

REVIEW ARTICLE

Synthesis, Structure and Properties of Dihydratetrathiafulvalenes

Abstract: Although less well known than their fully unsaturated analogues, dihydratetrathiafulvalenes (dihydro-TTFs) have been of considerable recent interest as components of organic conducting materials. In this article the various methods for their synthesis are reviewed and this is followed by a survey of their structure and properties, including those of charge transfer salts, and an account of their reactions.

ARTICLE HISTORY

Received:
Revised:
Accepted:

DOI:

Keywords: Dihydratetrathiafulvalenes, synthesis, X-ray structures, conductivity, cyclic voltammetry, reactions.

1. INTRODUCTION

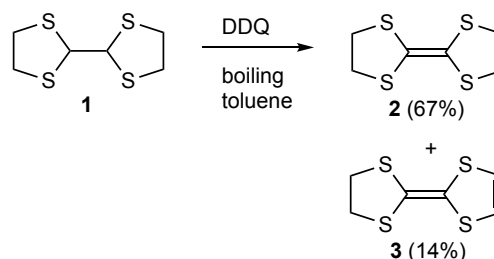
Ever since its discovery in 1972 [1], and the report in 1973 [2] that it forms conducting charge-transfer complex with tetracyano-p-quinodimethane (TCNQ), tetrathiafulvalene (TTF) has had a central role in the area of molecular electronics. Numerous substituted derivatives have been prepared and new publications involving TTF currently amount to over 200 per year. In contrast, dihydratetrathiafulvalenes where one of the five-membered rings lacks a double bond are much less common, although the parent compound was actually first reported the year before TTF. Much of the work in this area is due to Professor Jun-ichi Yamada and the reader is referred to two previous review articles [3,4] summarising his work, however as far as we are aware, the dihydratetrathiafulvalenes have not been specifically reviewed before.

2. SYNTHESIS

In this section we survey the different approaches taken to the synthesis of dihydratetrathiafulvalenes. These are arranged in roughly chronological order and all the relevant examples are listed under each synthetic method.

2.1 Dehydrogenation of Hexahydratetrathiafulvalene

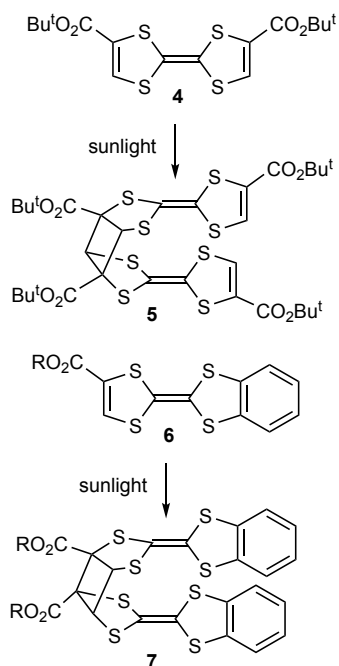
This was the first method used to obtain the parent compound **3** in 1971 (Scheme 1) [5]. Treatment of the saturated precursor **1** with the oxidant DDQ in boiling toluene for 1 h gave a mixture of the dehydrogenation products **2** and **3** from which **3** could be separated in low yield by chromatography.



Scheme 1. Synthesis of **3** by dehydrogenation

2.2 Photochemical [2+2]-Dimerisation of TTFs

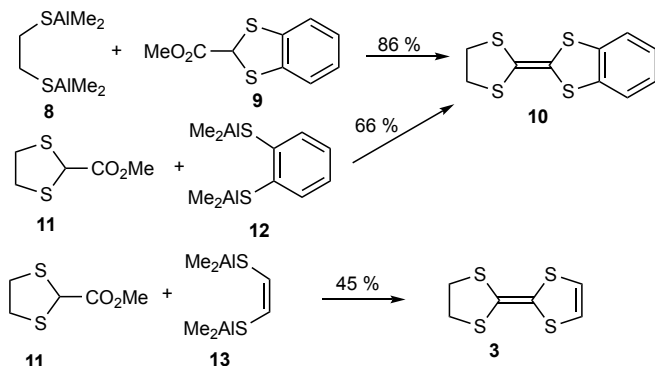
An unexpected observation first made by a Russian group in 1989 [6] was that the TTF diester **4** underwent photochemical [2+2]-cycloaddition in the solid state simply by exposing the crystals to sunlight (Scheme 2). The formation of the head to tail dimer **5** was later examined in a study which included determination of the crystal structure of **4** [7]. More recently the benzo-fused analogues **6** were studied and it was found that while the acid (R = H) undergoes dimerisation only to a trace extent, the methyl ester (R = Me) gives the head to head dimer **7** in 75% yield [8]. This allowed functionalisation of the dimer **7** for attachment to an electrode surface by installation of silane-containing side-chains [9].



Scheme 2. Synthesis by [2+2]-cycloaddition

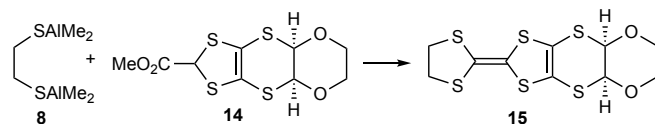
2.3 Synthesis Using Organoaluminium Thiolates

In 1992 Mori described a new direct method for synthesis of dihydro-TTFs involving condensation of organoaluminium thiolates with dithiol(an)e-2-carboxylates (Scheme 3) [10]. As shown the saturated part could come from either component with the dihydrobenzo-TTF **10** being formed in good yield either from **8** and **9** or from **11** and **12**. Reaction of the same ester **11** with aluminium enedithiolate **13** provided a higher yielding synthesis of the parent compound **3**. The esters **9** and **11** are readily prepared from the relevant dithiol with methyl dichloroacetate while the aluminium compounds **8** and **12** come from treating the dithiol with trimethylaluminium. Synthesis of **13** involves reaction of the sodium enedithiolate with dimethylaluminium chloride.



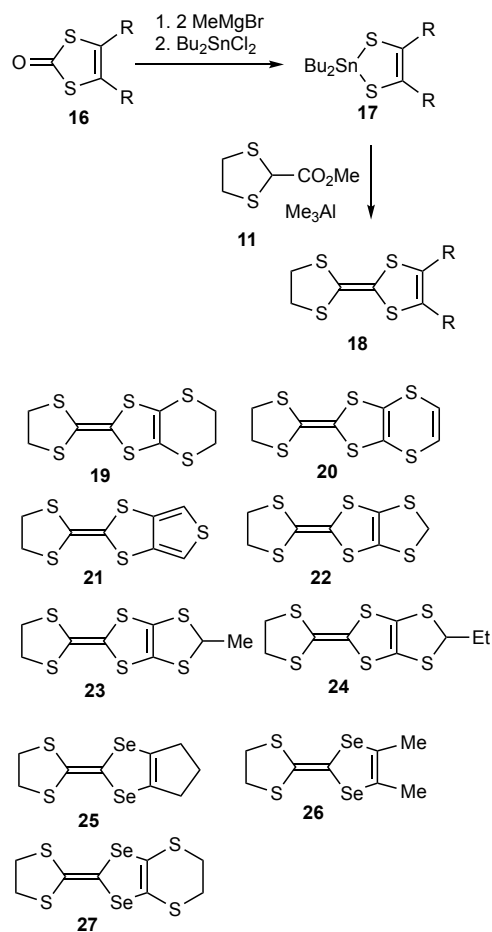
Scheme 3. Synthesis using organoaluminium thiolates

More recently this method has also been used in the synthesis of compound **15** by reaction of ester **14** with aluminium reagent **8** (Scheme 4) [11].

Scheme 4. Synthesis of **15** using an organoaluminium thiolate

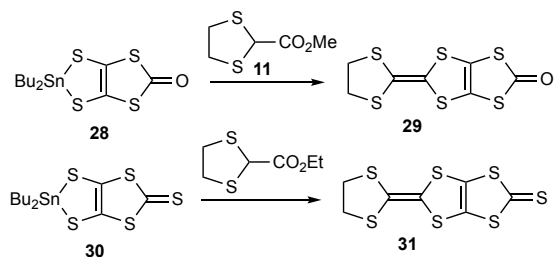
2.4 Synthesis using Organotin Thiolates

A more general variant of the previous method involves the use of cyclic dibutyltin dithiolates **17**. These can be prepared as shown by treatment of a dithiol-2-one **16** with methylmagnesium bromide followed by dibutyltin dichloride (Scheme 5) [12,13]. Subsequent reaction with dithiolane-2-ester **11** in the presence of trimethylaluminium has been used to gain access to a wide range of dihydro-TTF products **18** including **19**, **20** and **21** [12,13], **22** [13,14], **23** and **24** [15]. Starting from the diselenium analogue of **17**, the dihydrodithiadiselenafulvalenes compounds **25**, **26** [12,13] and **27** [13,14] were similarly obtained.



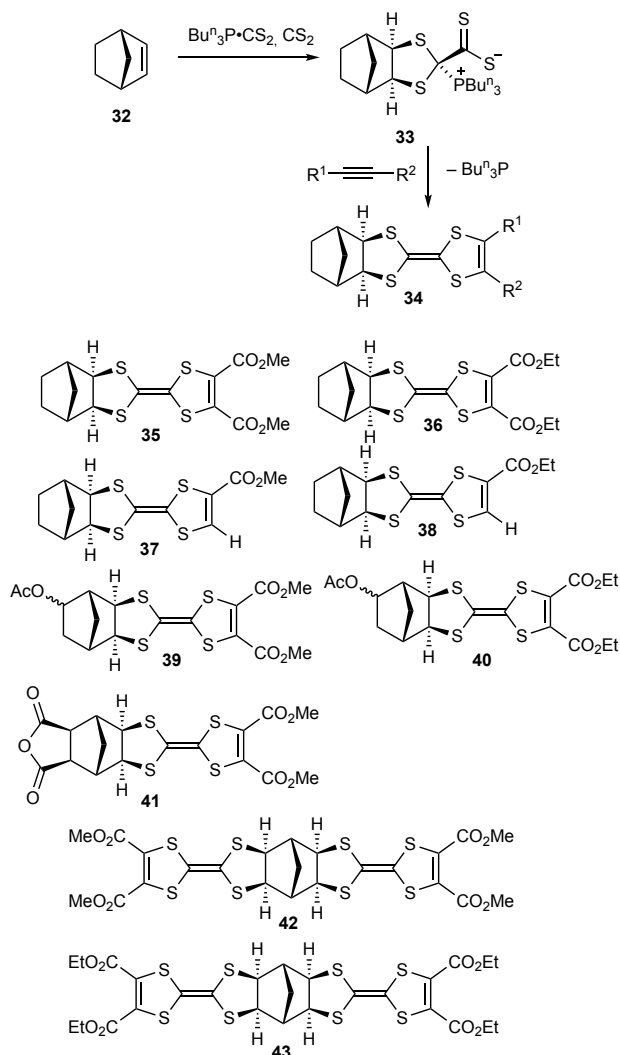
Scheme 5. Synthesis using cyclic organotin thiolates

A further valuable extension to this method involves reaction of the dithiole-2-one and -thione organotin compounds **28** and **30** with dithiolane ester **11** or its ethyl analogue to afford the products **29** and **31** which can then be condensed with further components using trimethyl phosphite to give extended dihydro-TTF compounds as described later in Section 2.6 (Scheme 6) [13,15].

Scheme 6. Formation of intermediates **29** and **31**

2.5 Cycloaddition of Tributylphosphine Carbon Disulfide Adduct and Acetylenic Esters to Strained Double Bonds

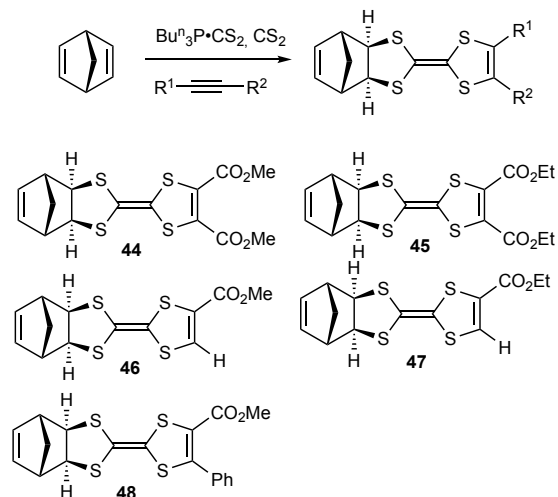
A new method first reported by Aitken in 1997 [17,18] involves the reaction of strained alkenes such as norbornene **32** with the crystalline adduct formed between tributylphosphine and carbon disulfide to generate a stable zwitterionic compound **33** which reacts with acetylenic esters to give dihydro-TTF products **34** (Scheme 7). In this way compounds such as **35–38** were prepared and by starting from substituted norbornenes the method could be extended to synthesis of **39–41**.



Scheme 7. Synthesis using tributylphosphine carbon disulfide adduct

By starting with norbornadiene, the reaction occurred on both double bonds to afford bis(dihydro-TTFs) **42** and **43** [18].

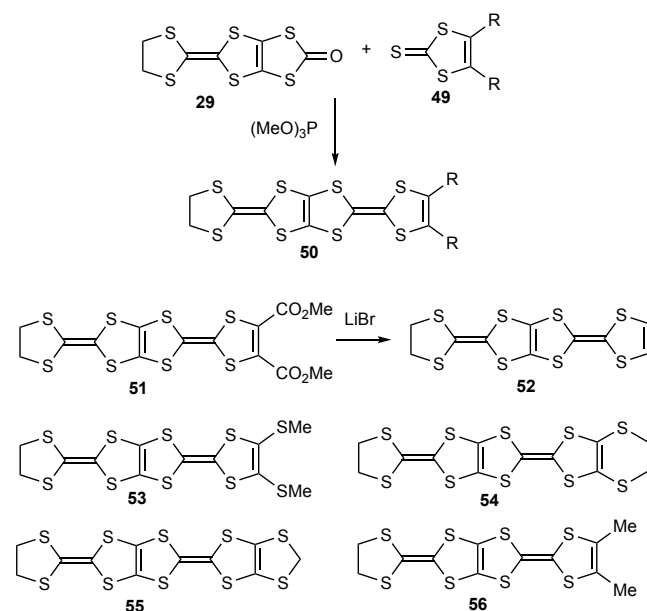
It was later reported that the mono adducts **44** and **45** could also be obtained in low yield by application of this method to norbornadiene and with less highly activated alkynes only mono adducts **46–48** were obtained (Scheme 8) [19,20].



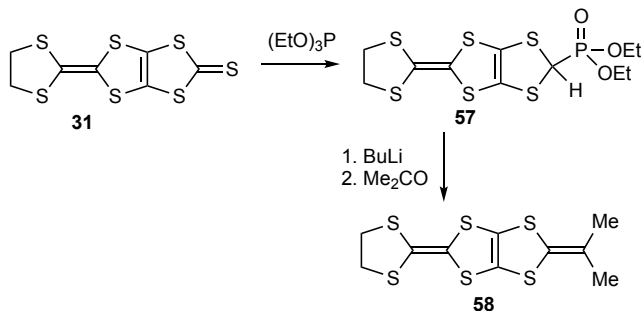
Scheme 8. Synthesis using norbornadiene and tributylphosphine carbon disulfide adduct

2.6 Phosphite-induced Condensation of Dithiolones and Dithiolethiones Already Containing a Dihydro-TTF unit

As mentioned in Section 2.4, the organotin method can be used to obtain dihydro-TTF compounds **29** and **31** which can then be further elaborated. Trimethyl phosphite-mediated condensation of **29** with a range of dithiole-2-thiones **49** gives products **50** (Scheme 9) [13]. Specific examples prepared in this way include **51** which could be subsequently reacted with lithium bromide to afford **52** [21], and **53–55** [13] as well as the dimethyl compound **56** [22].

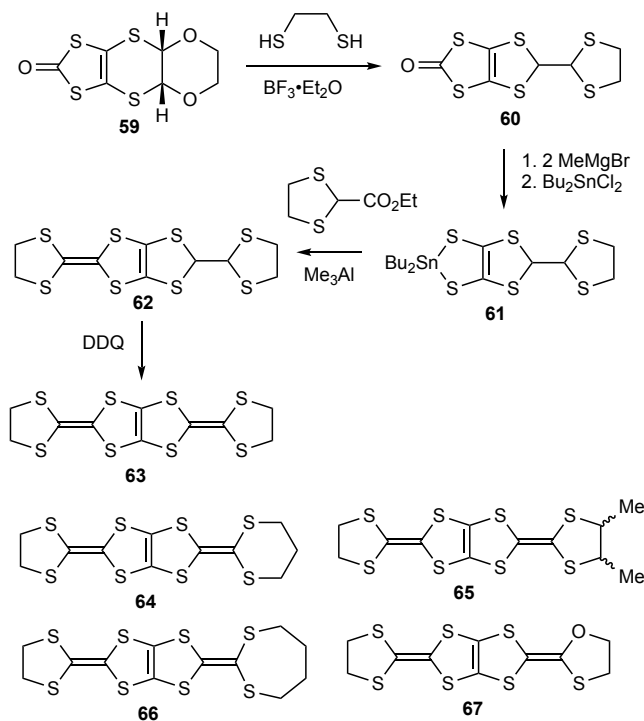
Scheme 9. Synthesis by phosphite-mediated condensation of **29**

A somewhat similar approach using the thione **31** involves treatment with triethyl phosphite to give the phosphonate **57** which is then reacted with butyllithium and acetone to give the 2-propylidene product **58** (Scheme 10) [16].

Scheme 10. Synthesis from thione **31**

2.7 Synthesis Starting from a 1,4-Dithiane-fused 1,4-Dioxane

An unusual and interesting entry to dihydro-TTFs comes from treatment of the 1,4-dioxane-containing dithiole-2-thione **59** with ethanedithiol in the presence of boron trifluoride etherate which gives compound **60** containing a tetrahydro-TTF unit (Scheme 11) [23]. This can then be converted into the dibutyltin compound **61** and condensed with the dithiolane ester using the method of Section 2.4 to give **62**. A final dehydrogenation using DDQ affords the symmetrical bis(dihydro-TTF) **63**.



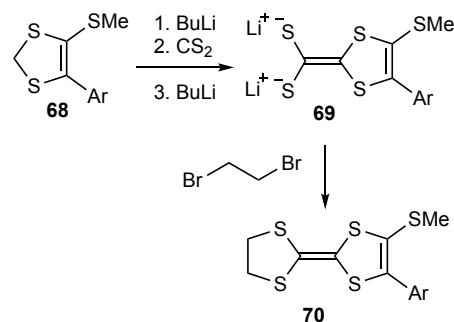
Scheme 11. Synthesis involving rearrangement of a dioxane

The same sequence but using propane-1,3-dithiol in the first step affords the homologue **64** [24], while using butane-2,3-dithiol gives dimethyl compound **65** as a mixture of isomers [25], and butane-1,4-dithiol gives the seven-membered ring

compound **66** [26]. For synthesis of the oxygen-containing compound **67** reaction of **59** with mercaptoethanol gave a mixture of products but the mono-oxygen analogue of **61** was obtained indirectly and the remainder of the sequence went smoothly through to **67** [27].

2.8 Synthesis from a Dithiolide Anion, Carbon Disulfide and Dibromoethane

This method has only been described in a single short paper and starts from a 4-aryl-5-methylmercapto-1,3-dithiole **68** (Scheme 12) [28]. Deprotonation followed by addition of carbon disulfide and a further deprotonation gives the dithiolate dianion which reacts with dibromoethane to afford the products **70**. This sequence was reported for three different aryl groups and, additionally, for two of them with 3,5-dinitrobenzylthio in place of the *S*-methyl group.



Scheme 12. Synthesis from a dithiolate anion

3. STRUCTURE AND PROPERTIES

Since the reason for interest in these compounds is their application in organic conductors, properties commonly investigated include their crystal and molecular structure as determined by X-ray diffraction, their oxidation and reduction potential as determined by cyclic voltammetry, and the conductivity and magnetic properties of the compounds and derived charge transfer salts. In the following Tables, a compilation of such data with literature references is presented (Tables 1-3).

Table 1. X-Ray Diffraction Studies of Dihydro-TTFs and Derived Charge-transfer Complexes

Compound	Reference
7 (R = H)	[8]
7 (R = Me)	[8]
15	[15]
(15) ₂ PF ₆	[11]
(15) ₂ AsF ₆	[11], [29]
(15) ₂ BF ₄ H ₂ O	[15], [29], [30]
(15) ₂ FeCl ₄	[31]
22	[15]
(22) ₂ AuI ₂	[15]

23	[15]
24	[15]
42	[18]
(52) Cr (isoquinoline) ₂ (NCS) ₄	[32]
(52) Cr (phenanthroline) ₂ (NCS) ₄	[33]
(52) ₆ Hg ₃ Br ₉	[34]
(54) ₂ AuI ₂	[21]
(56) ₂ PF ₆	[22]
(56) ₂ AsF ₆	[22]
63	[23]
(63) ₂ PF ₆	[23]
(63) Cr (isoquinoline) ₂ (NCS) ₄	[35]
(63) Fe (isoquinoline) ₂ (NCS) ₄	[35]
(63) ₂ FeCl ₄	[36]
(63) ₄ Hg(NCS) ₄	[37]
(63) ₆ Hg(NCS) ₃ Hg(NCS) ₄	[37]
(63) ₄ Hg ₃ Cl ₈	[34]
(63) ₄ Hg ₃ Br ₈	[34]
(63) ₂ FeBr ₄	[38]
(63) ₄ CoCl ₄ (H ₂ O) ₅	[39]
(63) ₄ MnCl ₄ (H ₂ O) ₅	[39]
(63) ₄ CoBr ₄ CH ₂ Cl ₂	[39]
(63) ₄ MnBr ₄ CH ₂ Cl ₂	[39]
(63) ₄ MnBr ₄ CH ₂ Br ₂	[39]
(63) ₂ chiral spiroboronate	[40]
(64) ₂ PF ₆	[24]
(65) ₂ BF ₄	[25]
(65) ₂ AsF ₆	[25]
(66) ₂ AuI ₂	[26]
67	[27]
(67) ₂ AuI ₂	[27]

Table 2. Cyclic Voltammetry Studies of Dihydro-TTFs

Compound	Reference
3	[5]
7 (R = Me)	[9]
15	[11]
19	[14]

20	[14]
21	[14]
22	[14]
23	[15]
24	[15]
25	[14]
26	[14]
27	[14]
52	[21]
53	[21]
54	[21]
63	[23]
64	[24]
65	[25]

Table 3. Conductivity Measurements and Studies of Magnetic Properties

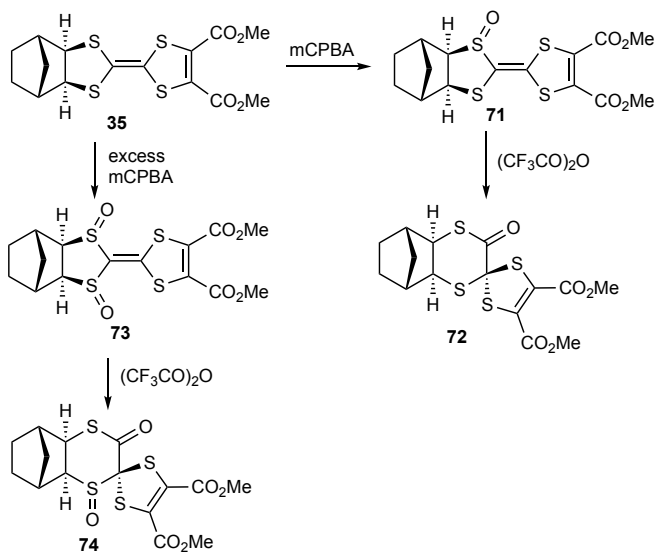
Compound	Counterion(s)	Reference
15	BF ₄	[30]
15	PF ₆ , AsF ₆	[11]
15	FeCl ₄	[31]
19	I ₃ , BF ₄ , ClO ₄ , ReO ₄ , PF ₆ , AsF ₆	[14]
20	BF ₄ , ClO ₄	[14]
22	BF ₄ , AuCl ₂ , AuI ₂	[14]
25	ClO ₄	[14]
26	ClO ₄	[14]
27	BF ₄ , ClO ₄ , ReO ₄	[14]
52	TCNQ, ClO ₄ , AsF ₆ , AuI ₂	[21]
52	Cr(isoquinoline) ₂ (NCS) ₄	[32]
52	Cr(phenanthroline) ₂ (NCS) ₄	[33]
52	Hg ₃ Br ₉	[34]
53	TCNQ, I ₃ , BF ₄ , ClO ₄ , PF ₆ , AsF ₆	[21]
54	TCNQ, I ₃ , BF ₄ , ClO ₄ , PF ₆ , AsF ₆ , AuI ₂	[21]
55	I ₃ , AuI ₂	[21]
56	PF ₆ , AsF ₆ , SbF ₆	[22]
58	AsF ₆	[16]
63	TCNQ, TCNQ-F ₄ , I ₃ , BF ₄ , ClO ₄ , PF ₆ , AsF ₆ , AuI ₂	[23]

63	Cr(isoquinoline) ₂ (NCS) ₄	[35]
63	Fe(isoquinoline) ₂ (NCS) ₄	[35]
63	FeCl ₄	[36]
63	Hg(SCN) ₄ , Hg(SCN) ₃	[37]
63	Hg ₃ Cl ₈ , Hg ₃ Br ₈	[34]
63	FeCl ₄ , FeBr ₄	[41]
63	CoCl ₄ , MnCl ₄ , CoBr ₄ , MnBr ₄	[39]
63	chiral spiroboronate	[40]
64	TCNQ, TCNQ-F ₄ , I ₃ , BF ₄ , ClO ₄ , PF ₆ , AsF ₆ , SbF ₆ , AuI ₂	[24]
64	SbF ₆	[42]
65	BF ₄ , PF ₆	[25]
66	I ₃ , BF ₄ , ClO ₄ , PF ₆ , AsF ₆ , AuI ₂	[26]
67	AuI ₂	[27]
67	BF ₄ , PF ₆ , AsF ₆	[43]

Raman spectroscopy studies have also been carried out on (63)₂Hg₃Cl₈ and (63)₂Hg₃Br₈ [44].

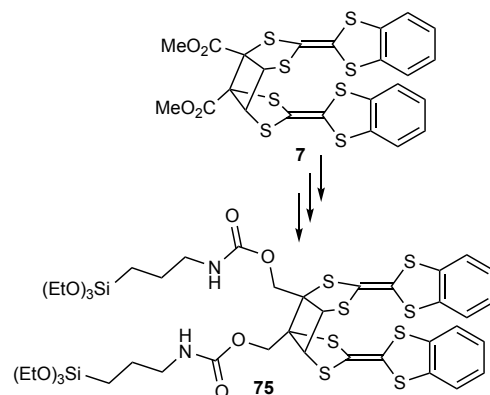
4. REACTIVITY

While the main interest in this area has been preparation of dihydro-TTFs to study their properties and applications, there are a few cases where their subsequent reactions have been reported. In an attempt to obtain the fully unsaturated TTF, compound **35** was oxidised to the monosulfoxide **71** and then treated with trifluoroacetic anhydride. This resulted in an unexpected rearrangement to give the spiro dithiane-dithiole **72** as confirmed by an X-ray structure and the corresponding disulfoxide **73** reacted similarly to give **74** (Scheme 13) [45]. There have been a few studies where functionality has been



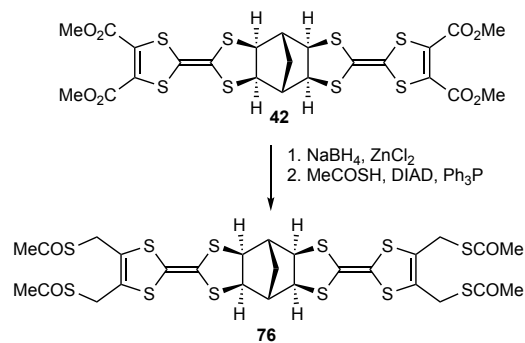
Scheme 13. Rearrangement of dihydro-TTFs under Pummerer conditions

introduced onto a dihydro-TTF to allow binding to a surface. Thus for example the cyclobutane diester **7** was converted in a few conventional steps into the derivative **75** whose properties were examined as a self-assembled monolayer on a glass surface (Scheme 14) [9].



Scheme 14. Functionalisation of **7** for attachment to a surface

Similarly reduction of the tetraester **42** followed by Mitsunobu condensation with thioacetic acid afforded **76** whose properties were investigated on a gold surface (Scheme 15) [46].



Scheme 15. Functionalisation of **42** for attachment to a gold surface

CONCLUSION

Although less well known than their fully unsaturated analogues, the dihydro-TTFs have played a part in the search for new organic conductors with applications in electronics. A variety of effective methods for their synthesis have been developed and the structure and properties of the donors themselves as well as a wide range of their charge-transfer salts have been investigated. In terms of charge transfer complexes exhibiting interesting conductivity and magnetic properties, compounds **15**, **52**, **63** and **64** have been investigated in most detail. Potential new directions in this area include the design of dihydro-TTF compounds which will have intermolecular interactions, either with the same molecule leading to supramolecular chemistry, or with solid surfaces allowing surface science and molecular electronics studies. No doubt further applications of such materials will be developed in the future.

FUNDING

We are grateful to the School of Chemistry, University of St Andrews for a studentship (FMF).

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

CONSENT FOR PUBLICATION

Not applicable.

ACKNOWLEDGEMENTS

None declared.

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