DITHIOLENE CHEMISTRY
Synthesis, Properties, and Applications

Special volume edited by
EDWARD I. STIEFEL
DEPARTMENT OF CHEMISTRY, PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY

PROGRESS IN INORGANIC CHEMISTRY

Series edited by
KENNETH D. KARLIN
DEPARTMENT OF CHEMISTRY, JOHNS HOPKINS UNIVERSITY
BALTIMORE, MARYLAND

VOLUME 52

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Dieter Sellmann
(1941–2003)

With the agreement of all of the authors, this volume is dedicated to our colleague Dieter Sellmann, who died unexpectedly shortly after completing his contribution to this book. Dieter was a marvelous synthetic chemist whose beautiful molecules are amply displayed in Chapter 11 (written with Jörg Sutter) of this collection. But, Dieter was more than someone who created novel and beautiful molecules. He brought insight and understanding to these structures and, especially, to their reactivity with important small molecules. He was inspired by biology, by the reactions of nitrogenase, and by nitrogen oxide interconversions. Indeed, some of his synthetic creations laid bare the possibilities of binding of reactive intermediates in glorious detail, about which others could only speculate. His molecules will continue to give us important clues about the reactivity of enzymes and other catalytic systems. We will miss Dieter's creativity, insights, and good humor, but we also remember and honor a life of great scientific accomplishment, which his article in this volume beautifully represents.

Dieter was an outstanding scientist, a wonderfully warm and vibrant human being, and a good friend. He will be sorely missed.

Preface

This volume of *Progress in Inorganic Chemistry* documents the intense current interest and bright future prospects for research on the chemistry and uses of dithiolene complexes. Over the last forty years, complexes of these remarkable ligands have gone from an important and interesting subclass of inorganic coordination chemistry to a field that, while generating continued interest in structure, bonding, and reactivity, now has impact on a far larger stage. The findings that dithiolene complexes have useful reactivity and sensing properties, that they are at the core of a large number of biologically essential enzymes, and that they display remarkable (super)conductivity, optical, and magnetic properties in the solid state, together have given great impetus to work in this field. These new and, in many cases, quite unexpected findings are documented in this volume side by side with continued discussions of the basic synthetic, structural, spectroscopic, bonding, and reactivity properties of the complexes. The size and scope of this volume and the quality of the individual contributions reveal a vital field that is just entering its prime. It is our hope that, by collecting comprehensive reviews on the various subfields of dithiolene chemistry in a single place, we will contribute toward the stimulation of this now burgeoning field of interdisciplinary research.

Although there had been some very early work (pre-1960) on the use of certain dithiolene ligands in quantitative analysis of metal ions, these initial studies were largely empirical and never explored the highly colored complexes at the structural level. The modern era of dithiolene research started in the early 1960s with contributions from three research groups: those of Schrauzer and co-workers (at Munich and the University of California at San Diego); Gray and co-workers (at Columbia); and Davison and Holm and co-workers (at Harvard). The combined work of these research groups first established the square-planar nature, redox activity, and broad scope of the highly colored bis(dithiolene) complexes of the late transition metals. From the outset, there was contention about the electronic structures of these complexes, as the redox capacity of the ligands (i.e., their noninnocence) made the assignment of oxidation state difficult, or, in some cases, ambiguous, at best. Interest in the area was further heightened by the synthesis and structural characterization of the tris(dithiolene) complexes of early transition metals. In addition to sharing the unusual properties of the bis complexes, members of the tris(dithiolene) family were shown to be the first molecular examples of trigonal-prismatic coordination by Eisenberg and Ibers (at Columbia and Brookhaven).

Work on dithiolene chemistry continued through the 1960s and 1970s fueled by continued interest in the remarkable coordination chemistry of dithiolene complexes. However, in the last 20 years tremendous added impetus to research in the area arose from discoveries in materials science, enzymology, analytical science, and reactivity that broadened the impact and import of dithiolene chemistry. This volume seeks to capture the interplay of basic work on dithiolene complexes with the growing biological, sensor, reactivity, and materials science implications and applications that have made dithiolene chemistry a vibrant and growing field.

Chapter 1 deals with synthesis, where we learn that there are many ways to make dithiolene complexes, either from preformed ligands or through the chemical reactivity of bound sulfur species. Synthesis is at the core of most of the coordination chemistry that has been done on dithiolene complexes. Chapter 2 deals with structures and structural trends of the most common simple dithiolene complexes. Indeed, it was the square-planar nature of most late transition metal bis(dithiolene) complexes and the unprecedented trigonal-prismatic six-coordination of some of the tris(dithiolene) complexes that was one of three major drivers for early work in the field.

In addition to structure, early work was also driven by two other prominent features: electronic structural uniqueness and one-electron redox activity. The second major driver, the electronic structural uniqueness of dithiolene complexes of the transition metals, was manifested in their highly colored nature (i.e., large extinction coefficients). This feature lead to extensive spectroscopic, magnetic, and theoretical studies, which continue through the present with great intensity. Electronic structural studies, reviewed in Chapter 3, reveal the many intricate and interesting features of dithiolene complexes, including the oxidation state ambiguity that can arise from the noninnocence of the ligands. Chapter 4 deals explicitly with the vibrational spectroscopy (IR and Raman), where the spectra are extremely valuable in probing the binding in the ligands and complexes. The material in Chapters 3 and 4 also show the great utility of the spectroscopic and computational tools in probing the molybdenum and tungsten dithiolene cofactors found in biological systems.

The third feature of dithiolene chemistry that attracted early attention was the chemical and electrochemical one-electron redox reactivity of the complexes, which allowed a given complex stoichiometry (M/L ratio) to be isolated with several different charges (i.e., different states of oxidation, albeit not necessarily different oxidation states of the metal). Chapter 5 deals with the electrochemical and chemical reactivity of dithiolene complexes, wherein it is seen that the chemical reactivity goes beyond simple redox reactivity and includes reactions that are often ligand, rather than metal, based.

Chapters 6 and 7 show how the unique electronic structural features of dithiolene complexes manifest themselves in luminescent and photochemical behavior. Chapter 6 reveals that the excited states of dithiolene complexes and

their photochemistry can be understood in those cases where the luminescent activity can be dissected in detail. Chapter 7 describes particular examples wherein the luminescent behavior has been exploited in the development of effective sensors for molecular oxygen and, with great promise, for other molecules as well.

Chapter 8 reviews the considerable work that has been done on solid-state systems. These systems combine the structural features of planar dithiolene complexes, wherein specifically discovered and/or designed ligands form complexes that coalesce into extended lattices, with unusual conductive, magnetic, and/or optical properties. The extensive interest in this field is nurtured by the truly unusual nature of the extended structures, which, in turn, clearly exploit some of the unique structural and electronic structural features of the simpler dithiolene complexes.

Chapters 9 and 10 deal with our now extensive knowledge of dithiolene centers in molybdenum and tungsten enzymes and in their chemical model systems, respectively. Chapter 9 introduces the families of molybdenum and tungsten enzymes that contain the pyranopterin dithiolene ligand, reveals the array of reactions catalyzed by these enzymes, and describes the active site protein structures that have come to light in recent years through X-ray crystallography. The enzyme work provides great impetus and added importance to studies of model systems outlined in Chapter 10. Work on these simpler systems reveals structural trends, electronic structural details, and reactivity modes that are essential to the full understanding of the structures, spectra, and reactivity of the enzymes, many of which are important in medical, agricultural, and environmental systems.

Last, but not least, Chapter 11 reveals how the dithiolene unit has been used as a building block to construct more complex organic ligands. These ligands form a remarkable variety of novel complexes (see dedication) that display new forms of reactivity, which may yet reveal ways in which important small molecules are activated and converted by enzyme systems in the transition metal dithiolene family.

The 11 chapters in this volume reveal a vigorous field that may just be entering its prime. The new results from synthesis, structure elucidation, spectroscopy, biology, bioinorganic chemistry, analytical science, solid-state materials chemistry, and reactivity define a rich field that has far to go before reaching maturity. It is also clear that, as we learn more about dithiolene complexes, we will see new applications arising that exploit our fundamental understanding of chemical, material, and biological systems. It is our hope that this monograph, by bringing together the myriad aspects of dithiolene chemistry in a single volume, will serve as a comprehensive archival reservoir, stimulate further advancement of the field, and impel its growing interface with diverse areas of science and technology.

Princeton, New Jersey   EDWARD I. STIEFEL

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Synthesis of Transition Metal Dithiolenes

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CONTENTS

I.   INTRODUCTION

Research on metal dithiolenes has remained continuously active since its inception in the early 1960s. Initially, the area was driven by the distinctive redox and structural characteristics of these coordination compounds. After this discovery phase, dithiolene chemistry was fueled by its connections to materials science with respect to photonics and electronic conductors. These developments paralleled growth in the area of organic metals; in fact, the preparative chemistry of dithiolene complexes has greatly benefited from advances in tetrathiafulvalene chemistry (1). This direction remains active (2, 3). In the 1990s, research on dithiolenes was energized by recognition that virtually all Mo- and W-containing enzymes feature dithiolene ligands, which are in turn incorporated into the heterocyclic pyranopterins (4–7). Parallel with the aforementioned developments—discovery, materials-driven studies, and biologically driven studies—dithiolene complexes continue to appear in many contexts, often unexpected ones, due to the great stability of the $MS_2C_2R_2$ ring.

This chapter discusses the synthesis of transition metal dithiolene complexes and is current to late 2002. Dithiolene chemistry has been reviewed several times previously, but this is the first review dedicated to synthetic aspects. Emphasis is placed on more contemporary methods, and the reader should consult the older reviews, especially those by Mueller-Westerhoff et al. (8) and McCleverty (9) for discussions of earlier literature. An effort was made to be comprehensive with respect to methods and the range of complexes examined, but the chemistry of metal dithiolenes is so vast that it is not practical to be exhaustive.

In this chapter, the term dithiolene refers to a ligand of the formula $R_2C_2S_2$, which depending on one's formalism could be described as an alkene-1,2-dithiolate dianion, a 1,2-dithione, or some oxidation state between these two extremes (Fig. 1). Benzenedithiolates, their derivatives, and analogues are also included.

This chapter is divided into two main parts. The first part focuses on reactions where the dithiolene ligand is generated independently of the metal center. For the most part, these preparations give alkenedithiolate dianions, which ordinarily are treated with metal electrophiles to form dithiolene complexes. In the second part, transition metals actively participate in the assembly of the dithiolenes, usually via the reaction of a metal sulfido species with an alkyne or hydrocarbon in an equivalent oxidation state.

When considering the synthesis of a dithiolene complex, it is essential to bear in mind that dithiolenes vary widely in their electronic properties. If one simply seeks an unsaturated chelating dithiolate, the most convenient options are benzenedithiolate and the inorganic dithiolenes 1,3-dithiole-2-thione-4,5-dithiolate ($dmit^{2-}$) and 1,2-maleonitrile-1,2-dithiolate (1,2-dicyanoethene-1,2-dithiolate) (mnt^{2-}). Large-scale syntheses of these ligands are available. Dithiolenes
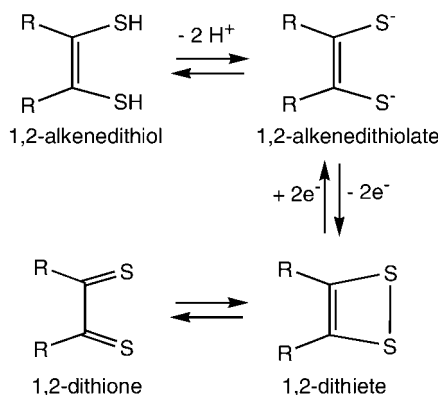

Figure 1.   Relationships and nomenclature for common dithiolene precursors.

such as mnt^{2-} and dmit^{2-} that have electronegative substituents behave like bidentate pseudohalides, and their complexes are usually synthesized via simple salt metathesis reactions. Akyl-substituted dithiolenes (e.g., [Me$_2$C$_2$S$_2$]$^{2-}$), are powerful π donors, useful for stabilizing metals in high formal oxidation states. Syntheses of complexes of such strongly donating dithiolenes often require redox steps after the initial formation of a metal dithiolene complex.

II.   SYNTHESIS FROM PREFORMED ALKENEDITHIOLATES, 1,2-DITHIONES, AND THEIR EQUIVALENT

A.   From Benzenedithiol and Related Derivatives

1.   Arene Derivatives

Arene-1,2-dithiols are completely stable and are valuable precursors to dithiolene complexes. Benzenedithiol is the most common member of this class of ligands, but related derivatives include toluene-3,4-dithiol (10), 3,4,5,6-tetrachlorobenzenedithiol (11), 3,4,5,6-tetramethylbenzenedithiol (12), 2,3-naphthalenedithiol (13), and quinoxalinedithiol (14) (Fig. 2).

Benzenedithiols are traditionally prepared by reductive dealkylation of 1,2-C$_6$R$_4$(SR′)$_2$, which in turn are obtained by treatment of dibromobenzenes with alkali metal or cuprous thiolates. The methodology continues to be used, for example, for crown ether-appended derivatives (15). A newer and more powerful synthesis of 1,2-benzenedithiol and its derivatives has been developed (16). This method (17) involves reaction of the benzenethiol with 2 equiv of BuLi to give 2-LiC$_6$H$_4$(SLi), which reacts with elemental sulfur to give the dithiolate (Eq. 1).

$$\text{(1)}$$
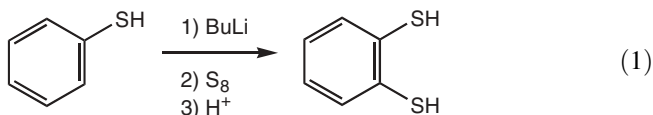
This method has been extended to the synthesis of the bulky benzenedithiol 3-(Ph$_3$Si)C$_6$H$_3$-1,2-(SH)$_2$ (18) as well as a series of mixed chalcogenides such as [1,2-C$_6$H$_4$(S)(Te)]$^{2-}$ (19).

Typically, transition metal benzenedithiolates (and related derivatives) are prepared by the following methods: salt elimination reactions using a metal halide and the dithiolate dianion, thiol exchange, and condensation of the free thiol with oxo, alkoxo, and amido precursors. In one example, the dithiol was
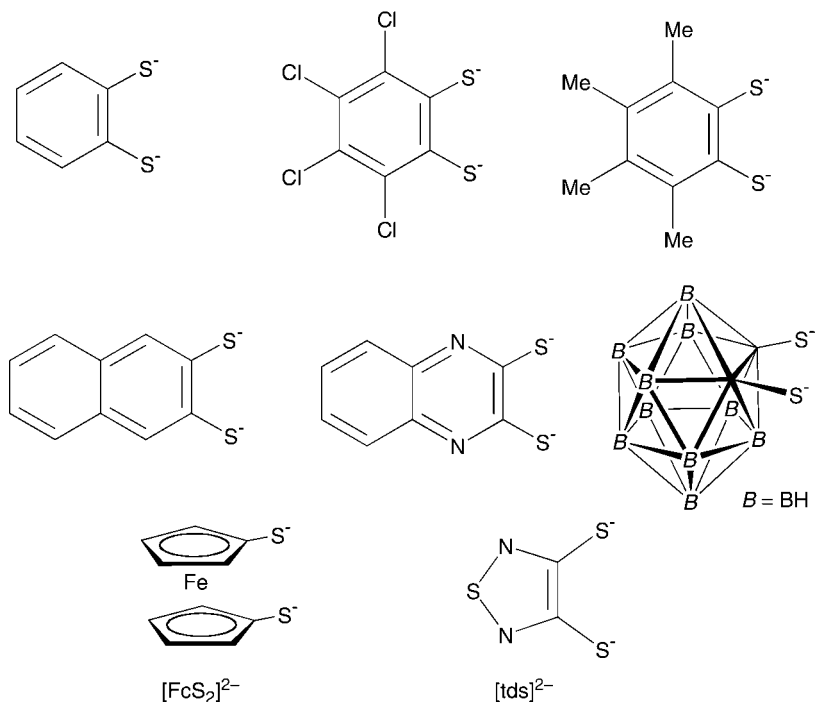
Figure 2.   Structures of important arenedithiolate and related ligands.

treated with a metal methyl compound concomitant with the elimination of methane (Eq. 2) (20).

$$WMe_6 + 3\ C_6H_4(SH)_2 \rightarrow W(S_2C_6H_4)_3 + 6\ CH_4 \qquad (2)$$
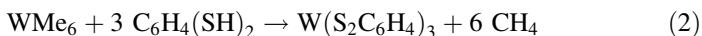
Homoleptic dithiolene complexes, for example, $[Ni(S_2C_6R_4)_2]^z$ and $[M(S_2C_6R_4)_3]^z$ (M = Mo, W), are generally prepared by reaction of the metal halide and the dithiolate, often followed by oxidation of the initially formed complexes. An illustrative study is the synthesis of $[Ni(S_2C_6H_2(t\text{-}Bu)_2)_2]^{2-}$, which can be oxidized to the monoanion and neutral derivatives using air and iodine, respectively (21). Reactions of $MoCl_5$ and WCl_6 with the benzene-dithiolate salts give $M(S_2C_6R_4)_3$ (15, 22) or reduced derivatives. Similarly, treatment of $Ti(NMe_2)_4$ with $C_6H_4(SH)_2$ gives $(NMe_2H_2)_2[Ti(S_2C_6H_4)_3]$, wherein the amido ligand serves not only as a proton acceptor but also generates the countercation (23). The tris(dithiolenes) are so robust and so easily formed that they plague syntheses of the oxo-dithiolenes $[MO(S_2C_6R_4)_2]^z$ (24). In the case of Mo derivatives, the metathetical reactions can be conducted

$$[WO(SPh)_4]^- \xrightarrow{C_6H_4(SH)_2} [WO(S_2C_6H_4)_2]^-$$

$$\Big\downarrow BH_4^-$$

$$[WO_2(S_2C_6H_4)_2]^{2-} \xleftarrow{Me_3NO} [WO(S_2C_6H_4)_2]^{2-}$$
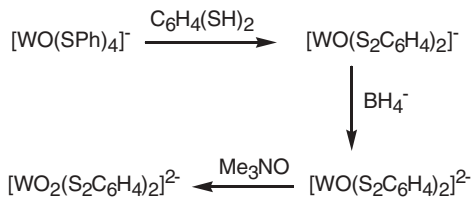
Figure 3.   Illustrative syntheses of oxo-tungsten dithiolenes (25).

in the presence of donor ligands, which inhibit the formation of the tris(dithiolene) complexes. For example, treatment of $Na_2(S_2C_6R_4)$ with $MoCl_4(MeCN)_2$ in the presence of donor ligands L affords $Mo(S_2C_6R_4)_2L_2$ (L = PPh_2Me or MeNC; R = H, Me) (12). These derivatives are closely related to the corresponding dicarbonyls (L = CO; see Section II.G.2).

Compounds of the type $[MO(S_2C_6H_4)_2]^{n-}$ (M = Mo, W) have received much attention. A direct approach to $[WO(S_2C_6H_4)_2]^-$ proceeds via the reaction of $WOCl_3(thf)_2$ (where thf = tetrahydrofuran) benzenedithiol, and Et_3N (24). Alternatively, thiol exchange routes can be advantageous as a means to minimize redox processes and formation of $[M(S_2C_6H_4)_3]^{n-}$. For example, $[WO(SPh)_4]^-$ and benzenedithiol give $[W^{V}O(S_2C_6H_4)_2]^-$, which can be subsequently reduced with $NaBH_4$ to give $[W^{IV}O(S_2C_6H_4)_2]^{2-}$ (Fig. 3) (25). Related thiol exchange reactions involve conversion of $[MoO(SC_6H_4R)_4]^{n-}$ (R = Cl, n = 2; R = H, n = 1) into $[MoO(S_2C_6H_3R)_2]^{n-}$ (R = H, Me, Ph_3Si) (18, 26).

The oxo-bis(dithiolenes) are amenable to further reactions. Treatment of $[MO(S_2C_6H_4)_2]^{2-}$ Me_3NO (13) affords $[M^{VI}O_2(S_2C_6H_4)_2]^{2-}$ (M = Mo, W) (25, 27). Silylation of the oxo-bis(dithiolene) complexes gives $[M^{VI}(OSiR_3)$-$(S_2C_6H_4)_2]^-$ (M = Mo, W), which are versatile precursors to diverse coordination sets on the bis(dithiolene) framework (12, 24). For example, such $[M^{VI}(OSiR_3)(S_2C_6H_4)_2]^-$ derivatives can be oxidized using Me_3NO to give $[M^{VI}(O)(OSiR_3)(S_2C_6H_4)_2]^-$ (M = Mo, W) and, in the W case, sulfided using dibenzyltrisulfide to give $[W^{VI}(S)(OSiR_3)(S_2C_6H_4)_2]^-$.

The mildly electrophilic complex $MeReO_3$ condenses with 2 equiv of benzenedithiol to give $MeRe(O)(S_2C_6H_4)_2$ (28), a rare alkyl metal dithiolene.

Thiol exchange has been employed to probe the strength of metal ligand bonds as illustrated by the reactions of dicysteinyl peptide-bound derivatives of $[Fe_2S_2(SR)_4]^{2-}$ with toluene-3,4-dithiol. For strongly chelating dipeptides, $[Fe(SR)_2(S_2C_6H_3Me)]^-$ derivatives (R = protein) form with H_2S elimination, whereas less strongly chelating dipeptides are displaced by this dithiol to give $[Fe_2S_2(S_2C_6H_3Me)_2]^{2-}$ (29).

Since several molybdoenzymes feature a single dithiolene ligand active site (30), the synthesis of monodithiolene complexes has been of interest. Two general approaches can be envisioned. Stepwise installation of dithiolene
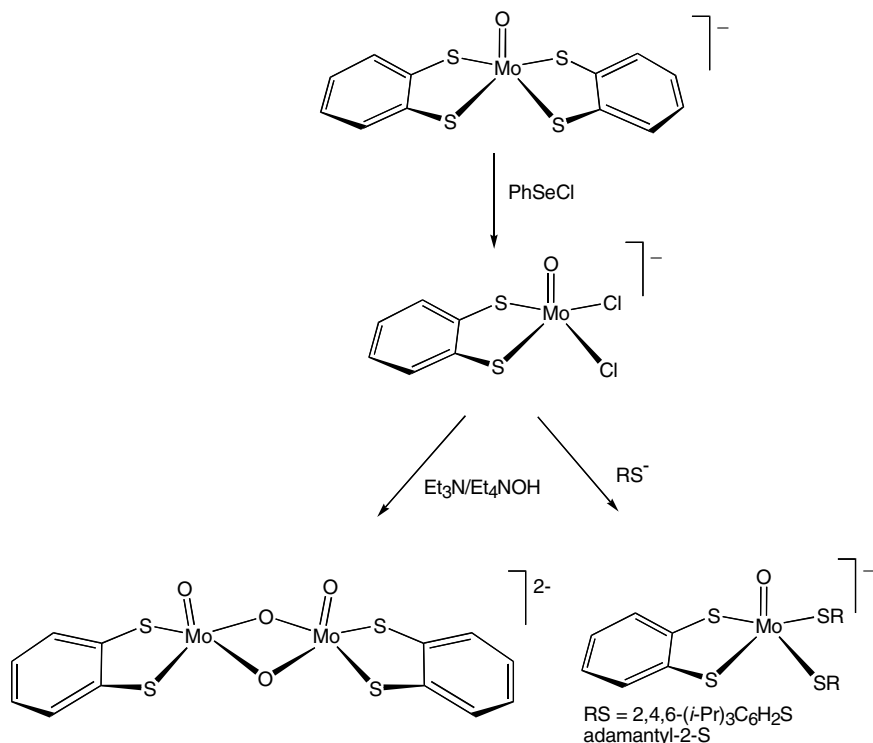
Figure 4. Routes to monodithiolene derivatives of Mo (30).

ligands or removal of dithiolenes from bis- and tris(dithiolene) precursors. One dithiolene can be removed from $[MoO(S_2C_6H_4)_2]^-$ using PhSeCl to give monodithiolene $[MoOCl_2(S_2C_6H_4)]^-$ together with $(PhSeS)_2C_6H_4$ (30). The chloro ligands in $[MoOCl_2(S_2C_6H_4)]^-$ undergo ready substitution to give diverse mixed-ligand derivatives as shown in Fig. 4. Thiolate–siloxide exchange was employed to prepare $[MoO_2(OSiPh_3)(S_2C_6H_4)]^-$ via the reaction of $MoO_2(OSiPh_3)_2$ with $Li_2S_2C_6H_4$.

Benzenedithiolates can also be prepared by H_2 elimination when using low-valent precursor complexes (Eq. 3) (31).

$$Cp_2V + C_6H_4(SH)_2 \rightarrow Cp_2VS_2C_6H_4 + H_2 \qquad (3)$$
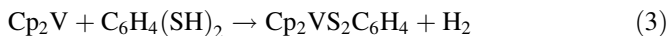
This H_2-elimination route from 1,2-benzenedithiol was also employed in the synthesis of $Fe_2(S_2C_6H_4)(CO)_6$ (32) and the coordinatively unsaturated $[Mn(CO)_3(S_2C_6H_4)]^-$ (33). A series of related coordinatively unsaturated species $[Cr(CO)_3(S_2C_6R_4)]^{2-}$ (R = H, Cl, Me) were prepared by displacement of the

Figure 5.   Synthetic routes to Fe(S$_2$C$_6$H$_4$)–CO complexes (38, 39).

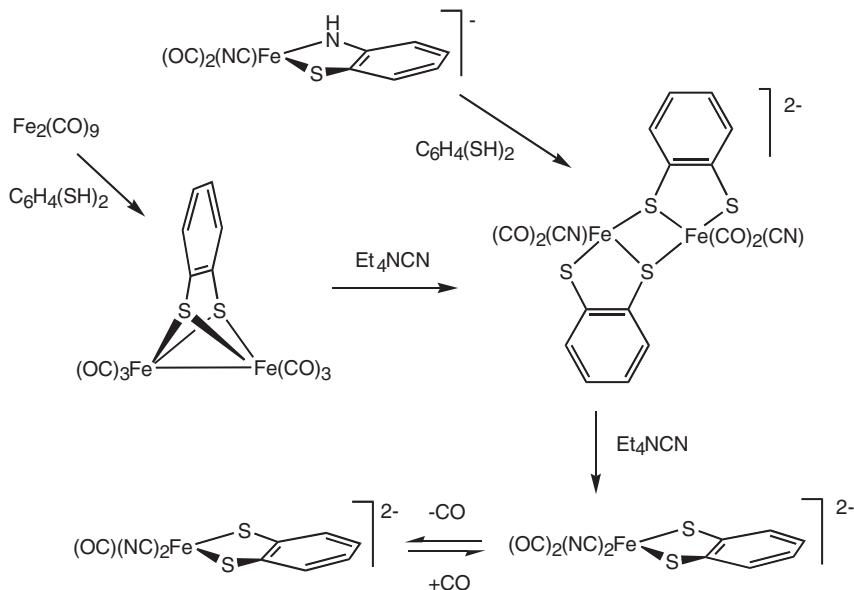solvento ligands from Cr(CO)$_3$(MeCN)$_3$. At higher metal stoichiometry, one obtains the binuclear [Cr$_2$(CO)$_6$(μ-CO)(μ-η^2:η^2-S$_2$C$_6$R$_4$)]$^{2-}$ (34). Other coordinatively unsaturated dithiolenes have been prepared by salt-forming methods, for example, [triphos]Fe(S$_2$C$_6$H$_4$) (35), [η^4-C$_4$Me$_2$(t-Bu)$_2$]Pd(S$_2$C$_6$H$_4$) (36), and (C$_5$Me$_5$)Ir(S$_2$C$_6$H$_4$) (37). The species Fe$_2$(S$_2$C$_6$H$_4$)(CO)$_6$ undergoes ready degradation upon treatment with Et$_4$NCN, giving rise to both mono- and diiron derivatives (Fig. 5) (38).

2.   Linked Bis(benzenedithiolate) Complexes

Relatively elaborate benzenedithiol ligands have been prepared via ortho lithiation of 1,2-benzenedithiol with 3 equiv BuLi, which affords 3-LiC$_6$H$_3$-(SLi)$_2$. This trilithiated compound undergoes carbonation to give 2,3-dimercaptobenzoic acid. This carboxy-functionalized dithiolene can be linked via amide formation to give the bis(benzenedithiol), isolated as its Cp$_2$Ti^{IV} derivative (see also Section II.G.1) (40, 41). Such ligands can be converted to chelating bis(dithiolene) complexes (Fig. 6). The use of 2,3-dimercaptobenzoic acid derivatives is inspired by the naturally occurring chelators derived from 2,3-dihydroxybenzoate (42).

An improved and very promising methodology to such linked dithiolenes begins with the ortho lithiation of 1,2-C$_6$H$_4$(S-i-Pr)$_2$, generated on a large scale
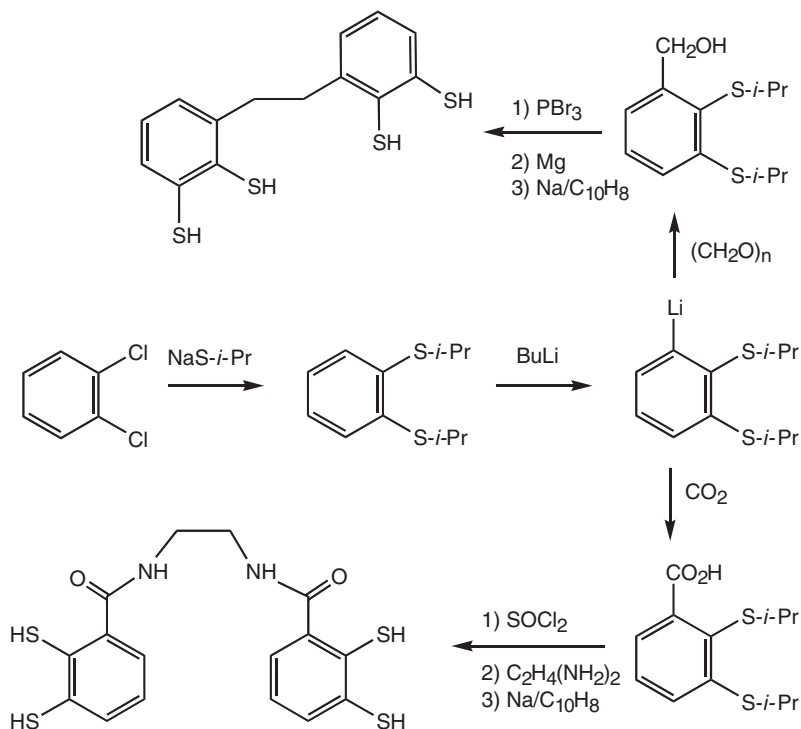
Figure 6. Hahn's methodology to bis(benzenedithiolates).

from $1,2\text{-}C_6H_4Cl_2$, to give the versatile nucleophile $3\text{-}LiC_6H_3\text{-}1,2\text{-}(S\text{-}i\text{-}Pr)_2$ (43). This revised metalation procedure was employed in the synthesis of the ethylene-linked dithiolene $1,2\text{-}C_2H_4[3\text{-}C_6H_3\text{-}1,2\text{-}(SH)_2]_2$, which forms bimetallic complexes with a staircase-like structure (Fig. 7).
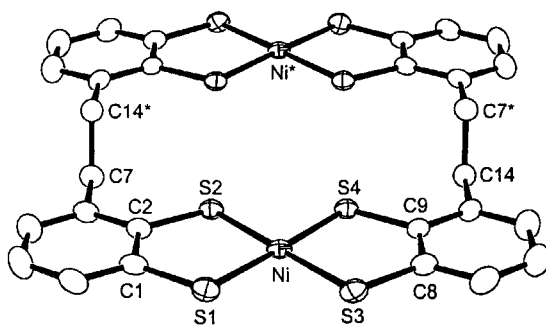
Figure 7. Structure of $\{Ni_2[(S_2C_6H_3)_2C_2H_4]_2\}^{4-}$ (40).

3.   Heterocyclic and Heteroatomic Dithiolates

Heterocyclic analogues of benzenedithiolates are also available. 3,4-Thio-phene-dithiolate is generated from the corresponding dibromothiophene (44). The isoelectronic but inorganic 1,2,5-thiadiazole-3,4-dithiolate, $[SN_2C_2S_2]^{2-}$ (tdas, see Fig. 2) can be prepared by sulfidation of $SN_2(CCl)_2$; the dianion forms bis(chelate) derivatives of Ni(II) and Fe(III) (45).

Complexes of 1,1′-ferrocenedithiolate ($[FcS_2]^{2-}$) exhibit properties like arenedithiolates, one difference being the potential for dative Fe $\rightarrow$ M bonding (46). Ferrocenedithiol and its salts are well known and have been widely employed as ligands. Some illustrative complexes are $Ni(S_2Fc)(PMe_2Ph)$ (47) and $TpRe(O)[S_2Fc]$ (48). The olefin polymerization precatalysts $FcS_2M(NMe_2)_2$ (M = Ti, Zr) were prepared by treatment of $M(NMe_2)_4$ with $Fc(SH)_2$, concomitant with elimination of $HNMe_2$ (49). 1,2,1′,2′-Ferrocenetetrathiol (50) could in principle be employed for the synthesis of multimetallic derivatives.

1,2-Dicarboranedithiolate can be generated by deprotonation of 1,2-dicarbor-ane followed by sulfidation (51–53). The resulting $Li_2S_2C_2B_{10}H_{10}$ reacts with metal dihalides to give the corresponding dithiolates.
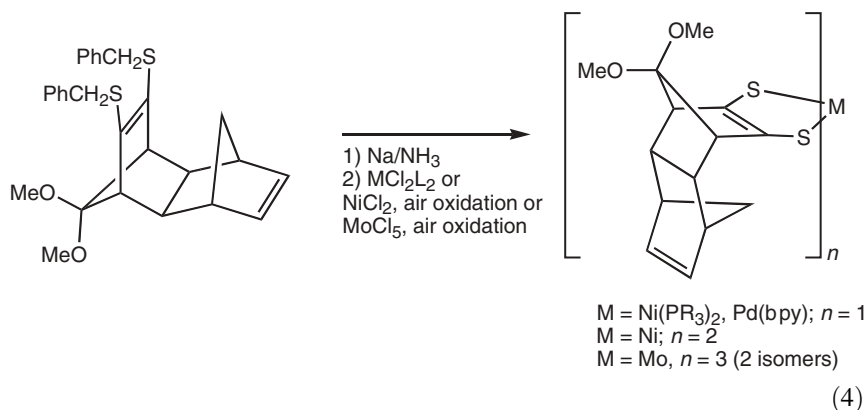
B.   From 1,2-Alkenedithiolates

1.   Via Reductive Dealkylation

In contrast to arenedithiols, 1,2-alkenedithiols are usually unstable. The corresponding alkenedithiolate dianions are, however, valuable precursors to dithiolene complexes, although they vary widely in their ease of manipulation. Salts of the required cis-$[C_2R_2S_2]^{2-}$ can be generated by the reductive cleavage of cis-1,2-bis(benzylthio)alkenes using Na/NH_3 (few alkali metal salts of dithiolenes have in fact been characterized in any detail). The reductive deal-kylation was discussed above as a route to benzene- and thiophenedithiolates (15, 43, 44).

Generally speaking, alkenedithiolates derived by this dealkylation route are strongly reducing and should be handled with complete exclusion of oxidants and electrophiles (e.g., chlorinated solvents, water). After their isolation as solids, the disodium dithiolates are generally treated with the metal halide to give the corresponding dithiolene complexes. In some cases, intermediate anionic dithiolene complexes are allowed to undergo oxidation by air or solvent prior to isolation of the final complex. Illustrative is the traditional route to the $M(S_2C_2H_2)_n$ complexes (M = Ni, n = 2; M = Mo, n = 3) (54, 55), the synthesis of which begins with the Na/NH_3 cleavage of cis-1,2-bis(benzylthio)ethene,

which can be made on a large scale from *cis*-dichloroethene and benzylthiolate salts (56). Solutions of *cis*-$C_2R_2S_2Na_2$ are treated with divalent metal salts (e.g., Ni, Co, Fe, Cu) to give intermediate anionic species that are subsequently oxidized to give neutral or monoanionic complexes. Third-row metal centers resist reduction, thus treatment of $(C_5Me_5)TaCl_4$ with *cis*-$C_2H_2S_2Na_2$ gives the expected $(C_5Me_5)Ta(S_2C_2H_2)_2$ (57). The compound *cis*-1,2-$C_2H_2[SC(O)Me]_2$, prepared by treatment of *cis*-1,2-$C_2H_2(SNa)_2$ with acetyl chloride (54, 58), is a promising if untested precursor to the dithiolene dianion (55). The reductive cleavage of the corresponding *trans*-1,2-bis(benzylthio)ethene gives *trans*-C_2H_2-$(SNa)_2$, which does not normally form molecular complexes (55) (a complex derived from a *trans*-alkenedithiolate is described in Section III.F.3). The cleavage of benzylthioethers has more recently been used to generate nonplanar dithiolene ligands shown in Eq. 4 (59).

1) Na/NH$_3$
2) MCl$_2$L$_2$ or
NiCl$_2$, air oxidation or
MoCl$_5$, air oxidation

M = Ni(PR$_3$)$_2$, Pd(bpy); n = 1
M = Ni; n = 2
M = Mo, n = 3 (2 isomers)

(4)

Because of the nonplanarity of these dithiolenes, the Mo(dithiolene)$_3$ derivative exists as two isomers, one with C_3 symmetry and the other with C_s symmetry.

2. *By Base Hydrolysis of Dithiocarbonates (Dithiole-2-ones) and Related Derivatives*

A powerful route to dithiolene complexes employs alkenedithiolate dianions generated by the hydrolysis of cyclic unsaturated dithiocarbonates, which are formally called 1,3-dithiole-2-ones. Representative of the many examples (60), the base hydrolysis route has been used to prepare the ferrocene-substituted dithiolene $Ni[S_2C_2H(C_5H_4)FeCp]_2$ (61), the sulfur-rich dithiolene $[Ni(S_2C_2S_2\text{-}C_2H_4)_2]^-$ (62), the cyano(dithiolenes) *trans*-$\{Ni[S_2C_2H(CN)]_2\}^n$ (n = 1, 2) (63), 2,3-thiophenedithiolates $[Au(S_2C_4H_2S)_2]^-$ (64), and the tris(styryldithiolate)
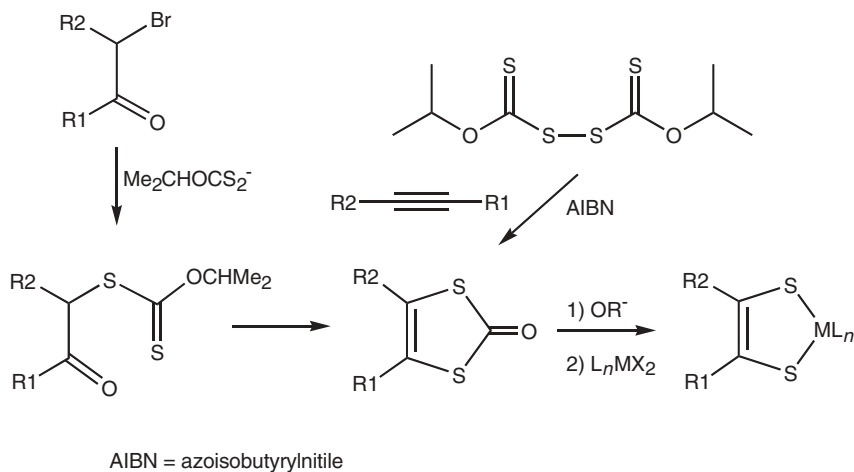
Figure 8.   Synthetic routes to alkene dithiocarbonates (dithioles) and their conversion to dithiolene complexes.

$Mo[S_2C_2H(Ph)]_3$ (65). As is typical throughout dithiolene chemistry, initially produced anionic dithiolene complexes are often allowed to undergo air-oxidation to give more conveniently isolated derivatives, for example, of the type $[Ni(S_2C_2R_2)_2]^-$ and $Mo(S_2C_2R_2)_3$.

The required 1,3-dithiol-2-ones can be prepared in several ways. Commonly used precursors are α-haloketones, which are often commercially available or can be prepared by halogenation of the ketones (66, 67). The overall procedure involves a series of efficient steps with well-defined intermediates (Fig. 8). A key step is the acid-catalyzed cyclization of a α-ketoxanthate ester [RC(O)CH₂-SC(S)OR] in neat H_2SO_4 to give the dithiocarbonate (68). The corresponding reaction using α-keto dithiocarbamate ester [RC(O)CH₂SC(S)NR₂] generates the iminium analogues of the cyclic dithiocarbonates (69), although the xanthate approach still appears preferable.

1,3-Dithiole-2-ones have also been efficiently prepared from alkynes via the addition of the equivalent of "CS₂O", which in turn is derived from diisopropyl xanthogen disulfide (70) (Fig. 8). The reaction, which is effected using the free radical initiator AIBN, has been used to prepare 2-thienyl substituted dithiolenes, which can undergo subsequent electropolymerization (71). Xanthate derivatives of hydroxymethylalkynes (e.g., HOCH₂C₂R) also convert to 1,3-dithioles (72). The use of 1,3-dithiole-2-ones is compatible with functionalized backbones, for example, the attachment of heterocyclic side groups to the dithiolene backbone (70, 72).

The 1,3-dithiole-2-ones can be prepared via displacement of ethylene from ethylenetrithiocarbonate with electrophilic alkynes (73). The modified trithiocarbonate is then converted to the corresponding dithiocarbonate, base hydrolysis of which provides $[(MeO_2C)_2C_2S_2]^{2-}$. This route was employed in the synthesis of $\{Ni[S_2C_2(CO_2Me)_2]_2\}^-$ (73), although such complexes are more routinely generated by the addition of $C_2(CO_2Me)_2$ to metal sulfido complexes (see Section III.A). Displacement of ethylene from ethylenetrithiocarbonate using the electrophile di(2-thienoyl)acetylene (74) gives 2,2′-dithienyldithiolenes (Eq. 5), which are susceptible to electropolymerization (75, 76).


$$[Z = CO_2Me, C(O)\text{-}2\text{-}C_4H_3S]$$

(5)
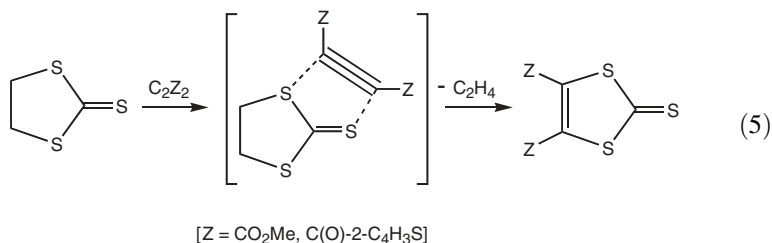
The dithiole-2-thione $(NC)_2C_2S_2CS$, which is derived from mnt^{2-} (see II.C.5), has been converted to a variety of dithiolene precursors such as the amide $[H_2NC(O)]_2C_2S_2CS$, the diacid $(HO_2C)_2C_2S_2CS$, and the unsubstituted derivative $H_2C_2S_2CS$ (77). Butadiene-1,2,3,4-tetrathiolate $[S_4C_4H_2]^{4-}$ has been prepared from the bis(dithiocarbonate). This tetraanion is a precursor to the coordination polymer $[Ni(S_4C_4H_2)]_n$ (78).

The conversion of the dithiocarbonates into alkenedithiolates involves base hydrolysis, which is usually effected with sodium alkoxides in alcohol. With the dianion in hand, the synthesis of complexes follows the usual course, as described above. Obviously, oxophilic metal centers, for example, Ti(IV) and Nb(V) (62), are incompatible with the usual alcohol solutions of *in situ* generated alkenedithiolates. In such cases, the anhydrous salts $Na_2S_2C_2R_2$ are employed in nonhydroxylic solvents, although after complex formation protic solvents are typically employed for cation exchange.

The dithiocarbonate methodology has been used to prepare a number of molybdenum–dithiolene complexes. In these syntheses, particular attention must be paid to the molybdenum precursor in order to avoid formation of the highly stable (and biologically irrelevant) tris(dithiolene) species. For example, treatment of $Ph(H)C_2S_2Na_2$ with $MoO_2(pentane\text{-}2,4\text{-}dionate)_2$ gave $M[S_2C_2\text{-}H(Ph)]_3^{n-}$ (M = V, Mo, W) with displacement of the oxo group (79). The use of $[MoO_2(CN)_4]^{4-}$ inhibits the formation of the tris complex (80), allowing one to

obtain the mixed-ligand complex $\{MoO[S_2C_2H(Ar)]_2\}^{2-}$, which exists as both cis and trans isomers (Eq. 6).


(X = NMe_2^+, O)　　　　　　　　　　　　　　　　(and trans isomer)

(6)
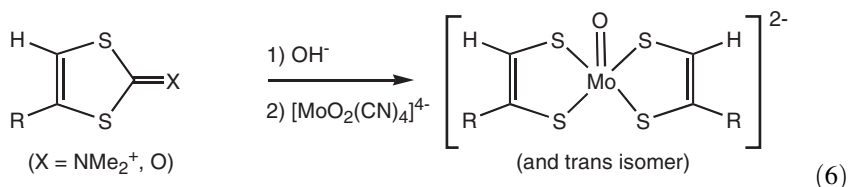
R = Ph; 2-, 3-, 4-C_5H_4N,
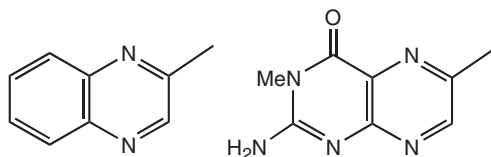
The use of cyanide ligands to suppress persubstitution by dithiolenes has also been applied to the synthesis of $[Ni(CN)_2(dithiolene)]^{2-}$ (81).

Whereas complexes of ethylenedithiolate $[H_2C_2S_2]^{2-}$ are typically prepared by the reductive S-dealkylation of cis-$H_2C_2(SCH_2Ph)_2$ (Section II.B), a viable alternative route involves base hydrolysis of 1,3-dithiol-2-one, $H_2C_2S_2(CO)$. The parent $H_2C_2S_2CO$ can in turn be prepared on a multigram scale from chloroacetaldehyde (82). This 1,3-dithiol-2-one can be functionalized via deprotonation followed by C-alkylation (72), thus opening the way to a variety of functional dithiolenes (Eq. 7).

(7)

1) $LiNR_2$
2) E^+
3) OR^-
4) $L_n MX_2$
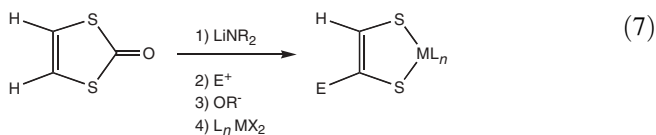
A versatile route to RS-substituted dithiolenes entails S-alkylation of the trithiocarbonate $dmit^{2-}$ (see Section II.C.1), which provides an efficient means to introduction of diverse functionality to the dithiolene backbone. Subsequent to S-alkylation, the resulting $S=CS_2C_2(SR)_2$ is converted to the dithiocarbonate $O=CS_2C_2(SR)_2$ with $Hg(OAc)_2$ in acetic acid (63, 83, 84). Such dithiocarbonates are more easily hydrolyzed than the trithiocarbonates (72, 85). This approach has been used for the synthesis of $Ni[S_2C_2(S(CH_2)_nMe)_2]_2$ ($n = 2$–11) (86) and related complexes with pendant alkene substituents (Eq. 8) (87).

$$(8)$$
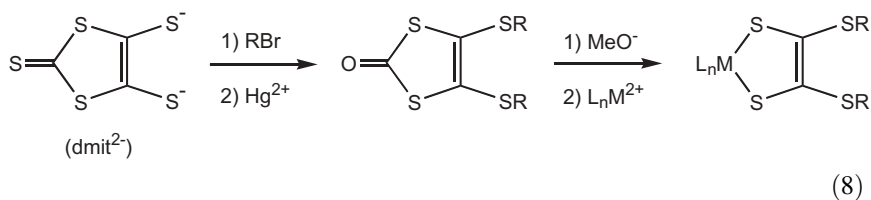
The direct reaction of $[Zn(dmit)_2]^{2-}$ with 1,2,-dibromoethylether affords the ethoxy-substituted trithiocarbonate, which eliminates ethanol to give a sulfur-rich dithiolene with extended unsaturation (Eq. 9) (88).

$$(9)$$
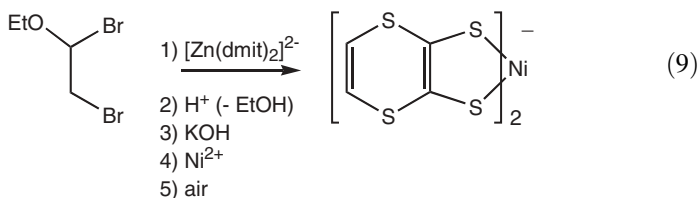
Recently, it was found that treatment of $[Zn(dmit)_2]^{2-}$ with certain alkylating agents gives unsymmetrically functionalized derivatives such as $S=CS_2C_2H$-(SR) $(R = 3-CH_2C_5H_4N, C_2H_4CN)$. Although mechanism of the C—S scission remains obscure, these trithiocarbonates are promising precursors to unsymmetrical dithiolenes (89).

C.   From Selected 1,2-Alkenedithiolate Dianions

1.   4,5-Dimercapto-1,3-dithiole-2-thione (dmit^{2-})

The heterocycle dmit^{2-}, occasionally referred to as $[\alpha\text{-}C_3S_5]^{2-}$, is one of the most important dithiolene ligands. The literature on dmit^{2-} is vast, but an overview of the ligand chemistry including many useful experimental procedures is available (1) as are reviews on specific aspects of the coordination chemistry (2, 3, 90–92). Most studies on dmit^{2-} are directed toward applications in materials chemistry, for example, the photonic or electronic properties (90, 93).

The synthesis of dmit^{2-} involves treatment of a dimethylformamide (DMF) solution of CS_2 with Na to give a mixture of dmit^{2-} and CS_3^{2-}. Recent work has shown that in the presence of CS_2, dmit^{2-} actually exists as its deep red thioxanthate, $[dmit \cdot CS_2]^{2-}$ (94). The breakthrough discovery that enabled the proliferation of this ligand was the finding by Hoyer and co-workers (95) that dmit^{2-} can be conveniently isolated in multigram scale as quaternary ammonium salts of $[Zn(dmit)_2]^{2-}$ (Fig. 9).
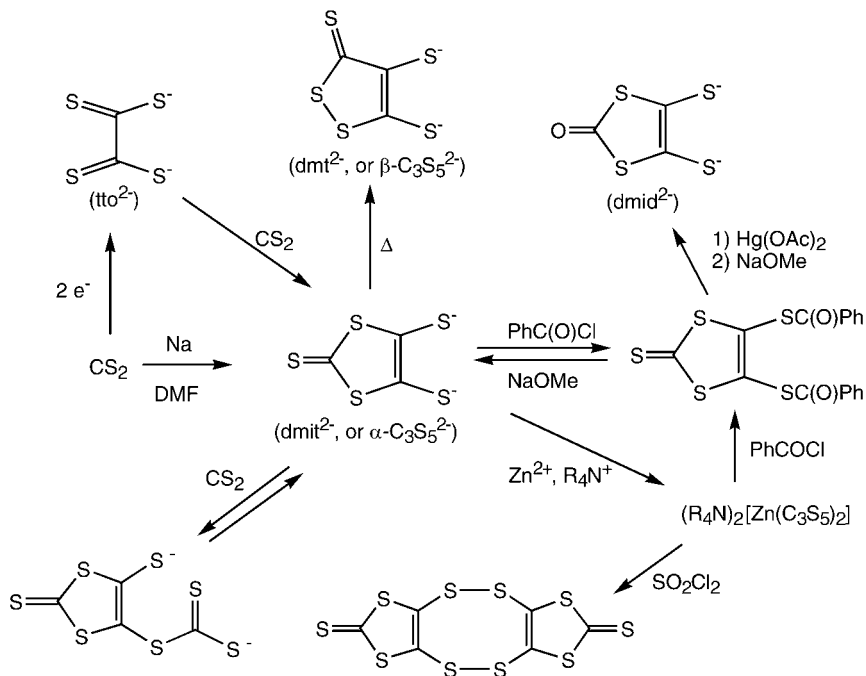
Figure 9.   Synthetic interrelationships involving $dmit^{2-}$ and other CS_2-derived species.

In principle, oxidized derivatives of $dmit^{2-}$ $(C_3S_5)_n$ and $[(C_3S_5)_2]^{2-}$ could be employed for the synthesis of dmit complexes (83).

Salts of $[Zn(dmit)_2]^{2-}$ are air stable in contrast to alkali metal salts of $dmit^{2-}$ itself (94). Diverse organic cations, for example, $[CpFe(C_5H_4CH_2NMe_3)]^+$, have been used in the isolation of $[Zn(dmit)_2]^{2-}$ (96). The basic Hoyer–Steimecke synthesis of $[Zn(dmit)_2]^{2-}$ has been subjected to numerous optimizations, mainly aimed at large-scale syntheses (>50 g) (1, 97–99), although the original procedure (95) is excellent. The method has been revised so that it consumes CS_2 more efficiently, facilitating its preparation from $^{13}CS_2$ (94). In one interesting modification, CS_2 and Na are first combined in the reaction flask and the electron-transfer process is controlled by the addition of DMF (98, 99). Although the reductive coupling of CS_2 has long been assumed to cogenerate equimolar amounts of $dmit^{2-}$ and $[CS_3]^{2-}$, recent reports show that under appropriate conditions, formation of $[CS_3]^{2-}$ can be suppressed (97).

Complexes of $dmit^{2-}$ are commonly generated either via ligand transfer from $[Zn(dmit)_2]^{2-}$ (see Section III.G) or by salt metathesis using Na_2dmit. Alkali metal salts of $dmit^{2-}$ are prepared by hydrolysis of the thioester $dmit[C(O)Ph]_2$. This dithioester is prepared by treatment of $[Zn(dmit)_2]^{2-}$ with $PhC(O)Cl$ and