.42(4)
C(5)-C(6)	1.35(4)	C(6)-C(7')	1.72(4)
C(6)-C(7)	1.9(2)	Fe(2A)-C(7)	1.91(3)
Fe(2A)-C(8)	1.90(3)	Fe(2A)-C(11)	1.97(3)
Fe(2A)-C(9)	1.95(3)	Fe(2A)-C(10)	2.00(3)
Fe(2A)-C(15)	1.88(2)	Fe(2A)-C(16)	1.86(2)
Fe(2A)-C(14)	2.01(2)	Fe(2A)-C(12)	1.98(3)

Fe(2A)-C(13)	2.06(3)	C(7)-C(11)	1.276(7)
C(7)-C(8)	1.276(7)	C(8)-C(9)	1.276(7)
C(9)-C(10)	1.276(7)	C(10)-C(11)	1.276(7)
C(12)-C(13)	1.276(7)	C(12)-C(16)	1.276(7)
C(12)-C(15)	2.064(11)	C(12)-C(14)	2.065(11)
C(13)-C(14)	1.276(7)	C(13)-C(15)	2.065(11)
C(13)-C(16)	2.065(11)	C(14)-C(15)	1.276(7)
C(14)-C(16)	2.065(11)	C(15)-C(16)	1.276(7)
Fe(2B)-C(8')	1.90(3)	Fe(2B)-C(7')	1.91(3)
Fe(2B)-C(9')	1.95(3)	Fe(2B)-C(15')	1.88(2)
Fe(2B)-C(16')	1.86(2)	Fe(2B)-C(11')	1.97(3)
Fe(2B)-C(10')	2.00(3)	Fe(2B)-C(14')	2.01(2)
Fe(2B)-C(12')	1.98(2)	Fe(2B)-C(13')	2.06(2)
C(7')-C(11')	1.283(7)	C(7')-C(8')	1.283(7)
C(8')-C(9')	1.283(7)	C(9')-C(10')	1.283(7)
C(10')-C(11')	1.283(7)	C(12')-C(13')	1.269(2)
C(12')-C(16')	1.270(2)	C(13')-C(14')	1.269(2)
C(14')-C(15')	1.269(2)	C(15')-C(16')	1.269(2)
C(17)-C(21)	1.42(2)	C(17)-C(18)	1.42(2)
C(18)-C(19)	1.42(2)	C(19)-C(20)	1.42(2)
C(20)-C(21)	1.42(2)	C(22)-C(23)	1.44(2)
C(22)-C(26)	1.44(2)	C(23)-C(24)	1.44(2)
C(24)-C(25)	1.44(2)	C(25)-C(26)	1.44(2)
C(28)-C(31)	1.41(3)	C(29)-C(30)	1.43(6)
C(29)-C(29')	1.58(8)	C(29')-C(30)	1.67(7)
C(33)-C(36)	1.38(4)	C(34)-C(35)	1.40(5)

Bond Angles (°)

C(28)-S(2)-C(29)	97(2)	C(31)-S(3)-C(30)	103.6(13)
C(27)-S(4)-C(31)	96.5(13)	C(32)-S(5)-C(33)	95.6(12)
C(33)-S(6)-C(34)	100(2)	C(36)-S(7)-C(35)	102(2)
C(32)-S(8)-C(36)	96.4(13)	C(2)-C(1)-C(17)	127(3)
C(1)-C(2)-C(3)	129(3)	C(27)-C(3)-C(2)	127(2)
C(27)-C(3)-C(4)	120(2)	C(2)-C(3)-C(4)	113(2)
C(32)-C(4)-C(5)	121(3)	C(32)-C(4)-C(3)	115(2)
C(5)-C(4)-C(3)	124(3)	C(6)-C(5)-C(4)	122(3)

C(5)-C(6)-C(7)	117(10)	C(11)-C(7)-C(8)	108.0
C(11)-C(7)-C(6)	130(10)	C(8)-C(7)-C(6)	122(10)
C(9)-C(8)-C(7)	108.0	C(10)-C(9)-C(8)	108.0(2)
C(8)-C(9)-Fe(2A)	68(2)	C(9)-C(10)-C(11)	108.01(11)
C(10)-C(11)-C(7)	108.00(7)	C(13)-C(12)-C(16)	108.01(12)
C(13)-C(12)-C(15)	72.0	C(16)-C(12)-C(15)	36.0
C(13)-C(12)-C(14)	36.0	C(16)-C(12)-C(14)	72.00(9)
C(15)-C(12)-C(14)	36.00(6)	C(12)-C(13)-C(14)	108.00(8)
C(12)-C(13)-C(15)	71.99(6)	C(14)-C(13)-C(15)	36.00(10)
C(12)-C(13)-C(16)	36.00(6)	C(14)-C(13)-C(16)	72.00(11)
C(15)-C(13)-C(16)	35.99(7)	C(15)-C(14)-C(13)	107.99(11)
C(15)-C(14)-C(12)	71.99(6)	C(13)-C(14)-C(12)	36.0(2)
C(15)-C(14)-C(16)	35.99(8)	C(13)-C(14)-C(16)	72.00(9)
C(12)-C(14)-C(16)	36.0	C(16)-C(15)-C(14)	108.01(6)
C(16)-C(15)-Fe(2A)	69.2(9)	C(16)-C(15)-C(12)	36.01(5)
C(14)-C(15)-C(12)	72.0	C(16)-C(15)-C(13)	72.00(6)
C(14)-C(15)-C(13)	36.0	C(12)-C(15)-C(13)	36.00(6)
C(15)-C(16)-C(12)	107.99(11)	C(15)-C(16)-C(13)	72.00(6)
C(12)-C(16)-C(13)	36.0	C(15)-C(16)-C(14)	36.00(13)
C(12)-C(16)-C(14)	72.00(10)	C(13)-C(16)-C(14)	36.0
C(11')-C(7')-C(8')	108.0	C(11')-C(7')-C(6)	126(3)
C(8')-C(7')-C(6)	126(3)	C(9')-C(8')-C(7')	108.0
C(8')-C(9')-C(10')	108.0	C(7')-C(11')-C(10')	108.0
C(13')-C(12')-C(16')	108.0	C(14')-C(13')-C(12')	108.0
C(13')-C(14')-C(15')	108.0	C(16')-C(15')-C(14')	108.0
C(15')-C(16')-C(12')	108.0	C(21)-C(17)-C(18)	108.0
C(21)-C(17)-C(1)	127(2)	C(18)-C(17)-C(1)	125(2)
C(20)-C(19)-C(18)	108.0	C(20)-C(19)-Fe(1)	72.9(9)
C(18)-C(19)-Fe(1)	68.1(9)	C(19)-C(20)-C(21)	108.0
C(19)-C(20)-Fe(1)	66.3(9)	C(21)-C(20)-Fe(1)	71.4(8)
C(17)-C(21)-C(20)	108.0	C(17)-C(21)-Fe(1)	67.5(8)
C(20)-C(21)-Fe(1)	69.0(8)	C(23)-C(22)-C(26)	108.0
C(23)-C(22)-Fe(1)	69.5(9)	C(26)-C(22)-Fe(1)	70.3(9)
C(22)-C(23)-C(24)	108.0	C(22)-C(23)-Fe(1)	69.6(9)
C(24)-C(23)-Fe(1)	70.2(9)	C(25)-C(24)-C(23)	108.0
C(25)-C(24)-Fe(1)	70.2(9)	C(23)-C(24)-Fe(1)	69.0(9)
C(24)-C(25)-C(26)	108.0	C(24)-C(25)-Fe(1)	69.3(9)
C(26)-C(25)-Fe(1)	69.4(9)	C(25)-C(26)-C(22)	108.0
C(25)-C(26)-Fe(1)	70.1(9)	C(22)-C(26)-Fe(1)	69.0(9)

C(3)-C(27)-S(4)	124(2)	C(3)-C(27)-S(1)	121(2)
S(4)-C(27)-S(1)	115(2)	C(31)-C(28)-S(2)	126(2)
C(31)-C(28)-S(1)	117(2)	S(2)-C(28)-S(1)	117(2)
C(30)-C(29)-C(29')	67(3)	C(30)-C(29)-S(2)	114(3)
C(29')-C(29)-S(2)	58(3)	C(29)-C(29')-C(30)	52(3)
C(29)-C(29')-S(2)	71(3)	C(30)-C(29')-S(2)	112(4)
C(29)-C(30)-C(29')	61(3)	C(29)-C(30)-S(3)	118(3)
C(29')-C(30)-S(3)	108(3)	C(28)-C(31)-S(4)	117(2)
C(28)-C(31)-S(3)	128(2)	S(4)-C(31)-S(3)	114.8(14)
C(4)-C(32)-S(8)	123(2)	C(4)-C(32)-S(5)	121(2)
S(8)-C(32)-S(5)	115(2)	C(36)-C(33)-S(6)	128(2)
C(36)-C(33)-S(5)	117(2)	S(6)-C(33)-S(5)	115(2)
C(35)-C(34)-S(6)	115(3)	C(34)-C(35)-S(7)	118(3)
C(33)-C(36)-S(7)	130(2)	C(33)-C(36)-S(8)	115(2)
S(7)-C(36)-S(8)	116(2)		

A.1.6 Crystallographic data for 2-(1,3-dithiole-2-ylidene)-6-[1-cyclopentadienyl(cyclopentadienyl)iron]-3a,4,5,6-tetrahydro-1,3-benzodithiole-4,4,5,5-tetracarbonitrile 194:acetonitrile solvate

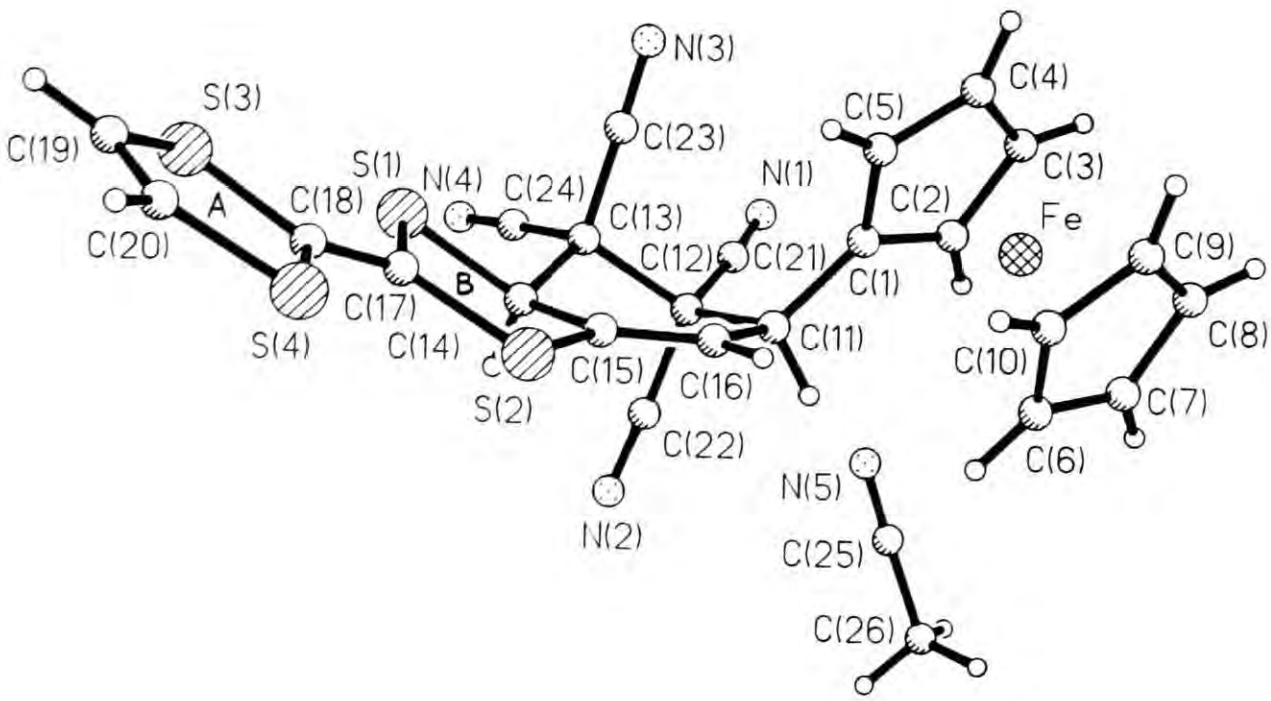

Figure A.1.6: X-Ray molecular structure of compound **194**:acetonitrile solvate and crystallographic numbering scheme.

Crystal Data

Empirical Formula	$C_{26}H_{17}FeN_5S_4$
Formula Weight	583.5
Crystal Colour, Habit	dark yellow, plate
Crystal Dimensions (mm)	0.10 x 0.45 x 0.50
Crystal System	Triclinic
Lattice Parameters	a = 7.008 (2) Å
	b = 11.660 (3) Å
	c = 17.065 (4) Å
	α = 80.43 (2)°
	β = 82.46 (2)°
	γ = 74.27 (2)°
Volume	1318.2 (5) $Å^3$
Space Group	PI
Z Value	2
Density (calc.)	1.470 mg/m^3
F_{000}	596
Absorption Coefficient	0.914 mm^{-1}

Intensity Measurements

Radiation	MoKα (λ = 0.71073 Å)
Temperature	293 K
2θ Range	5.0 to 50.0°
No. of Reflections Measured	Total: 4503
	Unique: 4309

Solution and Refinement

Structure solution	Direct Methods
Refinement Method	Full-Matrix Least-Squares
Residuals: R, R_w	0.038, 0.047
Goodness-of-Fit Indicator	1.72

Bond Lengths (Å)

Fe-C(1)	2.043 (4)	Fe-C(2)	2.024 (4)
Fe-C(3)	2.035 (4)	Fe-C(4)	2.035 (5)
Fe-C(5)	2.036 (5)	Fe-C(6)	2.030 (5)
Fe-C(7)	2.020 (7)	Fe-C(8)	2.023 (7)
Fe-C(9)	2.032 (5)	Fe-C(10)	2.043 (4)
S(1)-C(14)	1.811 (5)	S(1)-C(17)	1.753 (4)
S(2)-C(15)	1.750 (4)	S(2)-C(17)	1.761 (5)
S(3)-C(18)	1.754 (5)	S(3)-C(19)	1.738 (5)
S(4)-C(18)	1.760 (4)	S(4)-C(20)	1.734 (7)
N(1)-C(21)	1.136 (5)	N(2)-C(22)	1.128 (6)
N(3)-C(23)	1.121 (6)	N(4)-C(24)	1.124 (6)
C(1)-C(2)	1.428 (6)	C(1)-C(5)	1.424 (6)
C(1)-C(11)	1.508 (5)	C(2)-C(3)	1.415 (6)
C(3)-C(4)	1.411 (7)	C(4)-C(5)	1.404 (6)
C(6)-C(7)	1.398 (9)	C(6)-C(10)	1.385 (8)
C(7)-C(8)	1.386 (9)	C(8)-C(9)	1.392 (9)
C(9)-C(10)	1.389 (7)	C(11)-C(12)	1.589 (5)
C(11)-C(16)	1.507 (5)	C(12)-C(13)	1.598 (6)
C(12)-C(21)	1.479 (5)	C(12)-C(22)	1.483 (6)
C(13)-C(14)	1.543 (5)	C(13)-C(23)	1.492 (6)
C(13)-C(24)	1.490 (6)	C(14)-C(15)	1.510 (6)
C(15)-C(16)	1.327 (6)	C(17)-C(18)	1.337 (6)
C(19)-C(20)	1.315 (9)	N(5)-C(25)	1.083 (9)
C(25)-C(26)	1.430 (12)		

Bond Angles (°)

C(1)-Fe-C(6)	109.4 (2)	C(2)-Fe-C(6)	122.2 (2)
C(3)-Fe-C(6)	156.3 (2)	C(4)-Fe-C(6)	162.5 (2)
C(5)-Fe-C(6)	126.5 (2)	C(1)-Fe-C(7)	125.7 (2)
C(2)-Fe-C(7)	107.5 (2)	C(3)-Fe-C(7)	120.2 (2)
C(4)-Fe-C(7)	155.2 (2)	C(5)-Fe-C(7)	163.1 (2)
C(1)-Fe-C(8)	161.2 (2)	C(2)-Fe-C(8)	123.3 (2)
C(3)-Fe-C(8)	106.0 (2)	C(4)-Fe-C(8)	120.3 (2)
C(5)-Fe-C(8)	155.8 (2)	C(1)-Fe-C(9)	157.6 (2)

C(2)-Fe-C(9)	160.1 (2)	C(3)-Fe-C(9)	123.7 (2)
C(4)-Fe-C(9)	108.1 (2)	C(5)-Fe-C(9)	122.0 (2)
C(1)-Fe-C(10)	123.1 (2)	C(2)-Fe-C(10)	157.8 (2)
C(3)-Fe-C(10)	160.9 (2)	C(4)-Fe-C(10)	125.8 (2)
C(5)-Fe-C(10)	109.7 (2)	C(14)-S(1)-C(17)	95.2 (2)
C(15)-S(2)-C(17)	96.0 (2)	C(18)-S(3)-C(19)	94.8 (2)
C(18)-S(4)-C(20)	94.3 (3)	C(2)-C(1)-C(5)	107.1 (3)
C(2)-C(1)-C(11)	125.4 (4)	C(5)-C(1)-C(11)	127.5 (4)
C(1)-C(2)-C(3)	108.3 (4)	C(2)-C(3)-C(4)	107.5 (4)
C(3)-C(4)-C(5)	109.0 (4)	C(1)-C(5)-C(4)	108.1 (4)
C(7)-C(6)-C(10)	107.6 (5)	C(6)-C(7)-C(8)	108.4 (5)
C(7)-C(8)-C(9)	107.4 (5)	C(8)-C(9)-C(10)	108.5 (5)
C(6)-C(10)-C(9)	108.0 (5)	C(1)-C(11)-C(12)	113.9 (3)
C(1)-C(11)-C(16)	112.5 (3)	C(12)-C(11)-C(16)	110.4 (3)
C(11)-C(12)-C(13)	111.2 (3)	C(11)-C(12)-C(21)	113.2 (3)
C(13)-C(12)-C(21)	107.6 (4)	C(11)-C(12)-C(22)	109.1 (3)
C(13)-C(12)-C(22)	106.5 (3)	C(21)-C(12)-C(22)	109.0 (3)
C(12)-C(13)-C(14)	108.7 (3)	C(12)-C(13)-C(23)	109.6 (3)
C(14)-C(13)-C(23)	111.4 (3)	C(12)-C(13)-C(24)	109.5 (3)
C(14)-C(13)-C(24)	109.8 (3)	C(23)-C(13)-C(24)	107.8 (4)
S(1)-C(14)-C(13)	110.8 (3)	S(1)-C(14)-C(15)	109.8 (3)
C(13)-C(14)-C(15)	110.1 (3)	S(2)-C(15)-C(14)	113.0 (3)
S(2)-C(15)-C(16)	123.8 (3)	C(14)-C(15)-C(16)	123.2 (3)
C(11)-C(16)-C(15)	126.9 (3)	S(1)-C(17)-S(2)	116.1 (2)
S(1)-C(17)-C(18)	120.6 (4)	S(2)-C(17)-C(18)	123.3 (3)
S(3)-C(18)-C(4)	114.3 (2)	S(3)-C(18)-C(17)	122.3 (3)
S(4)-C(18)-C(17)	123.2 (4)	S(3)-C(19)-C(20)	117.5 (4)
S(4)-C(20)-C(19)	118.8 (4)	N(1)-C(21)-C(12)	175.3 (6)
N(2)-C(22)-C(12)	177.3 (5)	N(3)-C(23)-C(13)	178.3 (4)
N(4)-C(24)-C(13)	178.3 (5)	N(5)-C(25)-C(26)	178.4 (7)

A.1.7 Crystallographic data for 1-[1-Cyclopentadienyl(cyclopenta-dienyl)iron]-1-[2,2'-bi(1,3-dithiolylidene)-4-yl]ethanol 229

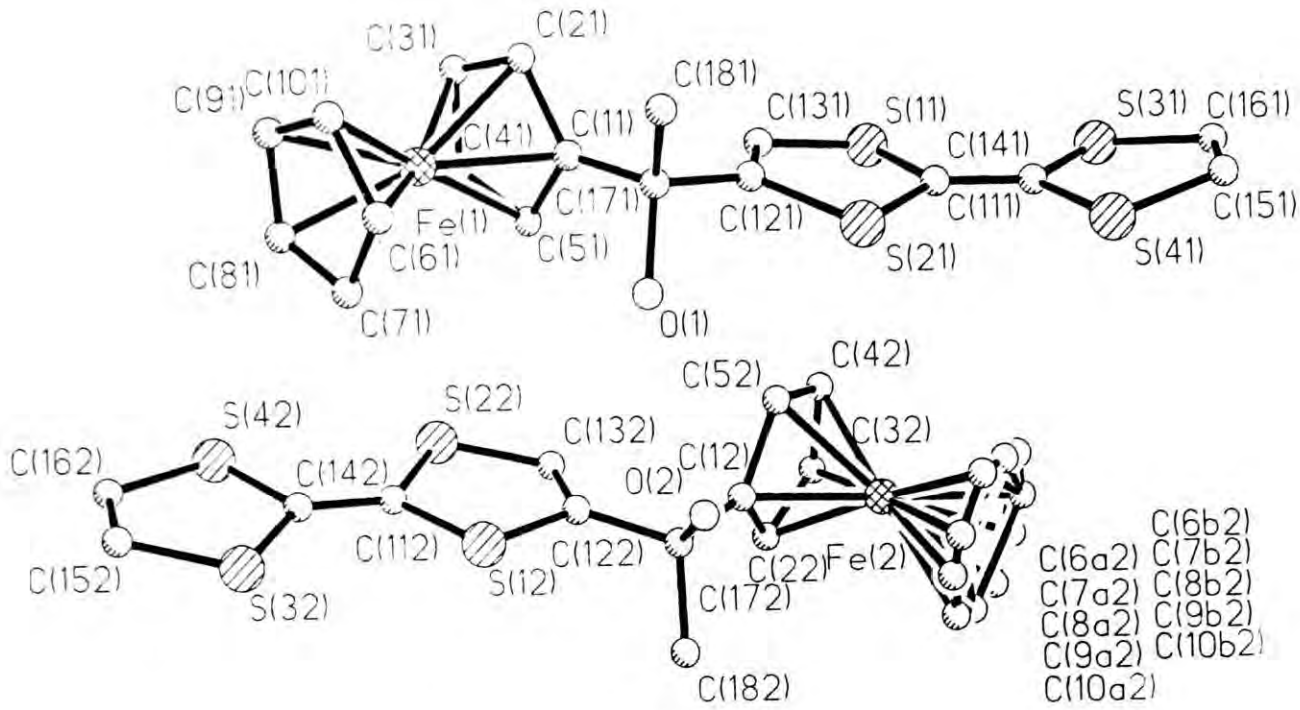

Figure A.1.7: X-Ray molecular structure of compound **229** and crystallographic numbering scheme.

Crystal Data

Empirical Formula	$C_{18}H_{16}FeOS_4$
Formula Weight	432.4
Crystal Dimensions (mm)	0.27 x 0.26 x 0.07
Crystal System	Triclinic
Lattice Parameters	a = 9.804 (3) Å
	b = 13.579 (4) Å
	c = 15.700 (4) Å
	α = 102.59 (2)°
	β = 106.32 (2)°
	γ = 108.09 (2)°
Volume	1796.9 (9) $Å^3$
Space Group	P-1 (No.2)
Z Value	4
Density (calc.)	1.598 mg/m^3
F_{000}	888
Absorption Coefficient	1.306 mm^{-1}

Intensity Measurements

Temperature	150 (2) K
2θ Range	2.52 to 25.00°
No. of Reflections Measured	Total: 6420
	Unique: 6129

Solution and Refinement

Structure solution	Direct Methods
Refinement Method	Full-Matrix Least-Squares
Residuals: R, R_w	0.042, 0.1022
Goodness-of-Fit Indicator	1.04

Bond Lengths (Å)

Fe(1)-C(41)	2.038 (5)	Fe(1)-C(91)	2.044 (5)
Fe(1)-C(61)	2.044 (5)	Fe(1)-C(81)	2.046 (6)
Fe(1)-C(101)	2.047 (5)	Fe(1)-C(71)	2.048 (5)
Fe(1)-C(51)	2.048 (5)	Fe(1)-C(11)	2.049 (5)
Fe(1)-C(31)	2.051 (5)	Fe(1)-C(21)	2.061 (5)
S(11)-C(111)	1.767 (5)	S(11)-C(121)	1.770 (5)
S(21)-C(131)	1.742 (5)	S(21)-C(111)	1.757 (5)
S(31)-C(151)	1.740 (6)	S(31)-C(141)	1.763 (5)
S(41)-C(161)	1.759 (6)	S(41)-C(141)	1.762 (5)
O(1)-C(171)	1.449 (7)	C(11)-C(21)	1.433 (7)
C(11)-C(51)	1.441 (7)	C(11)-C(171)	1.516 (7)
C(21)-C(31)	1.421 (7)	C(31)-C(41)	1.424 (8)
C(41)-C(51)	1.425 (8)	C(61)-C(101)	1.413 (8)
C(61)-C(71)	1.420 (9)	C(71)-C(81)	1.409 (8)
C(81)-C(91)	1.403 (9)	C(91)-C(101)	1.404 (8)
C(111)-C(141)	1.344 (7)	C(121)-C(131)	1.330 (7)
C(121)-C(171)	1.519 (7)	C(151)-C(161)	1.330 (8)
C(171)-C(181)	1.529 (8)	Fe(2)-C(7B2)	1.025 (11)
Fe(2)-C(6B2)	2.033 (9)	Fe(2)-C(10B2)	2.038 (9)
Fe(2)-C(10A2)	2.039 (14)	Fe(2)-C(9B2)	2.042 (9)
Fe(2)-C(9A2)	2.044 (11)	Fe(2)-C(12)	2.044 (4)
Fe(2)-C(22)	2.045 (5)	Fe(2)-C(42)	2.045 (5)
Fe(2)-C(52)	2.048 (5)	Fe(2)-C(32)	2.048 (5)

Fe(2)-C(8B2)	2.051 (10)	S(12)-C(112)	1.762 (5)
S(12)-C(122)	1.764 (5)	S(22)-C(132)	1.739 (5)
S(22)-C(112)	1.770 (5)	S(32)-C(152)	1.729 (6)
S(32)-C(142)	1.761 (5)	S(42)-C(162)	1.739 (7)
S(42)-C(142)	1.771 (5)	O(2)-C(172)	1.445 (6)
C(12)-C(22)	1.436 (6)	C(12)-C(52)	1.440 (7)
C(12)-C(172)	1.516 (6)	C(22)-C(32)	1.421 (7)
C(32)-C(42)	1.418 (7)	C(42)-C(52)	1.417 (7)
C(6A2)-C(10A2)	1.42 (2)	C(6A2)-C(7A2)	1.43 (2)
C(7A2)-C(8A2)	1.39 (2)	C(8A2)-C(9A2)	1.34 (2)
C(9A2)-C(10A2)	1.38 (2)	C(6B2)-C(10B2)	1.446 (14)
C(6B2)-C(7B2)	1.47 (2)	C(7B2)-C(8B2)	1.42 (2)
C(8B2)-C(9B2)	1.40 (2)	C(9B2)-C(10B2)	1.402 (14)
C(112)-C(142)	1.333 (7)	C(122)-C(132)	1.322 (7)
C(122)-C(172)	1.531 (6)	C(152)-C(162)	1.320 (9)
C(172)-C(182)	1.493 (6)		

Bond Angles (°)

C(111)-S(11)-C(121)	94.4 (2)	C(131)-S(21)-C(111)	94.3 (2)
C(151)-S(31)-C(141)	95.0 (2)	C(161)-S(41)-C(141)	94.5 (3)
C(21)-C(11)-C(51)	107.3 (4)	C(21)-C(11)-C(171)	124.4 (5)
C(51)-C(11)-C(171)	128.1 (5)	C(31)-C(21)-C(11)	108.3 (5)
C(21)-C(31)-C(41)	108.2 (5)	C(31)-C(41)-C(51)	108.4 (5)
C(41)-C(51)-C(11)	107.8 (5)	C(101)-C(61)-C(71)	108.3 (5)
C(81)-C(71)-C(61)	106.9 (5)	C(91)-C(81)-C(71)	108.8 (5)
C(81)-C(91)-C(101)	108.2 (5)	C(91)-C(101)-C(61)	107.7 (5)
C(141)-C(111)-S(21)	122.9 (4)	C(141)-C(111)-S(11)	122.8 (4)
S(21)-C(111)-S(11)	114.3 (3)	C(131)-C(121)-C(171)	127.2 (5)
C(131)-C(121)-S(11)	116.1 (4)	C(171)-C(121)-S(11)	116.6 (4)
C(121)-C(131)-S(21)	119.2 (4)	C(111)-C(141)-S(41)	122.3 (4)
C(111)-C(141)-S(31)	123.7 (4)	S(41)-C(141)-S(31)	114.0 (3)
C(161)-C(151)-S(31)	117.8 (4)	C(151)-C(161)-S(41)	117.5 (4)
O(1)-C(171)-C(11)	110.1 (4)	O(1)-C(171)-C(121)	105.0 (4)
C(11)-C(171)-C(121)	109.8 (4)	O(1)-C(171)-C(181)	110.7 (5)
C(11)-C(171)-C(181)	111.6 (5)	C(121)-C(171)-C(181)	109.3 (4)
C(112)-S(12)-C(122)	94.8 (2)	C(132)-S(22)-C(112)	94.1 (2)

C(152)-S(32)-C(142)	94.9 (3)	C(162)-S(42)-C(142)	94.2 (3)
C(22)-C(12)-C(52)	107.0 (4)	C(22)-C(12)-C(172)	126.6 (4)
C(52)-C(12)-C(172)	126.0 (4)	C(32)-C(22)-C(12)	108.2 (4)
C(42)-C(32)-C(22)	108.2 (4)	C(52)-C(42)-C(32)	108.5 (4)
C(42)-C(52)-C(12)	108.1 (4)	C(10A2)-C(6A2)-C(7A2)	105.6 (11)
C(8A2)-C(7A2)-C(6A2)	107.5 (10)	C(9A2)-C(8A2)-C(7A2)	109.0 (11)
C(8A2)-C(9A2)-C(10A2)	110.6 (12)	C(9A2)-C(10A2)-C(6A2)	107.4 (13)
C(10B2)-C(6B2)-C(7B2)	106.1 (9)	C(8B2)-C(7B2)-C(6B2)	107.8 (10)
C(9B2)-C(8B2)-C(7B2)	107.8 (10)	C(10B2)-C(9B2)-C(8B2)	110.6 (9)
C(9B2)-C(10B2)-C(6B2)	107.6 (8)	C(142)-C(112)-S(12)	123.2 (4)
C(142)-C(112)-S(22)	122.0 (4)	S(12)-C(112)-S(22)	114.7 (3)
C(132)-C(122)-C(172)	126.2 (4)	C(132)-C(122)-S(12)	116.7 (4)
C(172)-C(122)-S(12)	117.0 (3)	C(122)-C(132)-S(22)	119.6 (4)
C(112)-C(142)-S(32)	123.4 (4)	C(112)-C(142)-S(42)	122.4 (4)
S(32)-C(142)-S(42)	114.2 (3)	C(162)-C(152)-S(32)	118.2 (5)
C(152)-C(162)-S(42)	118.5 (5)	O(2)-C(172)-C(182)	105.3 (4)
O(2)-C(172)-C(12)	112.5 (4)	C(182)-C(172)-C(12)	111.5 (4)
O(2)-C(172)-C(122)	109.6 (4)	C(182)-C(172)-C(122)	109.8 (4)
C(12)-C(172)-C(122)	108.1 (4)		

A.1.8 Crystallographic data for 1,2-Bis[1-cyclopentadienyl(cyclopentadienyl)iron]ethene 146

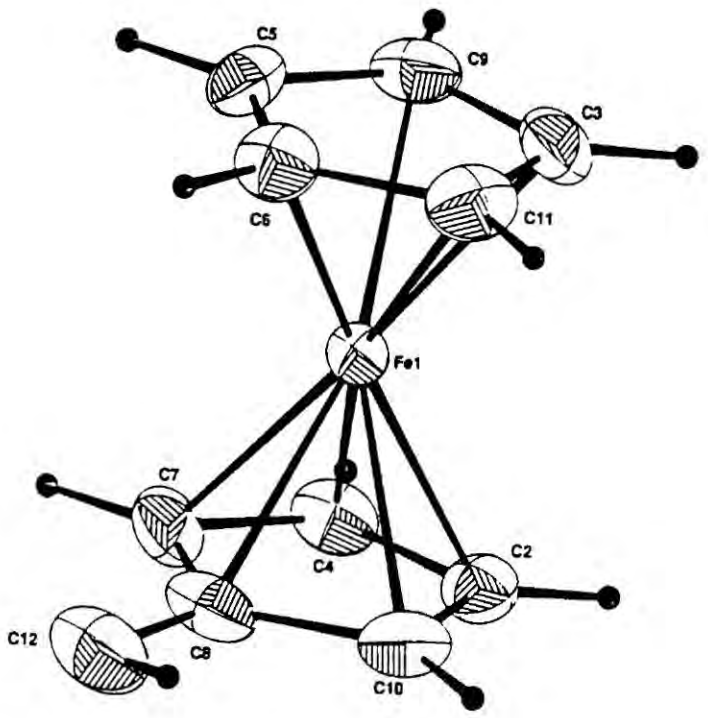

Figure A.1.8: X-Ray molecular structure of compound **146** and crystallographic numbering scheme.

Crystal Data

Empirical Formula	$C_{11}H_{10}Fe$
Formula Weight	198.04
Crystal Colour, Habit	dark orange, block
Crystal Dimensions (mm)	0.60 x 0.20 x 0.20
Crystal System	Monoclinic
Lattice Parameters	a = 7.642 (2) Å
	b = 10.374 (2) Å
	c = 10.918 (2) Å
	α = 90.0 (-)°
	β = 105.35 (2)°
	γ = 90.0 (-)°
Volume	834.65 (32) $Å^3$
Space Group	$P2_1/n$ (No.14)
Z Value	4
Density (calc.)	1.576 mg/m^3
F_{000}	408
Absorption Coefficient	1.74 mm^{-1}

Intensity Measurements

Radiation	MoKα (λ = 0.71073 Å)
Temperature	293 K
2θ Range	8.0 to 25.0°
No. of Reflections Measured	Total: 3835
	Unique: 1818

Solution and Refinement

Structure solution	Direct Methods
Refinement Method	Full-Matrix Least-Squares
Residuals: R, R_w	0.043, 0.046
Goodness-of-Fit Indicator	1.17

Bond Lengths (Å)

Fe(1)-C(2)	2.040 (3)	Fe(1)-C(3)	2.032 (3)
Fe(1)-C(4)	2.045 (3)	Fe(1)-C(5)	2.039 (3)
Fe(1)-C(6)	2.032)3)	Fe(1)-C(7)	2.031 (3)
Fe(1)-C(8)	2.046 (3)	Fe(1)-C(9)	2.042 (3)
Fe(1)-C(10)	2.040 (3)	Fe(1)-C(11)	2.031 (3)
C(2)-C(4)	1.408 (5)	C(2)-C(10)	1.412 (5)
C(3)-C(9)	1.404 (6)	C(3)-C(11)	1.418 (6)
C(4)-C(7)	1.420 (5)	C(5)-C(6)	1.405 (5)
C(5)-C(9)	1.400 (5)	C(6)-C(11)	1.428 (6)
C(7)-C(8)	1.424 (6)	C(8)-C(10)	1.414 (6)
C(8)-C(12)	1.479 (5)	C(12)-C(12)	1.26 (1)

Bond Angles (°)

C(2)-Fe(1)-C(3)	108.5 (1)	C(2)-Fe(1)-C(4)	40.3 (2)
C(3)-Fe(1)-C(4)	124.8 (2)	C(2)-Fe(1)-C(5)	157.9 (2)
C(3)-Fe(1)-C(5)	68.0 (2)	C(4)-Fe(1)-C(5)	122.4 (2)
C(2)-Fe(1)-C(6)	160.7 (2)	C(3)-Fe(1)-C(6)	68.8 (2)
C(4)-Fe(1)-C(6)	156.8 (2)	C(5)-Fe(1)-C(6)	40.4 (2)
C(2)-Fe(1)-C(7)	68.2 (2)	C(3)-Fe(1)-C(7)	161.1 (2)

C(4)-Fe(1)-C(7)	40.8 (2)	C(5)-Fe(1)-C(7)	107.5 (2)
C(6)-Fe(1)-C(7)	120.6 (2)	C(2)-Fe(1)-C(8)	68.3 (1)
C(3)-Fe(1)-C(8)	157.0 (2)	C(4)-Fe(1)-C(8)	68.6 (1)
C(5)-Fe(1)-C(8)	123.6 (2)	C(6)-Fe(1)-C(8)	106.3 (1)
C(7)-Fe(1)-C(8)	40.9 (2)	C(2)-Fe(1)-C(9)	123.1 (1)
C(3)-Fe(1)-C(9)	40.3 (2)	C(4)-Fe(1)-C(9)	108.9 (1)
C(5)-Fe(1)-C(9)	40.1 (2)	C(6)-Fe(1)-C(9)	68.0 (1)
C(7)-Fe(1)-C(9)	124.6 (2)	C(2)-Fe(1)-C(10)	40.5 (1)
C(3)-Fe(1)-C(10)	122.3 (2)	C(4)-Fe(1)-C(10)	68.1 (1)
C(5)-Fe(1)-C(10)	160.0 (2)	C(6)-Fe(1)-C(10)	123.6 (1)
C(7)-Fe(1)-C(10)	68.2 (2)	C(2)-Fe(1)-C(11)	124.3 (2)
C(3)-Fe(1)-C(11)	40.8 (2)	C(4)-Fe(1)-C(11)	161.0 (2)
C(5)-Fe(1)-C(11)	68.3 (2)	C(6)-Fe(1)-C(11)	41.2 (2)
C()-Fe(1)-C(11)	156.5 (2)	C(8)-Fe(1)-C(9)	160.5 (2)
C(8)-Fe(1)-C(10)	40.5 (2)	C(9)-Fe(1)-C(10)	158.2 (2)
C(8)-Fe(1)-C(11)	120.7 (2)	C(9)-Fe(1)-C(11)	68.1 (2)
C(10)-Fe(1)-C(11)	107.3 (2)	Fe(1)-C(2)-C(4)	70.0 (2)
Fe(1)-C(2)-C(10)	69.7 (2)	C(4)-C(2)-C(10)	108.3 (3)
Fe(1)-C(3)-C(9)	70.2 (2)	Fe(1)-C(3)-C(11)	69.5 (2)
C(9)-C(3)-C(11)	107.8 (3)	Fe(1)-C(4)-C(2)	69.7 (2)
Fe(1)-C(4)-C(7)	69.1 (2)	C(2)-C(4)-C(7)	107.7 (3)
Fe(1)-C(5)-C(6)	69.6 (2)	Fe(1)-C(5)-C(9)	70.0 (2)
C(6)-C(5)-C(9)	108.6 (3)	Fe(1)-C(6)-C(5)	70.1 (2)
Fe(1)-C(6)-C(11)	69.4 (2)	C(5)-C(6)-C(11)	107.5 (3)
Fe(1)-C(7)-C(4)	70.1 (2)	Fe(1)-C(7)-C(8)	70.1 (2)
C(4)-C(7)-C(8)	108.3 (3)	Fe(1)-C(8)-C(7)	69.0 (2)
Fe(1)-C(8)-C(10)	69.5 (2)	C(7)-C(8)-C(10)	107.1 (3)
Fe(1)-C(8)-C(12)	125.3 (3)	C(7)-C(8)-C(12)	133.7 (4)
C(1)-C(8)-C(12)	119.2 (4)	Fe(1)-C(9)-C(3)	69.5 (2)
Fe(1)-C(9)-C(5)	69.8 (2)	C(3)-C(9)-C(5)	108.6 (3)
Fe(1)-C(10)-C(2)	69.8 (2)	Fe(1)-C(10)-C(8)	70.0 (2)
C(2)-C(10)-C(8)	108.6 (3)	Fe(1)-C(11)-C(3)	69.6 (2)
Fe(1)-C(11)-C(6)	69.5 (2)	C(3)-C(11)-C(6)	107.5 (3)
C(8)-C(12)-C(12)	127.0 (7)		

APPENDIX 2

RESEARCH COLLOQUIA, LECTURES, SEMINARS AND CONFERENCES

A.2.1 List of Research Colloquia, Lectures and Seminars

There follows a list of research colloquia, seminars and lectures that have been addressed by external speakers and arranged by the Department of Chemistry during the period of the author's residence as a postgraduate student.

* Denotes presentations attended by the author.

Academic Year 1991-1992

17.10.91* Dr. J. A. Salthouse (University of Manchester)
Son et Lumiere: A Demonstration Lecture.

31.10.91* Dr. R. Keeley (Metropolitan Police, Forensic Science Dept.)
Modern Forensic Science.

06.11.91 Prof. B. F. G. Johnson (University of Edinburgh)
Cluster-Surface Analogies.

07.11.91* Dr. A. R. Butler (University of St. Andrews)
Traditional Chinese Herbal Drugs: a Different Way of Treating Disease.

13.11.91* Prof. D. Gani (University of St. Andrews)
The Chemistry of PLP-Dependent Enzymes.

20.11.91* Dr. R. More O'Ferrall (University College, Dublin)
Some Acid-Catalysed Rearrangements in Organic Chemistry.

28.11.91 Prof. I. M. Ward (University of Leeds, I.R.C.)
The SCI Lecture. Science and Technology of Orientated Polymers.

04.12.91* Prof. R. Grigg (University of Leeds)
Palladium-Catalysed Cyclisation and Ion-Capture Processes.

05.12.91* Prof. A. L. Smith (formerly of Unilever)
Soap, Detergents and Black-Puddings.

11.12.91	Dr. W. D. Cooper (Shell Research) Colloid Science: Theory and Practice.
22.01.92	Dr. K. D. M. Harris (University of St. Andrews) Understanding the Properties of Solid Inclusion Compounds.
29.01.92*	Dr. A. Holmes (University of Cambridge) Cycloaddition Reactions in the Service of the Synthesis of Piperidine and Indolizidine Natural Products.
30.01.92*	Dr. M. Anderson (Shell Research, Sittingbourne) Recent Advances in the Safe and Selective Chemical Control of Insect Pests.
12.02.92*	Prof. D. E. Fenton (University of Sheffield) Polynuclear Complexes of Molecular Clefts as Models for Copper Bio-sites.
13.02.92*	Dr. J. Saunders (Glaxo Group Research Ltd.) Molecular Modelling in Drug Discovery.
19.02.92*	Prof. E. J. Thomas (University of Manchester) Applications of Organostannanes to Organic Synthesis.
20.02.92*	Prof. E. Vogel (University of Cologne) *The Musgrave Lecture*. Porphyrins: Molecules of Interdisciplinary Interest.
25.02.92	Prof. J. F. Nixon (University of Sussex) *The Tilden Lecture*. Phospha-Alkynes: New Building Blocks in Inorganic and Organometallic Chemistry.
26.02.92	Prof. M. L. Hitchman (University of Strathclyde) Chemical Vapour Deposition.
05.03.92*	Dr. N. C. Billingham (University of Sussex) Degradable Plastics - Myth or Magic?
11.03.92	Dr. S. E. Thomas (Imperial College) Recent Advances in Organoiron Chemistry.
12.03.92	Dr. R. A. Hann (I.C.I. Imagedata) Electronic Photography - An Image of the Future.
18.03.92*	Dr. H. Maskill (University of Newcastle upon Tyne) Concerted or Stepwise Fragmentation in a Deamination-Type Reaction.
07.04.92	Prof. D. M. Knight (University of Durham, Dept. of Philosophy) Interpreting Experiments: the Beginning of Electrochemistry.
13.05.92	Dr. J.-C. Gehret (Ciba Geigy, Basel) Some Aspects of Industrial Agrochemical Research.

Academic Year 1992-1993

15.10.92	Dr. M. Glazer and Dr. S. Tarling (University of Oxford & Birkbeck College) The Chemist's Role as an Expert Witness in Patent Litigation.
20.10.92	Dr. H. E. Bryndza (Dupont Central Research) Synthesis, Reactions and Thermochemistry of Metal (Alkyl) Cyanide Complexes and Their Impact on Olefin Hydrocyanation Catalysis.
22.10.92*	Prof. A. Davies (University College, London) *The Ingold-Albert Lecture*. The Behaviour of Hydrogen as a Pseudometal.
28.10.92	Dr. J. K. Cockcroft (University of Durham) Recent Developments in Powder Diffraction.
29.10.92	Dr. J. Emsley (Imperial College, London) The Shocking History of Phosphorus.
04.11.92	Dr. T. P. Kee (University of Leeds) Synthesis and Coordination Chemistry of Silylated Phosphites.
05.11.92*	Dr. C. J. Ludman (University of Durham) Explosions: A Demonstration Lecture.
11.11.92*	Prof. D. Robins (University of Glasgow) Pyrrolizidine Alkaloids: Biological Activity, Biosynthesis and Benefits.
12.11.92*	Prof. M. R. Truter (University College, London) Luck and Logic in Host-Guest Chemistry.
18.11.92	Dr. R. Nix (Queen Mary College, London) Characterisation of Heterogeneous Catalysts.
25.11.92*	Prof. Y. Vallée (University of Caen) Reactive Thiocarbonyl Compounds.
25.11.92	Prof. L. D. Quin (University of Massachusetts, Amherst) Fragmentation of Phosphorus Heterocycles as a Route to Phosphoryl Species with Uncommon Bonding.
26.11.92*	Dr. D. Humber (Glaxo, Greenford) AIDS - The Development of a Novel Series of HIV Inhibitors.
02.12.92*	Prof. A. F. Hegarty (University College, Dublin) Highly Reactive Enols Stabilised by Steric Protection.
02.12.92*	Dr. R. A. Aitken (University of St. Andrews) The Versatile Cycloaddition Chemistry of $Bu_3P.CS_2$.
03.12.92	Prof. P. Edwards (University of Birmingham)

The SCI Lecture. What is a Metal?

09.12.92 Dr. A. N. Burgess (I.C.I. Runcorn)
The Structure of Perfluorinated Ionomer Membranes.

20.01.93 Dr. D. C. Clary (University of Cambridge)
Energy Flow in Chemical Reactions.

21.01.93 Prof. L. Hall (University of Cambridge)
NMR - Window to the Human Body.

27.01.93* Dr. W. Kerr (University of Strathclyde)
Development of the Pauson-Khand Annulation Reaction:
Organocobalt Mediated Synthesis of Natural and Unnatural Products.

28.01.93* Prof. J. Mann (University of Reading)
Murder, Magic and Medicine.

03.02.93* Prof. S. M. Roberts (University of Exeter)
Enzymes in Organic Synthesis.

10.02.93 Dr. D. Gillies (University of Surrey)
NMR and Molecular Motion in Solution.

11.02.93* Prof. S. Knox (University of Bristol)
The Tilden Lecture. Organic Chemistry at Polynuclear Metal Centres.

17.02.93 Dr. R. W. Kemmitt (University of Leicester)
Oxatrimethylenemethane Metal Complexes.

18.02.93 Dr. I. Fraser (I.C.I. Wilton)
Reactive Processing of Composite Materials.

22.02.93 Prof. D. M. Grant (University of Utah)
Single Crystals, Molecular Structure and Chemical-Shift Anisotropy.

24.02.93* Prof. C. J. M. Stirling (University of Sheffield)
Chemistry on the Flat-Reactivity of Ordered Systems.

10.03.93 Dr. P. K. Baker (University College of North Wales, Bangor)
Chemistry of Highly Versatile 7-Coordinate Complexes.

11.03.93 Dr. R. A. Y. Jones (University of East Anglia)
The Chemistry of Wine Making.

17.03.93* Dr. R. J. K. Taylor (University of East Anglia)
Adventures in Natural Product Synthesis.

24.03.93* Prof. I. O. Sutherland (University of Liverpool)
Chromogenic Reagents for Cations.

13.05.93 Prof. J. A. Pople (Carnegie-Mellon University, Pittsburgh)
The Boys-Rahman Lecture. Applications of Molecular Orbital Theory.

21.05.93 Prof. L. Weber (University of Bielefeld)
Metallophospha-Alkenes as Synthons in Organometallic Chemistry.

01.06.93* Prof. J. P. Konopelski (University of California, Santa Cruz)
Synthetic Adventures with Enantiomerically Pure Acetals.

02.06.93 Prof. F. Ciardelli (University of Pisa)
Chiral Discrimination in the Stereospecific Polymerisation of Alpha Olefins.

07.06.93 Prof. R. S. Stein (University of Massachusetts)
Scattering Studies of Crystalline and Liquid Crystalline Polymers.

16.06.93 Prof. A. K. Covington (University of Newcastle upon Tyne)
Use of Ion Selective Electrodes as Detectors in Ion Chromatography.

17.06.93 Prof. O. F. Nielsen (University of Copenhagen)
Low-Frequency IR and Raman Studies of Hydrogen Bonded Liquids.

Academic Year 1993-1994

13.09.93 Prof. Dr. A. D. Schlüter (Freie Universsität, Berlin)
Synthesis and Characterisation of Molecular Rods and Ribbons.

13.09.93 Dr. K. J. Wynne (Office of Naval Research, Washington, USA)
Polymer Surface Design for Minimal Adhesion.

14.09.93 Prof. J. M. DeSimone (University of North Carolina, Chapel Hill)
Homogeneous and Heterogeneous Polymerisations in Environmentally Responsible Carbon Dioxide.

28.09.93 Prof. H. Ila (North Eastern Hill University, India)
Synthetic Strategies for Cyclopentanoids *via* Oxoketene Dithioacetals.

04.10.93 Prof. F. J. Feher (University of California, Irvine)
Bridging the Gap between Surfaces and Solution with Sessilquioxanes.

14.10.93 Dr. P. Hubberstey (University of Nottingham)
Alkali Metals: Alchemist's Nightmare, Biochemist's Puzzle and Technologist's Dream.

20.10.93 Dr. P. Quayle (University of Manchester)
Aspects of Aqueous ROMP Chemistry.

21.10.93 Prof. R. Adams (University of South Carolina)
Chemistry of Metal Carbonyl Cluster Complexes: Development of Cluster Based Alkyne Hydrogenation Catalysts.

27.10.93 Dr. R. A. L. Jones (Cavendish Laboratory, Cambridge)

Perambulating Polymers.

10.11.93 Prof. M. N. R. Ashfold (University of Bristol)
High Resolution Photofragment Translational Spectroscopy: A New Way to Watch Photodissociation.

17.11.93 Dr. A. Parker (Rutherford Appleton Laboratory, Didcot)
Applications of Time Resolved Resonance Raman Spectroscopy to Chemical and Biochemical Problems.

24.11.93 Dr. P. G. Bruce (University of St. Andrews)
Structure and Properties of Inorganic Solids and Polymers.

25.11.93 Dr. R. P. Wayne (University of Oxford)
The Origin and Evolution of the Atmosphere.

01.12.93* Prof. M. A. McKervey (Queen's University, Belfast)
Synthesis and Applications of Chemically Modified Calixarenes.

08.12.93* Prof. O. Meth-Cohn (University of Sunderland)
Friedel's Folly Revisited - A Super Way to Fused Pyridines.

16.12.93 Prof. R. F. Hudson (University of Kent)
Close Encounters of the Second Kind.

26.01.94 Prof. J. Evans (University of Southampton)
Shining Light on Catalysts.

02.02.94 Dr. A. Masters (University of Manchester)
Modelling Water Without Using Pair Potentials.

09.02.94* Prof. D. Young (University of Sussex)
Chemical and Biological Studies on the Coenzyme Tetrahydrofolic Acid.

16.02.94 Prof. K. H. Theopold (University of Delaware)
Paramagnetic Chromium Alkyls: Synthesis and Reactivity.

23.02.94 Prof. P. M. Maitlis (University of Sheffield)
Across the Border: From Homogeneous to Heterogeneous Catalysis.

02.03.94* Dr. C. Hunter (University of Sheffield)
Noncovalent Interactions between Aromatic Molecules.

09.03.94 Prof. F. Wilkinson (Loughborough University of Technology)
Nanosecond and Picosecond Laser Flash Photolysis.

10.03.94* Prof. S. V. Ley (University of Cambridge)
New Methods for Organic Synthesis.

25.03.94 Dr. J. Dilworth (University of Essex)
Technetium and Rhenium Compounds with Applications as Imaging Agents.

28.04.94 Prof. R. J. Gillespie (McMaster University, Canada)

The Molecular Structure of some Metal Fluorides and Oxofluorides: Apparent Exceptions to the VSEPR Model.

12.05.94 Prof. D. A. Humphreys (McMaster University, Canada)
Bringing Knowledge to Life.

A.2.2 List of Conferences Attended

There follows a list of conferences attended by the author during the period when the research for the thesis was carried out.

June 1993	Science and Engineering Research Council, Graduate School (C.R.A.C.), University of Stirling.
August 1993	ESOC 8th Symposium on Organic Chemistry, Barcelona. A poster was presented entitled: "Covalently Attached Ferrocene and Tetrathiafulvalene Redox Systems".
April 1994	New Electronic Materials, RSC Conference, London.
May 1994	Graduate Symposium, University of Northumberland. An oral presentation was given entitled: "Functionalised Tetrathiafulvalenes in Supramolecular Chemistry".

APPENDIX 3

PUBLICATIONS

Parts of this work contained in this thesis have been reported in the following publications:

1) A.J. Moore, P.J. Skabara, M.R. Bryce, A.S. Batsanov, J.A.K. Howard and S.T.A.K. Daley, *J. Chem. Soc., Chem. Commun.*, 1993, 417.

2) M.R. Bryce, A.J. Moore, M.A. Coffin, G.J. Marshallsay, G. Cooke, P.J. Skabara, A.S. Batsanov, J.A.K. Howard and W. Clegg, *Phosphorus, Sulfur and Silicon,* 1993, **74**, 279.

3) M.R. Bryce, A.J. Moore, G. Cooke, G.J. Marshallsay, P.J. Skabara, A.S. Batsanov, J.A.K. Howard, S.T.A.K. Daley, *J. Chem. Soc., Perkin Trans. 1,* 1993, 1403.

4) M.R. Bryce, A.S. Batsanov, W. Devonport, J.N. Heaton, J.A.K. Howard, G.J. Marshallsay, A.J. Moore, P.J. Skabara and S. Wegener, Chapter in 'Molecular Engineering for Advanced Materials', Ed. J. Becher, Kluwer, Dordrecht, 1994, in press.