CHAPTER 1

Synthesis of Transition Metal Dithiolenes

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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$_2$C$_2$R$_2$ 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 \( \text{R}_2\text{C}_2\text{S}_2 \), 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

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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 $\pi$ 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)$^\prime$$_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).

$$\text{SH} \quad \text{SH} \quad \text{SH}$$

1) BuLi

$$\text{SH} \quad \text{SH}$$

2) S$_8$

$$\text{SH} \quad \text{SH}$$

3) H$^+$ (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 benzenedithiols (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
treated with a metal methyl compound concomitant with the elimination of methane (Eq. 2) (20).

\[
\text{WMe}_6 + 3 \text{C}_6\text{H}_4(\text{SH})_2 \rightarrow \text{W} (\text{S}_2\text{C}_6\text{H}_4)_3 + 6 \text{CH}_4
\]  

(2)

Homoleptic dithiolene complexes, for example, \([\text{Ni}(\text{S}_2\text{C}_6\text{R}_4)_2]^\circ\) and \([\text{M}(\text{S}_2\text{C}_6\text{R}_4)_3]^\circ\) (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 \([\text{Ni}(\text{S}_2\text{C}_6\text{H}_2(t-\text{Bu})_2)_2]^2^-\), which can be oxidized to the monoanion and neutral derivatives using air and iodine, respectively (21). Reactions of \(\text{MoCl}_5\) and \(\text{WCl}_6\) with the benzene-dithiolate salts give \(\text{M}(\text{S}_2\text{C}_6\text{R}_4)_3\) (15, 22) or reduced derivatives. Similarly, treatment of \(\text{Ti(NMe}_2)_4\) with \(\text{C}_6\text{H}_4(\text{SH})_2\) gives \((\text{NMe}_2\text{H}_2)_2[\text{Ti}(\text{S}_2\text{C}_6\text{H}_4)_3]\), 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 \([\text{MO}(\text{S}_2\text{C}_6\text{R}_4)_2]^\circ\) (24). In the case of Mo derivatives, the metathetical reactions can be conducted.
in the presence of donor ligands, which inhibit the formation of the tris(dithiolene) complexes. For example, treatment of Na₂(S₂C₆R₄) with MoCl₄(MeCN)₂ in the presence of donor ligands L affords Mo(S₂C₆R₄)₂L₂ (L = PPh₂Me 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(S₂C₆H₄)₂]ⁿ⁻ (M = Mo, W) have received much attention. A direct approach to [WO(S₂C₆H₄)₂]⁻ proceeds via the reaction of WOCl₃(thf)₂ (where thf = tetrahydrofuran) benzenedithiol, and Et₃N (24). Alternatively, thiol exchange routes can be advantageous as a means to minimize redox processes and formation of [M(S₂C₆H₄)₃]ⁿ⁻. For example, [WO(SPh)₄]⁻ and benzenedithiol give [W(V)O(S₂C₆H₄)₂]⁻, which can be subsequently reduced with NaBH₄ to give [W(V)O(S₂C₆H₄)₂]²⁻ (Fig. 3) (25). Related thiol exchange reactions involve conversion of [MoO(SC₆H₄R)₄]ⁿ⁻ (R = Cl, n = 2; R = H, n = 1) into [MoO(S₂C₆H₃R)₂]ⁿ⁻ (R = H, Me, Ph₃Si) (18, 26).

The oxo-bis(dithiolene) complexes are amenable to further reactions. Treatment of [MO(S₂C₆H₄)₂]²⁻ Me₃NO (13) affords [M(V)O₂(S₂C₆H₄)₂]²⁻ (M = Mo, W) (25, 27). Silylation of the oxo-bis(dithiolene) complexes gives [M(V)(OSiR₃)-(S₂C₆H₄)₂]⁻ (M = Mo, W), which are versatile precursors to diverse coordination sets on the bis(dithiolene) framework (12, 24). For example, such [M(V)(OSiR₃)(S₂C₆H₄)₂]⁻ derivatives can be oxidized using Me₃NO to give [M(V)(O)(OSiR₃)(S₂C₆H₄)₂]⁻ (M = Mo, W) and, in the W case, sulfided using dibenzyltrisulfide to give [W(V)(S)(OSiR₃)(S₂C₆H₄)₂]⁻.

The mildly electrophilic complex MeReO₃ condenses with 2 equiv of benzenedithiol to give MeRe(O)(S₂C₆H₄)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 [Fe₂S₂(SR)₄]²⁻ with toluene-3,4-dithiol. For strongly chelating dipeptides, [Fe(SR)₂(S₂C₆H₃Me)]⁻ derivatives (R = protein) form with H₂S elimination, whereas less strongly chelating dipeptides are displaced by this dithiol to give [Fe₂S₂(S₂C₆H₃Me)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
ligands or removal of dithiolenes from bis- and tris(dithiolene) precursors. One dithiolene can be removed from $[\text{MoO}(S_2C_6H_4)_2]^{-}$ using PhSeCl to give monodithiolene $[\text{MoOCl}_2(S_2C_6H_4)]^{-}$ together with $(\text{PhSeS})_2C_6H_4$ (30). The chloro ligands in $[\text{MoOCl}_2(S_2C_6H_4)]^{-}$ undergo ready substitution to give diverse mixed-ligand derivatives as shown in Fig. 4. Thiolate-siloxide exchange was employed to prepare $[\text{MoO}_2(\text{OSiPh}_3)(S_2C_6H_4)]^{-}$ via the reaction of $\text{MoO}_2(\text{OSiPh}_3)_2$ with $\text{Li}_2S_2C_6H_4$.

Benzenedithiolates can also be prepared by $\text{H}_2$ elimination when using low-valent precursor complexes (Eq. 3) (31).

$$\text{Cp}_2\text{V} + C_6H_4(\text{SH})_2 \rightarrow \text{Cp}_2\text{VS}_2C_6H_4 + \text{H}_2$$  \hspace{1cm} (3)

This $\text{H}_2$-elimination route from 1,2-benzenedithiol was also employed in the synthesis of $\text{Fe}_2(S_2C_6H_4)(\text{CO})_6$ (32) and the coordinatively unsaturated $[\text{Mn}(\text{CO})_5(S_2C_6H_4)]^{-}$ (33). A series of related coordinatively unsaturated species $[\text{Cr}(\text{CO})_3(S_2C_6R_4)]^{2-}$ (R = H, Cl, Me) were prepared by displacement of the
solvento ligands from Cr(CO)₃(MeCN)₃. At higher metal stoichiometry, one obtains the binuclear \([\text{Cr}_2(\text{CO})_6(\mu-\text{CO})(\mu-\eta^2:\eta^2-\text{S}_2\text{C}_6\text{R}_4)]^2^-\) (34). Other coordinatively unsaturated dithiolenes have been prepared by salt-forming methods, for example, \([\text{triphos}\text{Fe}(\text{S}_2\text{C}_6\text{H}_4)]\) (35), \([\text{Fe}(\text{S}_2\text{C}_6\text{H}_4)]\) (36), and \((\text{C}_5\text{Me}_5)\text{Ir}(\text{S}_2\text{C}_6\text{H}_4)\) (37). The species Fe₂(\text{S}_2\text{C}_6\text{H}_4)(\text{CO})₆ undergoes ready degradation upon treatment with \(\text{Et}_4\text{NCN}\), 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 \(\text{BuLi}\), which affords \(3-\text{LiC}_6\text{H}_3-(\text{SLi})_2\). 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 \(\text{Cp}_2\text{Ti}^{IV}\) 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 \(1,2-\text{C}_6\text{H}_4(\text{S-}\text{i-Pr})_2\), generated on a large scale.
from 1,2-C₆H₄Cl₂, to give the versatile nucleophile 3-LiC₆H₃-1,2-(S-i-Pr)₂ (43). This revised metatation procedure was employed in the synthesis of the ethylene-linked dithiolene 1,2-C₂H₄[S₂C₆H₃-1,2-(SH)₂]₂, which forms bimetallic complexes with a staircase-like structure (Fig. 7).

Figure 6. Hahn’s methodology to bis(benzenedithiulates).

Figure 7. Structure of \{Ni₂[(S₂C₆H₃)₂C₂H₄]₂\}⁻ (40).
3. Heterocyclic and Heteroatomic Dithiolates

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

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

1,2-Dicarboranedithiolate can be generated by deprotonation of 1,2-dicarbaborane followed by sulfdation (51–53). The resulting Li\(_2\)S\(_2\)C\(_2\)B\(_{10}\)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 dithiolenic complexes, although they vary widely in their ease of manipulation. Salts of the required cis-[\(\text{C}_2\text{R}_2\text{S}_2\)]\(^{2-}\) 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 dealkylation 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 dithiolenic 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(\(\text{S}_2\text{C}_2\text{H}_2\))\(_n\) 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-C₂R₂S₂Na₂ 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 (C₅Me₅)TaCl₄ with cis-C₂H₂S₂Na₂ gives the expected (C₅Me₅)Ta(S₂C₂H₂)₂ (57). The compound cis-1,2-C₂H₂[SC(O)Me]₂, prepared by treatment of cis-1,2-C₂H₂(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-C₂H₂-(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).

Because of the nonplanarity of these dithiolenes, the Mo(dithiolene)₂ derivative exists as two isomers, one with C₃ symmetry and the other with Cₛ 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[S₂C₂H(C₅H₄)FeCp]₂ (61), the sulfur-rich dithiolene [Ni(S₂C₂S₂-C₂H₄)₂]⁻ (62), the cyano(dithiolenes) trans-[Ni(S₂C₂H(CN)]₂⁻ (n = 1, 2) (63), 2,3-thiophenedithiolates [Au(S₂C₄H₂S)₂]⁻ (64), and the tris(styryldithiolate)
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 \(\alpha\)-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 \(\alpha\)-ketoxanthate ester \([RC(O)CH_2SC(S)OR]\) in neat H\(_2\)SO\(_4\) to give the dithiocarbonate (68). The corresponding reaction using \(\alpha\)-keto dithiocarbamate ester \([RC(O)CH_2SC(S)NR_2]\) 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 “CS\(_2\)O”, 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 dithio-lenes, which can undergo subsequent electropolymerization (71). Xanthate derivatives of hydroxymethylalkynes (e.g., HOCH\(_2\)C\(_2\)R) 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 ethylenetriothiocarbonate with electrophilic alkynes (73). The modified trithiocarbonate is then converted to the corresponding dithiocarbonate, base hydrolysis of which provides \([\text{MeO}_2\text{C}]_2\text{C}_2\text{S}_2\)^{2–}. This route was employed in the synthesis of \(\{\text{Ni[S}_2\text{C}_2(\text{CO}_2\text{Me})_2]_2\}^–\) (73), although such complexes are more routinely generated by the addition of \(\text{C}_2(\text{CO}_2\text{Me})_2\) to metal sulfido complexes (see Section III.A). Displacement of ethylene from ethylenetriothiocarbonate using the electrophile di(2-thienoyl)acetylene (74) gives \(2,2’\)-dithienyldithiolenes (Eq. 5), which are susceptible to electropolymerization (75, 76).

\[
\begin{align*}
\text{S} & \quad \text{S} & \quad \text{S} & \quad \text{S} \\
\text{C}2\text{S}2 & \quad \text{S} & \quad \text{Z} & \quad \text{C}2\text{H}4 & \quad \text{S} & \quad \text{S} \quad \text{Z} \\
\text{Z} & \quad \text{Z} & \quad \text{Z} & \quad \text{Z} & \quad \text{Z} & \quad \text{Z} \\
\end{align*}
\]

\[\text{[Z} = \text{CO}_2\text{Me}, \text{C(O)-2-C}_4\text{H}_3\text{S}]\]

The dithiole-2-thione \((\text{NC})_2\text{C}_2\text{S}_2\text{CS}\), which is derived from mnt\(^{2–}\) (see II.C.5), has been converted to a variety of dithiolene precursors such as the amide \([\text{H}_2\text{NC(O)}]_2\text{C}_2\text{S}_2\text{CS}\), the diacid \((\text{HO}_2\text{C})_2\text{C}_2\text{S}_2\text{CS}\), and the unsubstituted derivative \(\text{H}_2\text{C}_2\text{S}_2\text{CS}\) (77). Butadiene-1,2,3,4-tetrathiolate \([\text{S}_4\text{C}_4\text{H}_2]^{4–}\) has been prepared from the bis(dithiocarbonate). This tetraanion is a precursor to the coordination polymer \([\text{Ni}[\text{S}_4\text{C}_4\text{H}_2]]_n\) (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 \textit{in situ} generated alkenedithiolates. In such cases, the anhydrous salts \(\text{Na}_2\text{S}_2\text{C}_2\text{R}_2\) 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 \(\text{Ph}(\text{H})\text{C}_2\text{S}_2\text{Na}_2\) with \(\text{MoO}_2(\text{pentane}-2,4\text{-dionate})_2\) gave \(\text{M}[\text{S}_2\text{C}_2\text{-H(Ph)}]^n–\) \((\text{M} = \text{V}, \text{Mo}, \text{W})\) with displacement of the oxo group (79). The use of \([\text{MoO}_2(\text{CN})_4]^{4–}\) inhibits the formation of the tris complex (80), allowing one to
obtain the mixed-ligand complex {MoO[S₂C₂H(Ar)]₂}²⁻, which exists as both cis and trans isomers (Eq. 6).

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 [H₂C₂S₂]²⁻ are typically prepared by the reductive S-dealkylation of cis-H₂C₂(SCH₂Ph)₂ (Section II.B), a viable alternative route involves base hydrolysis of 1,3-dithiol-2-one, H₂C₂S₂(CO). The parent H₂C₂S₂CO 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).

A versatile route to RS-substituted dithiolenes entails S-alkylation of the trithiocarbonate dmit²⁻ (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≡CS₂C₂(SR)₂ is converted to the dithiocarbonate O≡CS₂C₂(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[S₂C₂(S(CH₂)ₙMe)₂]₂ (n = 2–11) (86) and related complexes with pendant alkene substituents (Eq. 8) (87).
The direct reaction of \([\text{Zn(dmit)}_2]^2-\) with 1,2-dibromoethylether affords the ethoxy-substituted trithiocarbonate, which eliminates ethanol to give a sulfur-rich dithiolene with extended unsaturation (Eq. 9) (88).

Recently, it was found that treatment of \([\text{Zn(dmit)}_2]^2-\) with certain alkylating agents gives unsymmetrically functionalized derivatives such as \(\text{S}-\text{C}_0/\text{C}_0/\text{C}_0/\text{C}_0/\text{C}_0/\text{CS}_2/\text{C}_2/\text{H}-\text{(SR)}\) (\(\text{R} = 3\text{-CH}_2/\text{C}_5/\text{H}_4/\text{N}, \text{C}_2/\text{H}_4/\text{CN}\)). Although mechanism of the \(\text{C}-\text{S}\) scission remains obscure, these trithiocarbonates are promising precursors to unsymmetrical dithiolenes (89).

C. From Selected 1,2-Alkenedithiolate Dianions

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

The heterocycle \(\text{dmit}^2-\), occasionally referred to as \([\alpha\text{-C}_3\text{S}_5]^2-\), is one of the most important dithiolene ligands. The literature on \(\text{dmit}^2-\) 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 \(\text{dmit}^2-\) are directed toward applications in materials chemistry, for example, the photonic or electronic properties (90, 93).

The synthesis of \(\text{dmit}^2-\) involves treatment of a dimethylformamide (DMF) solution of \(\text{CS}_2\) with Na to give a mixture of \(\text{dmit}^2-\) and \(\text{CS}_3^2-\). Recent work has shown that in the presence of \(\text{CS}_2\), \(\text{dmit}^2-\) actually exists as its deep red thioxanthate, \([\text{dmit}\cdot\text{CS}_2]^2-\) (94). The breakthrough discovery that enabled the proliferation of this ligand was the finding by Hoyer and co-workers (95) that \(\text{dmit}^2-\) can be conveniently isolated in multigram scale as quaternary ammonium salts of \([\text{Zn(dmit)}_2]^2-\) (Fig. 9).
In principle, oxidized derivatives of \( \text{dmit}^{2-} \) (\( \text{C}_3\text{S}_5 \))\(_n\) and \( [(\text{C}_3\text{S}_5)]^{2-}_2 \) could be employed for the synthesis of dmit complexes (83).

Salts of \( [\text{Zn(dmit)}]^{2-}_2 \) are air stable in contrast to alkali metal salts of \( \text{dmit}^{2-} \) itself (94). Diverse organic cations, for example, \( [\text{CpFe(C}_5\text{H}_4\text{CH}_2\text{NMe}_3)]^{+} \), have been used in the isolation of \( [\text{Zn(dmit)}]^{2-}_2 \) (96). The basic Hoyer–Steimecke synthesis of \( [\text{Zn(dmit)}]^{2-}_2 \) 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 \( \text{CS}_2 \) more efficiently, facilitating its preparation from \( ^{13}\text{CS}_2 \) (94). In one interesting modification, \( \text{CS}_2 \) 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 \( \text{CS}_2 \) has long been assumed to cogenerate equimolar amounts of \( \text{dmit}^{2-} \) and \( [\text{CS}_3]^{2-} \), recent reports show that under appropriate conditions, formation of \( [\text{CS}_3]^{2-} \) can be suppressed (97).

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

Figure 9. Synthetic interrelationships involving dmit\(^{2-}\) and other CS\(_2\)-derived species.
isolated as yellow crystals with favorable stability and solubility (1). Ionic complexes of $\text{dmit}^{2-}$ are usually synthesized in a three-step, one-pot procedure: (a) $\text{dmit}[\text{C}(\text{O})\text{Ph})]_2$ is hydrolyzed with NaOMe in MeOH; (b) an alcoholic or aqueous solution of the metal cation, for example, $\text{NiCl}_2(\text{H}_2\text{O})_6$, is then added to give the alkali metal salt of the metal dithiolene complex, for example, $\text{Na}_2[\text{Ni(dmit)}_2]$; and (c) an aqueous or methanolic solution of a quaternary salt, for example, $\text{R}_4\text{NCl}$ or $\text{Ph}_4\text{PCl}$ $\equiv \text{quat}^+\text{Cl}^-$, is added to precipitate $\text{(quat)}_m[\text{M(dmit)}_n]$ salts which are amenable to recrystallization from MeCN solution. This route is employed to access derivatives of $[\text{Ni(dmit)}_2]^{2-}$, the subject of many hundreds of publications (2, 100), which are discussed by Cassoux in chapter 8 of this volume (100). Starting from $\text{dmit}[\text{C}(\text{O})\text{Ph})]_2$, one can also isolate the anhydrous and air-sensitive $\text{Cs}^+$ and $\text{NMe}_4^+$ salts of $\text{dmit}^{2-}$ (1, 101, 102).

Numerous complexes of $\text{dmit}^{2-}$ have been prepared using $\text{in situ}$ generated $\text{Na}_2\text{dmit}$ (103–115), for example, $[\text{Mn(dmit)}_2]^{4-}$ (113), $[\text{Re}_2(\text{dmit})_5]^{2-}$ (114), and $[\text{Rh}(\text{dmit})_2]^{-}$ (103). With more inert precursors such as $\text{Cp}_2\text{MoCl}_2$ (116), alkali metal salts of $\text{dmit}^{2-}$ are used, whereas for more reactive metal electrophiles the transfer (see Section II.D) of $\text{dmit}^{2-}$ from $[\text{Zn(dmit)}_2]^{2-}$ is convenient, for example, for the synthesis of $\text{Cp}_2\text{Ti(dmit)}$ from $\text{Cp}_2\text{TiCl}_2$ (117). Note that the M—Cp linkage is not immune to substitution as shown by the conversion of $\text{Cp}_2\text{TiCl}_2$ into $[\text{CpTi(dmit)}_2]^{-}$ using $\text{Na}_2\text{dmit}$ (118). A related strategy for the preparation of $\text{dmit}^{2-}$ complexes involves the reaction of preformed $[\text{Ni(dmit)}_2]^{2-}$ and $[\text{Ni(MeCN)}_6]^{2+}$ in a 3:1 ratio to give $[\text{Ni}_2(\text{dmit})_3]^{2-}$, whose structure is shown in Fig. 10 (94).

![Figure 10. Structure of $[\text{Ni}_2(\text{dmit})_3]^{2-}$ (94).]
Whereas mixed-ligand dmit complexes are generally prepared by reaction of dmit$^{2-}$ sources with substituted metal halides, the displacement of dmit$^{2-}$ from homoleptic complexes represents an alternative route. For example, treatment of [Ni(dmit)$_2$]$^{2-}$ with triphos gives [Ni(dmit)(triphos)] (119).

2. Inorganic Dithiolates Related to dmit$^{2-}$

The coordination chemistry of the oxa derivative of dmit$^{2-}$, [OCS$_2$C$_2$S$_2$]$^{2-}$ (dmid$^{2-}$), has been well developed although the electronic properties of the resulting complexes have elicited only modest attention. This ligand is generated by the base-degradation of the bis(dithiocarbonate) tetrathiapentalenedione (TPD) (120). Otherwise, TPD has played an important role in the development of tetrathiafulvalenes and dithiolenes (121, 122); the reader is referred to Sections II.C and III.E for related methodology. The corresponding imine-containing dithiolates [RNCS$_2$C$_2$S$_2$]$^{2-}$ would be interesting ligands.

Isomeric with dmit$^{2-}$ is dmt$^{2-}$, (dmt$^{2-} = 4,5$-dimercapto-1,2-dithiole-3-thione) wherein the three carbon atoms are contiguous (see Fig. 10) (2). The synthesis of dmt$^{2-}$ starts with the dmit$^{2-}$ preparation followed by heating at $\sim$120–140 °C to effect the Steimecke rearrangement (123, 124). The complex (NEt$_4$)$_2$-[Zn(dmt)$_2$] is isolated as an oil before conversion to the thioester dmt[C(O)-Ph)$_2$, which is usually purified prior to conversion to its metal complexes. One unusual feature of dmt$^{2-}$ is the reactivity that is latent in the ligand backbone, illustrated by its reaction with dimethylacetylene dicarboxylate (DMAD) (123).

Tetrathiooxalate, [C$_2$S$_4$]$^{2-}$ (see Fig. 10), is not a true enedithiolate and strictly speaking falls outside the scope of this chapter. Nonetheless, the exploration of this ligand is closely tied to dithiolene chemistry. Early researchers mistook dmit$^{2-}$ for [C$_2$S$_4$]$^{2-}$ (125), not realizing that C$_2$S$_4^{4-}$ reacts with CS$_2$ to give dmit$^{2-}$ (126). Hydrolysis of the bis(dithiocarbonate) C$_2$(S$_2$CO)$_2$ yields [OCS$_2$C$_2$S$_2$]$^{2-}$ (see above) (127), not [C$_2$S$_4$]$^{4-}$ as has been claimed (128, 129) (see Section II.C). The alkene C$_2$(SMet)$_4$ has been generated by treatment of basic solutions of C$_2$(S$_2$CO)$_2$ with methylating agents, but this reaction proceeds via the intermediacy of OCS$_2$C$_2$(SMet)$_2$. An easy gram-scale route to (Et$_4$N)$_2$-C$_2$S$_4$ has been developed (130), based on a simplification of Jeroschewski’s electrosynthesis (125).

Numerous bi- and polynuclear complexes with M$_2$(C$_2$S$_4$) cores (monometallic derivatives of [C$_2$S$_4$]$^{n-}$ are unknown) are assigned as ethylenetetrathiolate derivatives as judged by structural criteria, specifically the C=C distance. Such complexes are often prepared by reductive coupling of CS$_2$ using low-valent metal complexes such as those of Ni(I), Fe(I), and Ti(II) (131). Tetrathiooxalate complexes, generated by salt metathesis from (Et$_4$N)$_2$C$_2$S$_4$ (130, 132), undergo reduction to give ethylenetetrathiolato complexes (Eq. 10) (133).
Partial oxidation of $\text{C}_2\text{S}_2^{2-}$ proceeds with loss of sulfur and coupling to give the vinylidene dithiolate derivative of dmit$^{2-}$. This planar dianion $\text{C}_4\text{S}_6^{2-}$ is isolated as its blue-purple $\text{Et}_4\text{N}^+$ salt (130). Treatment of this salt with metal halides affords di- and polymeric complexes, for example, $[\text{C}_4\text{S}_6][\text{RuCl(arene)}]_2$ and the semiconducting $[\text{NiC}_4\text{S}_6]_n$ (134) (Eq. 11).

$$
\begin{align*}
\text{S-S} & \quad \text{I}_2 \quad \text{Ni}^2+ \\
\text{S-S} & \quad \text{Ni}^2+ \\
\end{align*}
$$

3. Tetrathiafulvalene (TTF)-Derived Dithiolenes

Because of the close structural and preparative connections between the TTFs and dithiolene chemistry, it is only natural that extended dithiolenes have been developed with a TTF-like core. These complexes are generally prepared via the corresponding TTF-based di- or tetrathiolates.

Tetrathiafulvalenetetrathiolate, with the formula $[\text{C}_6\text{S}_8]^{4-}$ or $[\text{S}_2\text{C}_2\text{S}_2\text{C}=-\text{CS}_2\text{C}_2\text{S}_2]^{4-}$, has long been known, but only recently have well-defined molecular complexes been described. Solutions of $[\text{C}_6\text{S}_8]^{4-}$ can be generated by hydrolysis of the corresponding bis(dithiole) $\text{OCS}_2\text{C}_2\text{S}_2\text{C}=-\text{CS}_2\text{C}_2\text{S}_2\text{CO}$ (see Section II.C) or by lithiation–sulfidation of TTF itself. The former method has been applied to the synthesis of polymeric complexes (129). The latter method was employed in the synthesis of $\text{C}_6\text{S}_8[\text{TiCp}_2]_2$ (135), which has been fully characterized.

In contrast to the binucleating character of tetrathiafulvalenetetrathiolate, a variety of chelating tetrathiafulvalenedithiolates are also known, and these species give rise to complexes with especially interesting electrical properties. The synthetic routes to this family of ligands typically begin with dmit$^{2-}$ as illustrated in Fig. 11.

The synthesis of this hybrid TTF–dithiolene illustrates the use of the cyanoethyl group to protect the sulfur atoms of the dithiolene (81, 136, 137). The trimethylene-capped tetrathiafulvalenetetrathiolate forms a molecular...
species of the type \{\text{Ni}[\text{S}_2\text{C}_2\text{S}_2\text{C}═\text{CS}_2\text{C}_2\text{S}_2(\text{CH}_2)_3]_2\}^{2−}\). Electro-oxidization (138) is commonly employed to secure single crystals of dithiolene-based organic metals. When applied to \{\text{Ni}[\text{S}_2\text{C}_2\text{S}_2\text{C}═\text{CS}_2\text{C}_2\text{S}_2(\text{CH}_2)_3]_2\}^{2−}, one obtains crystals of the charge-neutral species \([\text{Ni}(\text{dithiolene})_2]\), an unusual single component metalloorganic electrical conductor (139).

4. From the Thiacarbons \([C_nS_n]^2−\) and Related Derivatives

The coordinating properties of the thiacarbons \([C_nS_n]^2−\) have been of intermittent interest (140). Beck et al. investigated the coordination chemistry of tetrathiasquarate, \([C_4S_4]^2−\) (141, 142). This dianion forms an extensive series of bimetallic complexes \([C_4S_4][\text{ML}_n]_2^{2−}\), where \(ML_n = \text{Rh(PPh}_3)_2^{+}, \text{Pt(PPh}_3)_2, \text{PdCl}_2, \text{Pt(PEt}_3)_2^{+}\) (141), and \(\text{Au(PMePh}_2)^{+}\) (142). Metal carbonyls form similar complexes as well as derivatives where the squarate is unidentate (143). Complexes with terminal \([C_4S_4]^2−\) ligands, for example, \(\text{L}_2\text{MC}_4\text{S}_4\) are apparently unknown. Benzenehexathiolato complexes include multimetallic complexes such as \(\text{C}_6\text{S}_6[\text{Au(PPh}_3)]_6\) (144), \(\text{C}_6\text{S}_6[\text{Pt(PR}_3)_2]_3\) (145), and \(\text{C}_6\text{S}_6[\text{TiCp}_2]_3\) (146). Such species are prepared by salt-metathesis reactions.
5. 1,2-Maleonitrile 1,2-dithiolate (mnt²⁻)

An easily prepared, versatile, and time-honored dithiolene ligand is maleonitriledithiolate, \([(\text{NC})_{2}C_{2}S_{2}]^{2-}\), or mnt²⁻. The subject of numerous studies, mnt complexes are well described in earlier reviews (9, 147). The sodium salt of mnt²⁻ species arises via the reaction of alkali metal cyanide with CS₂ followed by the spontaneous coupling of the intermediate \([\text{S}_2\text{CCN}]^-\) concomitant with loss of sulfur (148). Quaternary ammonium salts of mnt²⁻ do not appear to have been synthesized.

Most complexes of mnt²⁻ are prepared by straightforward salt metathesis reactions, as expected for this pseudohalide-like dithiolene. Recent studies on oxo Mo/W derivatives use less obvious methods. Sarkar and co-workers (149) synthesized \([\text{MoO}_2(\text{mnt})_2]^{2-}\) via the reaction of aqueous \([\text{MoO}_4]^{2-}\) with Na₂mnt buffered with citrate and phosphate. The phosphate buffer plays a significant role in this synthesis. The corresponding reaction with \(\text{HSO}_3^-\) in place of the buffer afforded \([\text{MoO}(\text{mnt})_2]^{2-}\), isolated as its quaternary ammonium salt (Eq. 12).

\[
\begin{align*}
\text{[MoO}_4]^{2-} & \xrightarrow{\text{mnt}^{2-}} \text{[MoO}_2(\text{mnt})_2]^{2-} \xrightarrow{\text{PPh}_3} \text{[MoO}(\text{mnt})_2]^{2-} \\
\end{align*}
\]

Direct access to \([\text{Mo}^{IV}(\text{mnt})_2]^{2-}\) involves the use of \([\text{MoOCl}_3]^{2-}\) (150), analogous to the routes to \([\text{TeO}(\text{mnt})_2]^-\), \([\text{OsN}(\text{mnt})_2]^-\), and related mixed-dithiolene complexes (151–153). Treatment of \([\text{MoOCl}(\text{MeCN})_4]^+\) with a mixture of \([\text{H}_2\text{C}_2\text{S}_2]^{2-}\) and mnt²⁻ gives \([\text{MoO}(\text{mnt})(\text{S}_2\text{C}_2\text{H}_2)]^{2-}\) (12), which, like \([\text{MoO}(\text{S}_2\text{C}_6\text{H}_4)_2]^{2-}\) (154), can be oxidized with Me₃NO.

The complex \([\text{W}^{IV}(\text{mnt})_2]^{2-}\) has attracted attention because, like the tungsten-containing enzyme acetylene hydratase, it catalyzes the hydration of alkynes. This complex is synthesized using aqueous \([\text{WO}_4]^{2-}\), mnt²⁻, and dithionite (155). The corresponding reaction of \([\text{WO}_4]^{2-}\), mnt²⁻, and \(\text{HSO}_3^-\) gave \([\text{W}^{VI}O_2(\text{mnt})_2]^{2-}\). The use of \(\text{HSO}_3^-\) is curious as it is normally considered a reductant, but the less oxidizing \(\text{W}^{(VI)}\) center apparently resists reduction. At low pH, both the \([\text{WO}_n(\text{mnt})_2]^{2-}\) derivatives convert to the \([\text{W}(\text{mnt})_3]^{2-}\), especially in the presence of excess mnt²⁻.

A rare example of a unidentate dithiolene is \(\text{Ru}^{1-}\text{mnt}(\text{CO})_2(\text{terpy})\) (terpy is \(2,2',6',2''\text{-terpyridine}\), prepared from the corresponding \([\text{RuCl}(\text{CO})_2(\text{terpy})]^{+}\) (156). The stability of this complex reflects the relatively low nucleophilicity of mnt²⁻.

D. Via Thiophosphate Esters (from \(\alpha\)-Hydroxyketones and \(\alpha\)-Diketones)

A historically significant route to dithiolenes starts from \(\alpha\)-hydroxyketones (also called acyloins) (157). This methodology is well suited for the large-scale
synthesis of homoleptic dithiolene complexes, especially those with aryl and simple alkyl substituents. Perhaps the most important complexes of this type are Ni(S₂C₂R₂)₂, where R = Me and Ph, which have gained recent attention as dithiolene-transfer agents for the synthesis of bis(dithiolene) derivatives of Mo and W (see Section II.G.2) (158).

In the thiophosphate strategy, an 1,2-enedithiol is recognized as a tautomer of an α-mercaptothione, which in turn is related via S-for-O exchanges to the corresponding α-hydroxyketone (Eq. 13).

Thus, treatment of α-hydroxyketones with P₄S₁₀ gives intermediate species described as thiophosphate esters (159), although such species have not been rigorously characterized. Hydrolysis of these thiophosphates followed by treatment with metal sources, for example, [WO₄]²⁻ (160), NiCl₂·(H₂O)₆ (160), or Cp₂NbCl₂ (161) gives dithiolene complexes. Schrauzer and Mayweg (160) describe a reliable, large-scale (45 g) procedure to Ni(S₂C₂R₂)₂, where R = Me and Ph.

1,2-Diketones (e.g., derivatives of benzil) can be used in place of α-hydroxyketones, a modification that broadens the utility of this method (71, 162), despite the fact that the dithione is the incorrect oxidation state to combine with metal salts. Large numbers of nickel diaryldithiolenes have been prepared via this sulfiting method (163–165). Representative of the dithiolene complexes prepared by the P₄S₁₀/diketone route are Ni[S₂C₂(Ph)(C₆H₄NMe₂)]₂, W[S₂C₂(C₆H₄NMe₂)₂]₃, and Ni[S₂C₂(C₆H₄OC₁₁H₂₃)₂]₂, which have interesting acid–base (162, 166–168) and liquid-crystal properties (65, 169).

E. From 1,2-Dithietes

1,2-Dithietes (170–172) are four-membered R₂C₂S₂ rings with adjacent sulfur atoms. Such heterocycles are isomeric with 1,2-dithiones and formally result from the two-electron oxidation of 1,2-alkenedithiolates (Fig. 1). Among the few known 1,2-dithietes, bis(trifluoromethyl)dithiete, (CF₃)₂C₂S₂, played a key role in the early stages of dithiolene chemistry. Preparation of this volatile (and poisonous) liquid dithiete involves the reaction of hexafluoro-2-butyne with molten sulfur (9). Oxidation of the dithiolene Cp₂TiS₂C₂(CO₂Me)₂ (Section III.A) gives the dithiete (MeO₂C)₂C₂S₂, which has been characterized crystallographically (173).
Because of its solubility in nonpolar solvents and its oxidizing character, (CF₃)₂C₂S₂ is well suited for synthesis of dithiolenes starting with nonpolar, low-valent organometallic precursors, for example, metal carbonyls (8). The synthesis of dithiolenes from dithietes is illustrated by the reaction of [CpMo(CO)₃]₂ and (CF₃)₂C₂S₂ to afford [CpMo{S₂C₂(CF₃)₂}]₂ via a dicarbonyl intermediate (Fig. 12) (174). An unusual method of exploiting the oxidative character of (CF₃)₂C₂S₂ involves its reaction with [MS₄]²⁻ (M = Mo, W) (175). Starting from mixed-oxo-metal sulfides one obtains oxo-dithiolenes such as {MoO[S₂C₂C₂(CF₃)₂]₂}²⁻ (Fig. 12). The same oxo-molybdenum species can be obtained by reduction of (CF₃)₂C₂S₂ followed by salt metathesis (12).

**F. From 1,2-Dithiones, Including Dithiaoxamides and Esters of Tetrathiaoxalate**

Few dithiolenes are prepared via reactions involving 1,2-dithioketones, a rare class of compounds prone to oligomerization. The first stable 1,2-dithione, 1,2-bis(4-dimethylaminophenyl)ethane-1,2-dithione, was generated by photolysis...
of the corresponding dithiocarbonate. The resulting dithione exists in equilibrium with the dithiete (176, 177). The corresponding diphenyl derivative exists exclusively in the dithiete form, indicating that π-donor substituents stabilize the dithione form. Cyclohexanedithione (178) (or its dithiete tautomer), has been trapped in situ with Mo(0) to give the poorly soluble tris(dithiolene) (Eq. 14).

A subset of the 1,2-dithiones are dialkyl tetrathiooxalate esters, C_2S_2(SR)_2. The parent C_2S_2(SMe)_2 exists in dynamic equilibrium with its dimer (Eq. 15) (179).

The compound C_2S_2(SMe)_2 exhibits oxidizing character; for example, it reacts photochemically with Ni(CO)_4 and Mo(CO)_6 to give dithiolene complexes Ni[S_2C_2(SMe)_2]_2 and Mo[S_2C_2(SMe)_2]_3 (an alternative synthesis of such complexes is described in Section III.E) (180, 181). The thermal reaction of Ni(cyclooctadiene)_2 and C_2S_2(SMe)_2 in the presence of bidentate ligands affords the mixed-ligand complexes Ni[S_2C_2(SMe)_2]L_2 (L_2 = tmeda, bpy or 2,2-bipyridine). The required S_2C_2(SMe)_2 is derived from dmit^2− via methyla- tion, conversion to the dithiocarbonate OCS_2C_2(SMe)_2 followed by photode-carbonylation (179). In principle, this methodology could give a range of SR-substituted dithiolenes.

Related to the dithioesters of dithiooxalic acid are the diamides R_2NC(S)C(S)NR_2, which are relatively more stable than ordinary dithiones (182, 183). These 1,2-dithiones are mildly oxidizing as illustrated by their reactions with Mo(CO)_2(PR_3)_2(MeCN)_2 with displacement of MeCN (184). Crystallographic studies (185) show that Mo(CO)_2(PBu_3)_2[S_2C_2(NC_5H_10)_2] (NC_5H_10 = piperidinyl) has some enedithiolate character (r_C=C = 1.37 Å). In contrast, the corresponding tetracarbonyls, Mo(CO)_4[S_2C_2(NR_2)_2], arising from Mo(CO)_4−(OPPh_3)_2, are described as Mo (0) derivatives (184).
Nickel complexes of unstable cyclic dithioamides are generated by sulfurizing the corresponding diamide in the presence of Ni powder using \((\text{MeO-C}_6\text{H}_4)_2\text{P}_2\text{S}_4\), a sulfiding agent akin to \(	ext{P}_4\text{S}_{10}\) (Eq. 16).

![Equation 16](image)

Yields are diminished if the thiation is conducted prior to the addition of the metal, indicative of the thermal instability of these dithioamides. Furthermore, the yields are lower when Ni(II) salts are used in place of Ni powder, consistent with the oxidative character of the dithioamide. Nickel dithiolenes of the dithioamides exhibit extraordinary extinction coefficients (\(~80,000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}\) at \(~1000 \text{ nm}\)) (186, 187).

**G. Via Intermetallic Dithiolene Transfer**

Two basic types of dithiolene exchange reaction are practiced, (1) non-redox reactions, which usually involve use of Zn\(^{II}\) and Cp\(_2\)Ti\(^{IV}\) based reagents, and (2) redox reactions, which commonly involve neutral bis(dithiolene) complexes of Ni.

**1. Non-Redox Routes**

Dithiolenes of Ti\(^{IV}\) and Zn\(^{II}\) (see Section III.A) transfer their alkene-dithiolate to softer metals. Chelate-transfer reactivity under mild conditions was first demonstrated with Cp\(_2\)Ti\(\text{S}_2\text{C}_2\text{R}_2\) (Z = CO\(_2\)Me, CF\(_3\)), which reacts with a variety of metal dichloro complexes, for example, [RhCl\(_2\)(CO)\(_2\)]\(^-\), NiCl\(_2\)(PR\(_3\))\(_2\), to give the corresponding late metal dithiolene and titanocene dichloride, which can be removed by filtration through silica gel with which it reacts (188). Related zinc complexes, for example, Zn(S\(_2\text{C}_2\text{R}_2\))(tmeda), where tmeda = tetramethylethlenediamine, also display this chelate-transfer reactivity and are perhaps still more versatile (see Section III.A) (189). Both the zinc and titanocene dithiolenes react with main group halides such as CXCl\(_2\) reagents (X = O, S), to give the corresponding XCS\(_2\text{C}_2\text{R}_2\). The hexametallic dithiolene [Pd\(_2\text{S}_2\text{C}_2\text{(CO}_2\text{Me})_2\)]\(_6\) (Fig. 13) was prepared by ligand transfer involving PdCl\(_2\)-(cyclooctadiene) and Zn[S\(_2\text{C}_2\text{(CO}_2\text{Me})_2\)](tmeda), concomitant with dissociation of the diene from Pd (190).

Organic salts of [Zn(dmit)]\(_2\)^{2-} readily undergo dithiolene-transfer reactions with metal chlorides. For example, this dianion reacts with Cp\(_2\)TiCl\(_2\), NbCl\(_5\),
VCl₃, and AuCl(PPh₃) to afford Cp₂Ti(dmit) (92, 117), [V(dmit)₃]²⁻ (191), [Nb₂S₄(dmit)₄]²⁻ (115), and dmit[Au(PPh₃)]₂ (192), respectively. Although other dmit complexes are rarely employed for dithiolene transfer CpNi(dmit) was prepared by treatment of [Ni(dmit)₂]⁺ (193).

2. Redox Routes

Schrauzer et al. (194) showed that Ni(S₂C₂R₂)₂ and metal carbonyls react upon photolysis resulting in transfer of dithiolene ligands. For example, Ni(S₂C₂R₂)₂ and Fe(CO)₅ react to give the binuclear dithiolene complexes Fe₂(S₂C₂R₂)(CO)₆ (R = H, Me, Ph); these species can also be prepared by the photoaddition of Fe₂S₂(CO)₆ to alkynes (195). More recent studies on this kind of reaction have revealed examples of incomplete transfer of dithiolene ligands, resulting in the formation of heterometallic complexes, Eq. 17 (Cp' = C₅Me₅, C₅H₄SiMe₃) (196).

\[
0.5 \left[ \text{Fe(S}_2\text{C}_2\text{Ph}_2)\right]_2 + 0.5 \text{Cp'}\text{Ru}_2(\text{CO})_4 \rightarrow \text{Cp'}\text{RuFe(S}_2\text{C}_2\text{Ph}_2)_3 + \cdots \quad (17)
\]

Photolysis of M(CO)₆ (M = Mo, W) and Ni(S₂C₂R₂)₂ gives modest yields of M(S₂C₂R₂)₂(CO)₂ (R = Me, Ph) (197). As expected for M(IV) derivatives, the carbonyl ligands are labile and can be displaced with a variety of donor ligands. For example, the chelating 1,2-bis(diphenylphosphino)ethane (dppe) reacts with W(CO)₂(S₂C₂R₂)₂ to give M(S₂C₂R₂)₂(dppe) (Fig. 14). A monodithiolene derivative, W(S₂C₂Me₂)(CO)₄, was also described, although the behavior of
this complex has not been examined [see related work on dithiaoxamide complexes of Mo (Section II.G)].

After a long hiatus, the dithiolene-transfer reaction involving Ni(S2C2R2)2 was rejuvenated by Holm and co-workers (198) who sought new routes to bis(dithiolene) complexes of molybdenum and tungsten as models for metalloenzymes. As discussed above, a synthetic challenge in the chemistry of molybdenum and tungsten dithiolenes is often preventing formation of the tris(dithiolene) complexes, which are substitutionally inert.

Dithiolene transfer from Ni(S2C2R2)2 to Mo/W (0) proceeds more efficiently when conducted thermally using preformed M(CO)3(MeCN)3. At the stoichiometry of Ni(S2C2R2)2/M(CO)3(MeCN)3 = 2, the yields of M(CO)2(S2C2R2)2 are ~30% (Mo) (198) and ~70% (W) (165, 199) (Eq. 18).

\[
2\text{Ni(S2C2R2)2} + \text{M(CO)3(MeCN)3} \rightarrow 2[\text{Ni(S2C2R2)2}]_n + \text{M(CO)2(S2C2R2)2}
\]

The required Ni(S2C2R2)2 complexes can be prepared on a large scale using the dithiophosphate route (Section II.E). The use of the labile M(CO)3(RCN)3 reagents, which are easily generated thermally (201), facilitates this chelate-transfer reaction. The resulting M(S2C2R2)2(CO)2 complexes have trigonal-prismatic structures, as anticipated by the characterization of the related Mo(CO)2-Se2C6H4 (202). The series \([\text{M(S2C2R2)2(CO)2}]^{n-}\) \((n = 0, 1, 2)\) has been characterized, the dianionic species having been generated by reduction of the neutral complex with potassium anthracenide, and the monoanion was obtained by comproportionation (203).

The carbonyl ligands in M(S2C2R2)2(CO)2 are readily substituted by sources of O2-, S2-, and Se2- (Fig. 15) (198, 199). Furthermore, phenoxides, arythiolates, and aryldiselenoates (198, 204, 205) also displace one or both of the carbonyl ligands, the determining factor apparently being the steric crowding around the M(IV) center.
The resulting anionic complexes closely resemble the proposed active site structures of the molybdopterin-based O-atom transfer enzymes such as dimethyl sulfoxide reductase (DMSOR) (4–6), which characteristically converts dimethyl sulfoxide (DMSO) to Me₂S. The complexes [M(S₂C₂Me₂)₂(OR)]⁻, for example, deoxygenate Me₃NO, DMSO, and Ph₂SeO, to give the reduced substrates and the oxo-metallates [MO(S₂C₂Me₂)₂(OR)]⁺ (M = Mo, W) (158, 200, 205). One dithiolene can be removed from [MoO(S₂C₂Me₂)₂]⁻ using PhSeCl to give mono(dithiolenes) [MoOCl₂(S₂C₂Me₂)]⁻ (30), analogous to the more extensively developed [MoOCl₂(S₂C₆H₄)]⁻ (Fig. 4). These monodithiolenes undergo substitution of the chlorides to give diverse alkoxy and thiolato derivatives, which are structural analogues of the active sites of sulfite.

Figure 15. Representative reactions of M(S₂C₂R₂)₂(CO)₂ (M = Mo, W) with anions (198, 199, 203–205).
oxidase and assimilatory nitrate reductase (30). As usual, the main challenge in the preparation of mono(dithiolene) Mo complexes is preventing formation of the very stable tris(dithiolene) derivatives.

Some insights into the details of dithiolene-transfer reactions are provided by a study of the reaction of CpCo(S$_2$C$_6$H$_4$)$_2$ with Mo(CO)$_3$ sources [e.g., Mo(CO)$_3$(py)$_3$/BF$_3$; py = pyridine]. The product is the trimetallic species Mo(CO)$_2$[CpCo(S$_2$C$_6$H$_4$)$_2$] (Fig. 16) (206). Structurally elated complexes have been prepared from [Ni(S$_2$C$_6$H$_4$)$_2$]$^-$ and sources of Cp$^*$Ru$^+$ (207).

III. TRANSITION METAL PROMOTED ROUTES TO DITHIOLENES

A. Addition of Electrophilic Alkynes to Metal Sulfides

Metal per- and polysulfido complexes react with electrophilic alkynes to give dithiolenes. The readily available diester DMAD is most commonly employed
in this reaction (12, 188, 208–222). Other electrophilic alkynes that have been used in this context are \( \text{C}_2(\text{CF}_3)\_2 \) (175, 223, 224), \( \text{HC}_2\text{CO}_2\text{Me} \) (189), \( \text{C}_2[\text{C}(\text{O})\text{Ph}]\_2 \) (225), and \( \text{C}_2[\text{C}(\text{O})\text{NH}_2]_2 \) (12, 226). Still more elaborate alkynes have been employed in the synthesis of pterin-related dithiolenes (217, 227). Terminal sulfido complexes also are known to add electrophilic alkynes as illustrated by additions to both \( \text{Tp}^*\text{WS}_2(\text{EPh}) \), where \( \text{E} = \text{O, Se} \); \( \text{Tp}^* = \) hydrido tris(3,5-dimethylpyrazolyl)borate (228) and \( \text{WS}_2(\text{OSiPh}_3)_2(\text{Me}_4\text{phen}) \) (229), where \( \text{Me}_4\text{phen} \) is tetramethylphenanthroline.

The prototype reaction of DMAD with sulfur-rich metal complexes involves treatment of \( \text{Cp}_2\text{TiS}_5 \) with DMAD to give \( \text{Cp}_2\text{TiS}_2\text{C}_2(\text{CO}_2\text{Me})_2 \) (Eq. 19) (188).

![Equation 19](image)

The reaction in Eq. 19 is first order in alkyne and polysulfido complex and is probably initiated by nucleophilic attack of a coordinated sulfur atom at the alkyne carbon followed by attack of the incipient carbanion on another part of the polysulfido chain. In some reactions, vinylpersulfido or sulfur-rich derivatives of dithiolenes are obtained, for example, the “\( \beta \) isomer” of \( \text{Cp}_2\text{TiS}_2\text{C}_2-(\text{CO}_2\text{Me})_2 \) (214) and \( \text{Cp}_2\text{MoS}_3\text{C}_2\text{R}_2 \) (217). These convert to dithiolenes upon heating or treatment with \( \text{PR}_3 \), respectively. The dithiolenes \( \text{Cp}_2\text{TiS}_2\text{C}_2\text{R}_2 \) are distinctively green in color and are readily purified. These and related titanocene complexes are of synthetic value because the dithiolene ligand can be removed as the free dianion or transferred to a “softer” metal center (Section II.H.1).

**DMAD is a highly reactive electrophile, so caution should be exercised in using this reagent.** Illustrative of the complications that one can encounter, the reaction of \( \text{Mo}(\text{S}_2)(\text{S}_2\text{CNEt}_2)_3 \) with DMAD gives “melded” dithiolene complexes wherein the \( \text{Et}_2\text{NC} \) fragment has inserted into the dithiolene \( \text{M}--\text{S} \) bond (230).

Subsequent to the development of the titanocene dithiolenes, related results were obtained starting with \( \text{ZnS}_6(\text{tmeda}) \), where \( \text{tmeda} = \) tetramethylene diamine and \( \text{ZnS}_4(\text{pmdta}) \) (189), where \( \text{pmdta} = \) pentamethyldiethylenetriamine (ligand). These species react with DMAD and \( \text{HC}_2\text{CO}_2\text{Me} \) to give dithiolene complexes, and the dithiolene can also be readily removed from the zinc center. The zinc complexes are more potent dithiolene-transfer agents than the titanocene complexes. The pentacoordinate complex \( \text{ZnS}_4(\text{pmdta}) \) reacts more rapidly with alkynes than the \( \text{tmeda} \) derivative (Fig. 17).

The reaction of phenylethynylquinoxaline and \( [\text{Mo}(\text{S})(\text{S}_4)_2]^{2-} \) gives \( \{\text{Mo}--[\text{S}_2\text{C}_2(\text{Ph})(\text{C}_8\text{H}_5\text{N}_2)]_3\}^{2-} \) (227), which probably exists as a mixture of rapidly
interconverting fac and mer isomers (231). These species are unremarkable except that they undergo oxidation (I₂) to produce thiophenic derivatives that are structurally related to the products resulting from the oxidative degradation of molybdopterin (5). Although the mechanism of this conversion remains unclear, the cyclization step is fairly general as illustrated by related oxidations of families W(IV) dithiolenes (Fig. 18) (228).

The conversion of dithiolenes into thiophenes has been known for many years (232). A related thiophene-forming reaction has also been observed using intact dithiolenes (Eq. 20) (233).
The ethanedithiolate complex $\text{Mo}_2\text{S}_4(\text{S}_2\text{C}_2\text{H}_4)_2$ reacts with DMAD to give the corresponding dithiolene $\text{Mo}_2\text{S}_2(\text{S}_2\text{C}_2\text{O}_2\text{Me})_2$ via a process that involves loss of ethylene. Precedent for this reaction is the reaction of ethylenedithiocarbonate with DMAD as discussed in Section II.B.2 (see Eq. 5).

**B. Addition of Unactivated Alkynes to Metal Sulfides**

Alkynes, even those lacking electron-withdrawing substituents, add to $\text{Cp}_2\text{Mo}_2\text{S}_4$ and derivatives to give dithiolenes. This discovery marked one of the seminal developments in the chemistry of metal sulfides because it foreshadowed the extensive reactivity of sulfido ligands toward diverse small molecule substrates. Alkynes displace alkenes from the bis(alkanedithiolates) $\text{Cp}_2\text{Mo}_2(\text{S}_2\text{C}_2\text{H}_3\text{R})_2$ to give the bis(dithiolene) derivatives $\text{Cp}_2\text{Mo}_2(\text{S}_2\text{C}_2\text{R}’_2)_2$ (234). For example, treatment of $\text{Cp}_2\text{Mo}_2(\text{S}_2\text{C}_2\text{H}_4)_2$ with acetylene gives ethylene and $\text{Cp}_2\text{Mo}_2(\text{S}_2\text{C}_2\text{H}_2)_2$ (Eq. 21). These reactions proceed via the initial loss of the alkene followed by the binding of the alkyne to the sulfido ligands. In contrast to the $\text{Cp}_2\text{Mo}_2\text{S}_4$ system, most metal sulfides react only with electrophilic alkynes (see Section III.A).
The dithiolene complex can be hydrogenated (2 atm, 60°C) to re-form the starting ethanedithiolate complex, thereby defining an alkyne–alkene hydrogenation cycle. An alternative entry into these dithiolenes involves reaction of alkyne with (MeC₅H₄)₂Mo₂(μ-S)₂(μ-SH)₂ with displacement of H₂ (235). Furthermore, it was found that anti-(MeC₅H₄)₂Mo₂(μ-S)₂(S)₂ and species described as (MeC₅H₄)₂Mo₂Sₓ react with acetylene to give (MeC₅H₄)₂Mo₂(S₂C₂H₂)₂ (236).

Treatment of Cp₂Mo₂S₂(SH)₂ with 1 equiv of PhC₂H in the presence of oxygen gives Cp₂Mo₂(O)(μ-S)₂[S₂C₂H(Ph)], which is also reactive toward H₂ (237). Similar oxo-dithiolenes can be obtained in low yields when Cp₂Mo₂-(S)(O)(μ-S)₂ is treated with acetylene (238). Of the many modifications of the Cp₂Mo₂S₄ system, perhaps the most widely studied is the methanedithiolate Cp₂Mo₂S₂(S₂CH₂), wherein the reactivity is focused on the pair of μ-S ligands. This species forms dithiolenes upon treatment with the alkynes C₂H₂, C₂Ph₂, and C₂Et₂, but following a general trend, it binds alkenes more weakly (239). Functionalized Cp ligands have been introduced, for example, C₅H₄R, where R = CH₂CH₂NMe₂, CH₂CO₂Me, CH₂CO₂⁻ (240); these allow dithiolene
formation to occur in water. Similarly, the complexes can be water-solubilized by functionalization of the methylenedithiolate, e.g., Cp₂Mo₂S₂(S₂CH-CH₂CO₂⁻).

Alkynes also add to organotungsten and rhenium sulfides, although, in contrast to the Cp₂Mo₂S₄ chemistry, these reactions are complicated by sulfur atom transfer processes. For example, Cp₂W₂S₂(μ-S)₂ reacts with acetylene over the course of days (room temperature) to give low yields of Cp₂W₂(S₂C₂H₂)₂. Longer reaction times favor the formation of more complex products such as Cp₂W₂S₃(S₂C₂H₂) and Cp₂W₂S₂(S₂C₂H₂)₂; in the latter two examples, the dithiolene ligands are nonbridging (241). The dithiolene ligands in Cp₂W₂S₂(S₂C₂H₂)₂, but not Cp₂W₂(S₂C₂H₂)₂, are hydrogenated under mild homogeneous conditions; the reaction forms ethylene and Cp₂W₂(S)-
(μ-S)₂(S₂C₂H₂), that is, with net change in the S/W ratio. As with the analogous Mo systems, alkynes displace ethylene from Cp₂W₂(S)(μ-S)₂(S₂C₂H₄) and Cp₂W₂S₂(S₂C₂H₄). Acetylene also binds to [(C₅Me₄Et)₂Re₂(μ-η²:η²-S₂)₂]²⁺ (242), but does not displace alkenes from Cp₂V₂(S₂C₂H₃R)₂ (241). In contrast to Mo analogues, Cp₂V₂S₄ adds only electrophilic alkynes (223).

The inorganic clusters [Mo₃(μ₃-S)(μ₂-E)(μ₂-S)₂(H₂O)₉]⁴⁺ (E = O, S) add acetylene at room temperature in aqueous 1 M HCl solution to give the dithiolene (243). The dithiolene ligand adopts an unusual bonding mode, wherein each thiolate sulfur atom bridges two metals (Fig. 19). The cluster

![Figure 19. Structure of the C₂H₂ adduct of [Mo₃(μ₃-S)(μ₂-O)(μ₂-S)₂(H₂O)₉]⁴⁺ (243).](image-url)
[Mo$_3$(μ$_3$-S)(μ$_2$-E)(μ$_2$-S$_2$C$_2$H$_2$)(H$_2$O)$_9$]$^{4+}$ is a rare example of a M-dithiolene-H$_2$O complex. A related alkyne addition involves the addition of PhC$_2$H to [Mo(Et$_2$dtc)$_2$][Rh(PPh$_3$)$_2$]S$_4$Cl, where dtc = dithiocarbamate which gives a dithiolene-bis(vinylthiolato) derivative, wherein one sulfur of the dithiolene is triply bridging and the second sulfur is doubly bridging. The reaction is thought to proceed via initial dissociation of PPh$_3$ (244).

The anion [ReS$_4$]$^-$, which is isoelectronic with the well-known $d^0$-oxo-transfer agents [MnO$_4$]$^-$ and OsO$_4$, binds a variety of unactivated alkynes (Fig. 20).

The alkyne $+$ [ReS$_4$]$^-$ reaction depends on the reactant ratio; additionally, the presence of elemental sulfur has a strong influence. A monomeric dithiolene [ReS$_2$(S$_2$C$_2$R$_2$)]$^-$ is initially produced, but it subsequently dimerizes (the corresponding monomeric alkanedithiolate [ReS$_2$(S$_2$C$_7$H$_9$)]$^-$ is stable) (245, 246). With a deficiency of alkyne, one obtains tetrametallic [Re$_4$S$_{12}$(S$_2$C$_2$R$_2$)$_2$]$^{4-}$ with an alkyne/Re ratio of 0.5. These derivatives arise via the addition of [ReS$_4$]$^-$ to [ReS$_2$(S$_2$C$_2$R$_2$)]$^-$ followed by dimerization. Treatment of [ReS$_4$]$^-$ with $\geq$2 equiv of alkyne in the presence of elemental sulfur gives [ReS(S$_2$C$_2$R$_2$)$_2$]$^-$; such

Figure 20. Synthetic relationships of dithiolenes derived from [ReS$_4$]$^-$. 

(one of two isomers)  (and cis isomer)  (R’ = H, Ph)
species adopt a square-pyramidal geometry common to \(d^2\) complexes (247). When the alkyne addition is conducted in the presence of RSH (R = H, alkyl, aryl) one obtains related derivatives [ReS(S\(_2\)C\(_2\)R\(_2\))(SH)(SR)]\(^-\) (R\(_2\) = PhC\(_2\), H; Ph, Ph). Furthermore, by using ethanedithiol it is possible to prepare mixed dithiolenedithiolate complexes, for example, [ReS[S\(_2\)C\(_2\)(tms)\(_2\)](S\(_2\)C\(_2\)H\(_4\))]\(^-\) (248), where tms = trimethylsilyl.

Related to these results is the finding that [Cp\(^*\)WS\(_3\)]\(^-\) adds Ph\(_2\)C\(_2\) to give the corresponding tungsten(IV) dithiolene (249). In contrast to [ReS\(_4\)]\(^-\), the dianion [WS\(_4\)]\(^{-2}\) does not bind Ph\(_2\)C\(_2\). The reactivity of metal sulfido complexes toward alkynes thus correlates with the charge on the metal sulfide: neutral complexes (e.g., Cp\(_2\)M\(_2\)S\(_4\)) being more reactive than monoanions, [Cp\(^*\)WS\(_3\)]\(^-\) and [ReS\(_4\)]\(^-\), which in turn are more reactive than [WS\(_4\)]\(^{-2}\).

The reaction of metal carbonyl complexes with elemental sulfur in the presence of alkynes has long been known to afford diithiolenes, for example, of Fe, Mo, and Ni, although usually in low yields (250). This route to dithiolenes is mechanistically interesting because binary metal sulfides are unreactive toward alkynes under mild conditions, thus dithiolene formation indicates the occurrence of reactive MS\(_x\) intermediates. Insights into this reaction have mostly come from studies on Cp metal carbonyls. Sulfdation of Cp\(_2\)Fe\(_2\)(CO)\(_4\) in the presence of alkynes gives dithiolenes, for example, Cp\(_2\)Fe\(_2\)(CO)S\(_2\)C\(_2\)-(CO\(_2\)Me)\(_2\) and the cubanes Cp\(_2\)[Ph(R)C\(_2\)S\(_2\)]\(_2\)Fe\(_4\)S\(_4\) (R = Ph, Et, Me) and Cp\(_2\)(Ph\(_2\)C\(_2\)S\(_2\))Fe\(_4\)S\(_5\) (251–253). These species are representative of other abiological Fe–S ensembles that feature dithiolenes in place of thiolate terminal ligands (254, 255).

Insight into the trapping of reactive metal sulfides with alkynes is provided by studies on the desulfurization of Cp\(_2\)Ru\(_2\)S\(_4\) in the presence of alkynes (256). This reaction gives Cp\(_2\)Ru\(_2\)(μ-η\(^3\)-η\(^4\)-S\(_2\)C\(_2\)R\(_2\)) via the intermediate Cp\(_2\)Ru\(_2\)S\(_2\). Otherwise, Ph\(_2\)C\(_2\) and Cp\(_2\)Ru\(_2\)S\(_4\) do not react, and when the desulfurization
agent (PBu$_3$) is added prior to the addition of the alkyne, only the unreactive 
Cp$_2$Ru$_2$S$_6$ cluster, not dithiolenes, results. The intermediacy of Cp$_2$Ru$_2$S$_2$ in this 
reaction has been independently confirmed because dehydrohalogenation of 
Cp$_2$Ru$_2$Cl$_2$(μ-SH)$_2$ in the presence of alkynes gives the same dithiolenes 
(Fig. 21) (257).

The CpCo/Rh promoted reaction with sulfur and alkynes is the basis of a 
catalytic synthesis of thiophenes (258).

**C. From Metal Sulfides and α-Haloketones and Related Precursors**

This method is somewhat related to the thiophosphate method (Section II.E). Metal complexes of the type L$_n$M(SH)$_2$ react with α-halogenated ketones to give the corresponding dithiolenes. The bis(thiol) complexes include Cp$_2$Mo(SH)$_2$ and M(SH)$_2$(dppe) (M = Ni, Pd, Pt) (259). The pathway for this dithiolene synthesis probably begins with the alkylation of one SH ligand, taking advantage of the nucleophilicity characteristic of such ligands (260, 261). The halide leaving group can be replaced by phosphate esters (262) (Eq. 22). The latter may have implications for the biosynthesis of molybdopterin cofactors, the precursors to which are α-phosphorylated ketones. Note that molybdopterin cofactor does not contain molybdenum, it is the organosulfur component that binds Mo and W.

\[
\begin{align*}
\text{L}_n\text{M} & \quad \text{SH} \\
\text{+} & \quad \text{O} \quad \text{R}_2 \\
\text{SH} & \quad \text{X} \quad \text{R}_1 \\
\text{- H}_2\text{O}, \text{HX} & \quad \text{L}_n\text{M} \quad \text{SH} \quad \text{SH} \\
\text{X} & = \text{Br, tosyl, OPO(OEt)}_2 \\
\text{R}_1 & = \text{H, Me, Ph} \\
\text{R}_2 & = \begin{array}{c}
\text{N} \\
\text{N} \\
\text{N} \\
\text{N}
\end{array}
\end{align*}
\]

This method has found particular use in the preparation of pyridine-substituted dithiolene complexes, which exhibit pH sensitive luminescence properties (263). The α-halocarbonyl starting materials could include related precursors used in the synthesis of unsaturated dithiocarbonates described in Section II.C.
D. By Dehydrogenation of Alkanedithiolates

Given the considerable stability of dithiolenes, it is not surprising that they can be generated by dehydrogenation of alkanedithiolato complexes. Indeed, Pt(S$_2$C$_2$H$_2$Ph$_2$)(bpyR$_2$)$_2$, where bpyR$_2$ is a substituted 2,2-bipyridine, dehydrogenates upon photolysis of its oxygenated solutions. Photooxidation of the corresponding ethanedithiolate gives S-oxygenated products instead (264). Conventional dehydrogenation agents, for example, dichloro-dicyanoquinone, do not appear to have been applied to the dehydrogenation of alkanedithiolates. Dehydrogenation has been employed in the synthesis of thiophenedithioles (Section II.B.2) from the corresponding tetrahydrothiophene derivatives (64).

Electrophilic alkenes react with ZnS$_4$(pmdeta) to give dithiolene complexes Zn(S$_2$C$_2$R$_2$)(pmdta). The following alkenes were employed in this reaction: cis- and trans-C$_2$H$_2$(CO$_2$Me)$_2$, C$_2$H$_3$CO$_2$Me, C$_2$H$_3$CN, 1,2-C$_2$H$_2$Me(CN), C$_2$H$_3$CHO, and 1,2-C$_2$H$_2$(CN)(Ph). The reaction proceeds via the reversible formation of a dipolar intermediate, as indicated by the ability of the polysulfido complexes to catalyze the cis–trans isomerization of C$_2$H$_2$(CO$_2$Me)$_2$ (Eq. 23) (265). Such dipolar intermediates are proposed to undergo ring closure to give alkanedithiolato intermediates. Independently prepared alkanedithiolate Zn[SiC$_2$H$_2$(CO$_2$Me)$_2$](pmdta) reacts with elemental sulfur to give the dithiolene Zn[SiC$_2$(CO$_2$Me)$_2$](pmdta). The dithiolene ligands can be removed from the Zn center, for example, with phosgene trimer (COCl$_3$)$_3$ and Cp$_2$TiCl$_2$ to give OCS$_2$C$_2$H(CN) and Cp$_2$TiS$_2$C$_2$H(CN), respectively (Section II.G.1).

\[
\text{Zn}S\text{NMe}_2\text{NMe}_2\text{S}R + S_8 - \text{H}_2\text{S} \rightarrow \text{Zn}S\text{NMe}_2\text{NMe}_2\text{S}R
\]  

(Eq. 23)

An esoteric example of a dehydrogenative route to a dithiolene involves the thermolysis of Cp$_2$TiS$_5$. In the product, two H atoms on one Cp ring have migrated to allow the formation of a cyclopentene-1,2-dithiolate derivative (Eq. 24) (266).

\[
\text{TiS}_5\text{S} \rightarrow \text{TiS}_5\text{S} \text{Cp}_2\text{TiS}_2\text{S}_2\text{Cp}_2\text{TiS}_5\text{S}
\]  

(Eq. 24)
The Kajitani–Sugimori group, which has conducted numerous studies on the ligand-centered reactions of dithiolenes (267), synthesized various CpCo-(S₂C₂RR') derivatives via the reaction of CpCo(CO)₂, electrophilic alkenes, and elemental sulfur (268). The reaction of [TcCl₆]²⁻ with ethanedithiol is claimed to generate small amounts of [Tc₂(S₂C₂H₄)₂(S₂C₂H₂)₂]²⁻ wherein the dithiolate, not the dithiolene is bridging (269), although the structure assignment has been disputed (270). The ethanedithiolate Cp*Re(S₂C₂H₄)Cl₂ upon thermolysis or treatment with O₂ gives the dithiolene Cp*Re(S₂C₂H₃)Cl₂ (271). Similarly, heating Cp*Re(S₂C₂H₃Et)Cl₂ and Cp*Re(S₂C₂H₂Me₂)Cl₂ gives the corresponding alkyl-substituted dithiolenes without C–C bond scission. The dehydrogenation follows first-order kinetics. Such reactions are relevant to the ability of metal sulfides to catalyze hydrogen-transfer reactions.

E. From Dithiocarbonates

As discussed in Section II.C, the hydrolysis of certain unsaturated dithiocarbonates, that is, dithiole-2-ones, gives alkenedithiolate dianions that react further with metal cations to give dithiolenes. In selected cases, dithiolenes can be prepared directly from reactions of metal complexes with dithiole-2-ones. This process has been demonstrated on two occasions using the electrophilic tetrathiapentalenedione. Treatment of TPD with [MoS₄]²⁻ affords [Mo-(C₅S₄O)₃]²⁻ and COS. Oxidation of this tris(dithiolene) complex to the charge-neutral Mo(VI) derivative followed by hydrolysis in the presence of BuBr gives Mo[S₂C₂(SBu)₂]₃ (Eq. 25) (272).

\[
\begin{align*}
\text{(TPD)} & \quad [\text{MoS}_4]^{2-} \quad - \text{COS, S} \quad [\text{Mo(S}_2\text{C}_2\text{S}_2\text{CO})_3]^{2-} \\
1) [\text{Cp}_2\text{Fe}]^+ & \quad 2) \text{NaOMe/RX} \\
\end{align*}
\]

In a similar reaction, [MoS₄]²⁻ reacts with C₄S₅O, the monothiocarbonyl derivative of TPD, to give the same products as above, showing the preferential reactivity of the thiometalate for the dithio- versus the trithiocarbonate. It was also found that the tetrasulfido complex ZnS₄(pmdta) (Section III.A) reacts with TPD to give Zn(S₂C₂S₂CO)(pmdta) (189).
Relevant to the quest for molybdopterin-related ligands, heterocycle-substituted trithiocarbonates were shown to give modest yields of the \(\text{CpCo}(\text{dithiolene})\) when treated with \(\text{CpCo}(\text{cod})\) (\(\text{cod} = 1,5\)-cyclooctadiene, Eq. 26) (85).

\[
\begin{align*}
\text{BnO}_2\text{C} & \quad \text{S} & \quad \text{S} & \quad \text{H} \\
\text{N} & \quad \text{OMe} & \quad \text{S} & \quad \text{S} & \quad \text{H} & \quad \text{BnO}_2\text{C} \\
\text{CpCo}(\text{alkene})_2 \\
\text{CpCo}(\text{dithiolene})
\end{align*}
\]

The \(\text{CpCo}\) platform has been employed to display and interrogate the dithiolene unit with respect to the ligand-based reactivity. The dithiolene ligand cannot, however, be readily removed from the \(\text{CpCo}\) site.

The reaction of dmit-derived trithiocarbonates (see Eq. 8) with \(\text{Cp}_2\text{Mo}_2[\text{C}_2-(\text{CO}_2\text{Me})_2](\text{CO})_4\) followed by treatment with elemental sulfur gives \(\text{Cp}_2\text{Mo}_2(\text{S})-\text{C}_2\text{C}_2\text{R}_2\) (273). The latter is a unique example of a complex of the tto-derived ligand \([\text{S}_2\text{C}_2[\text{SC(O)Ph}_2]_2]^{-}\).

F. Specialized Routes to Dithiolenes

Dithiolenes have been prepared by many unplanned or unusual methods, often involving organometallic intermediates (274). Whereas these transformations are presently classified as specialized, future work may show that these methods enjoy more significance than presently appreciated. The fact that dithiolenes appear in the products of so many reactions is testament to their considerable stability.

1. S-Dealkylation

Complexes of alkyl-linked \(o\)-benzenedithiolates eliminate ethylene to give benzenedithiolato complexes (Eq. 27) (275–277). This reaction is the reverse of the known addition of alkenes to \(\text{bis}(\text{dithiolene})\) complexes (278–281). Photolysis of the \(S\)-benzylated dithiolenes \(\text{M} \left(\text{PhCH}_2\text{S}_2\text{C}_2\text{Ph}_2\right)_2\) (\(\text{M} \equiv \text{Ni, Pd, Pt}\)) results in \(S\)-dealkylation with elimination of benzyl radicals (282). In general, however, the properties of \(S\)-alkylated dithiolenes have not been
thoroughly investigated (199, 283, 284) beyond the work on CpCo derivatives (267).

1,4-Dithiin derivatives (dithiabenzenes) have long been known to react with metal carbonyls to give dithiolenes (285). A recent illustration is provided by the finding that treatment CpCo(CO)₂ with 2-nitro-3,5-diphenyl-1,4-dithiin affords CpCoS₂C₂(Ph)H (286).

2. Insertion into Metal–Alkyne Bonds

Alkyne complexes of the early metals that are nucleophilic at carbon (i.e., have metallacyclopentene character) insert electrophiles such as elemental sulfur. Thus, zirconocene benzyne complexes, which are generated upon thermolysis of diarylzirconocene complexes, can be trapped in the presence of sulfur to give benzenedithiolato complexes (287, 288). Some insights into the mechanism of this process is provided by the finding that the vinylperthiolate form of Cp₂TiS₂C₂(CO₂Me)₂ rearranges intramolecularly to give the dithiolene (214, see also 215) (Eq. 28).

Addition of sulfur to the alkyne-bridged complex Cp₂Mo₂(CO)₄(C₂R₂) efficiently affords dithiolenes Cp₂Mo₂(S)(μ-S)₂S₂C₂R₂ [R₂ = H₂; H, Me; H, Ph; Et₂; (CO₂Me)₂] in good yields (273). Such complexes had previously been prepared by alkyne addition to Cp₂Mo₂Sₓ derivatives (238). Related dithiolene complexes have been made by the successive treatment of the same alkyne complexes with diorganotrithiocarbonates and elemental sulfur (273).
3. C–C Coupling Pathways

A remarkable method for the assembly of dithiolenes proceeds via coupling of the two RCS halves of the ligand mediated by a metal center. Reaction of \([\text{Mn(CO)}_5]^-\) with ArC(S)Cl (Ar = C_6H_5, 4-ClC_6H_4, 4-ClC_6H_4) gives the unusual example of a trans (or \(E\)-) dithiolene complex. This transformation has been rationalized by invoking a thioacyl Mn[C(S)Ph](CO)_5 intermediate, which due to the carbenoid character of the thioacyl ligand, undergoes C–C coupling even at very low temperatures (Eq. 29).

Decarbonylation of \((\text{trans-S}_2\text{C}_2\text{Ph}_2)[\text{Mn(CO)}_5]_2\) occurs at \(-30^\circ\text{C}\) to give \((\eta^2:\eta^5-\text{S}_2\text{C}_2\text{Ph}_2)[\text{Mn}_2(\text{CO})_6\) (289). Other examples of \(\eta^2:\eta^4\)-dithiolenes have the formula \(\text{Cp}_2\text{Ru}_2\text{S}_2\text{C}_2\text{R}_2\) (256, 290).

Reduction of \(\text{Fe}[\eta^2-\text{SCSMe})(\text{CO})_2\text{L}_2]^+\) gives the dithiolenes \(\text{Fe}_2[\text{S}_2\text{C}_2-(\text{SMe})_2](\text{CO})_4\text{L}_2\) [L = PPh_3, P(OMe)_3] (291). These species degrade in air to the deeply colored, 16 e\(^-\) monometalic derivatives \(\text{Fe}[\text{S}_2\text{C}_2(\text{SMe})_2]-(\text{CO})_2(\text{PPh}_3\), which are formally derived from dimethyltetraethiolatoxalate (Section II.F). Conceivably, these C–C coupling reactions are related to the reductive coupling of CS_2 by low-valent metal complexes, which leads to tetrathiooxalate (or ethylenetetrathiolato) complexes, for example, from \(\text{Cp}_2\text{Ti}^{\text{II}}\) and (triphos)Rh\(^{\text{I}}\) sources (131, 292, 293) (see also Section II.C.2).

The bis(alkylidyne) clusters \(\text{Cp}_3\text{Co}_3(\text{CR})_2\) react with elemental sulfur to give \(\text{CpCoS}_2\text{C}_2\text{R}_2\) (R = Bu, Ph, CO_2Me, C_2SiMe_3). Labeling studies show that the two alkylidyne units from the same cluster are coupled in this reaction, which probably begins with attack of sulfur on a Co–Co bond (294).

Werner reported the formation of a \(\text{CpCo(dithiolene)}\) complexes via a multistep process that begins with C-alkylation of \(\text{CpCo(PMe}_2\text{Ph})(\text{CNMe})\) followed by reaction with CS_2 and further sulfidation with elemental sulfur. The product is structurally related to \(\text{CpCo(dmit)}\) (295).

4. From Alkynes and Thiocarbonyl Derivatives

Dithiocarbamate complexes are known to react with alkynes to give low yields of dithiolenes and related ligands via pathways that can be difficult to
rationalize (296). For example, the bis(alkyne) complex W(dtc)$_2$(PhC$_2$H)$_2$ reacts photochemically with phenylacetylene to give W(C$_5$Ph$_2$H$_2$NMe$_2$)(S$_2$C$_2$H(Ph))(dtc) via a proposed dimethyamino carbyne intermediate (297).

The electron-rich complex Fe(CO)$_2$[(P(OMe)$_3$)$_2$(η$^2$-CS$_2$)] adds electrophilic alkynes via an apparent 1,3-dipolar addition process to give carbene derivatives that in turn undergo efficient air oxidation to afford the 16 e$^-$ dithiolene complexes Fe(CO)[(P(OMe)$_3$)$_2$(S$_2$C$_2$RR')] (R, R' = CO$_2$Me, Ph, CHO, etc.) (298).

5. Dithiolene Coupling

Unsubstituted dithiolenes can be coupled via dehydrogenation. Examples of this behavior come from studies on derivatives of CpCo, a standard platform for exploring the reactivity of dithiolenes (267). Treatment of CpCoS$_2$C$_2$H(Ph) with AlCl$_3$ gives small amounts of the 1,2,3,4-tetrathiobutadiene derivative [CpCo]$_2$(S$_4$C$_4$Ph$_2$) (299). The related benzenehexathiolate complex arises via dehydrogenative coupling of 3 equiv of CpCoS$_2$C$_2$H$_2$ (Eq. 30) (300).

Although inefficient and mechanistically mysterious, these transformations highlight the reactivity inherent in the C–H bond of unsubstituted dithiolenes, a fertile area for further research (see Eq. 20). Benzenehexathiolate complexes can also of course be prepared by reactions of metal salts with C$_6$(SH)$_6$ or its salts (see Section II.A) (144, 146).

Hoffman has shown that mnt$_2$ complexes form phthalocyanines that are decorated on their exteriors with metal dithiolenes (301, 302). The reaction is analogous to the conversion of phthalonitriles to phthalocyanines.

6. From Alkynyl Anions

The complex Fe$_2$(S$_2$(CO)$_6$ reacts with alkynyllithium reagents to give dithiolenes after treatment with electrophiles (303). The synthesis proceeds
via $\mu$-alkynylthiolato complexes, which add electrophiles ($H^+$, $Me_3SiCl$, $PhCHO$) at the carbon adjacent to sulfur.

IV. SUMMARY AND OUTLOOK

Dithiolene complexes can be prepared by incredibly diverse routes, the range of which is testament to the stability of the $MS_2C_2R_2$ ring. These routes are of interest not only for their synthetic utility but also for the insights that they provide on the electronic structure of the host–metal complex. Whereas dithiolenes occur widely as biological cofactors, the chemistry of synthetic catalysts based on dithiolenes remains minimal—the development of catalytic chemistry of metal dithiolenes will likely spawn many new synthetic methods.

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ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tr>
<td>AIBN</td>
<td>Azoisobutyronitrile</td>
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<td>bpy</td>
<td>2,2'-Bipyridine</td>
</tr>
<tr>
<td>cod</td>
<td>1,5-Cyclooctadiene</td>
</tr>
<tr>
<td>Cp</td>
<td>Cyclopentadienyl</td>
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<tr>
<td>$Cp^+$</td>
<td>Pentamethylcyclopentadienyl</td>
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<td>Dimethylacetylene dicarboxylate</td>
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<td>DMF</td>
<td>Dimethylformamide</td>
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<td>dmid$^{2-}$</td>
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<td>dmit$^{2-}$</td>
<td>4,5-Dimercapto-1,2-dithiole-3-thione-4,5-dithiolate</td>
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<td>DMSO</td>
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<td>Dimethyl sulfoxide reductase</td>
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<td>Dithiocarbamate</td>
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<td>dppe</td>
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<td>Me$_4$phen</td>
<td>Tetramethylphenanthroline</td>
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<td>mnt$^{2-}$</td>
<td>Maleonitrile-1,2-dithiolate</td>
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<td>(1,2-dicyanoethane-1,2-dithiolate)</td>
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REFERENCES