Dehydrogenative Route to Metallo Dithiolenes: The Reaction of Zinc Polysulfides and Alkenes

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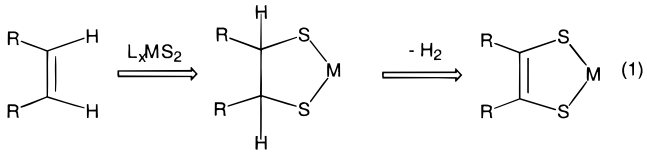
Complexes of the type ZnS_6(TMEDA), ZnS_4(PMDETA), and ZnS_4(Me_3TACN) react with electrophilic alkenes to give dithiolene complexes $ZnS_2C_2R_2(amine)_n$. The Me_3TACN complex is the most reactive, while the more conveniently prepared PMDETA complex also undergoes this reaction at useful rates. The following alkenes were successfully tested: $C_2H_2(CO_2Me)_2$ (cis and trans isomers), $C_2H_3(CO_2Me)$, $C_2H_3(CN)$, 1,2-$C_2H_2Me(CN)$, $C_2H_3(CHO)$, and 1,2-$C_2H_2(CN)(Ph)$. Crystallographic analysis shows that the highly reactive complex ZnS_4(Me_3TACN) is structurally similar to ZnS_4(PMDETA), including the presence of an elongated $Zn-N_{ax}$ bond. Model studies indicate that the reaction of alkenes with L_nZnS_x proceeds via the reversible formation of a dipolar intermediate, as indicated by the ability of the polysulfido complexes to catalyze the isomerization of *cis*-$C_2H_2(CO_2Me)_2$. It is proposed that such dipolar species undergoes ring closure to give alkanedithiolato intermediates, e.g., $Zn[S_2C_2H_2(CO_2Me)_2]$(PMDETA). The dithiolato complexes $Zn[S_2C_2H_2(CO_2Me)_2]$(PMDETA) and $Zn[S_2C_2H_2(CO_2Me)_2]$(TMEDA) were prepared from $ZnMe_2$, the di- and triamines, and the dithiol *meso*-$(HS)_2C_2H_2(CO_2Me)_2$. These dithiolates undergoes dehydrogenation upon treatment with S_8 to give the dithiolene $Zn[S_2C_2(CO_2Me)_2]L_n$ at a rate that is independent of the ancillary ligand L. The dithiolene ligands can be removed from the Zn center by treatment with $[COCl_2]_3$ and Cp_2TiCl_2; in this way $Zn[S_2C_2H(CN)]$(PMDETA) was converted to $OCS_2C_2H(CN)$ and $Cp_2TiS_2C_2H(CN)$.

Introduction

Metal dithiolenes are receiving increasing attention because of their role in biological and materials chemistry. For example, all known Mo- and W-containing enzymes, except the nitrogenases, feature the molybdopterin cofactor, an alkenedithiolate (dithiolene) linked to a nucleotide.[1] Bis(dithiolene) metal complexes have been of interest in the materials science community because of their utility as laser dyes and their high electrical conductivity.[2] Research on metal dithiolenes has been further invigorated by the discovery of large nonlinear optical responses in nickel dithiolenes[3] and the luminescent properties of platinum dithiolenes.[4−7]

The intense research on metal dithiolenes has spawned many syntheses of such complexes. Virtually all routes begin with alkynes or their equivalent, such as α-hydroxyketones, α-haloketones,[8] and unsaturated dithiocarbonates.[9] The synthesis of dithiolenes from alkenes would be advantageous because alkenes are available with a wider range of substituents than alkynes. The metal sulfide-promoted conversion of an alkene to a dithiolene formally requires two steps, the initial addition of the equivalent of S_2^{2-} across the double bond to give an alkanedithiolate followed by dehydrogenation (eq 1).



(1)

We have found that zinc polysulfido complexes, especially those bearing triamine coligands, effect this dehydrogenative conversion of alkenes to dithiolenes. The new methodology is of additional interest because it is employs inexpensive reagents and, once prepared, the resulting dithiolene ligands can be removed from the host metal.

Results and Discussion

Synthesis of Dithiolenes from Alkenes. Acetonitrile solutions of ZnS_4(PMDETA) (**1**, PMDETA = *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine) react with the dimethyl maleate and dimethyl fumarate over the course of several hours to give the same pale yellow product, $Zn[S_2C_2(CO_2Me)_2]$(PMDETA) (**3a**). This complex had been previously prepared from dimethyl acetylenedicarboxylate (DMAD) and **1**.[10] Dimethyl maleate also reacts slowly with ZnS_6(TMEDA) (**2**) to give the dithiolene $Zn[S_2C_2(CO_2Me)_2]$(TMEDA) (**4a**). While the dehydrogenative route to **3a** is slower than the direct reaction of DMAD with **1**, it is virtually quantitative. In terms of mass balance, the reaction

(1) Kisker, C.; Schindelin, H.; Rees, D. C. *Annu. Rev. Biochem.* **1997**, *66*, 233−267.
(2) Cassoux, P.; Valade, L.; Kobayashi, H.; Kobayashi, A.; Clark, R. A.; Underhill, A. E. *Coord. Chem. Rev.* **1991**, *110*, 115−160.
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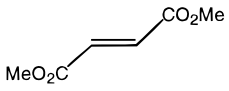
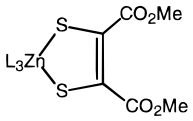
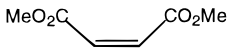
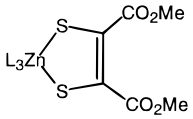
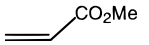
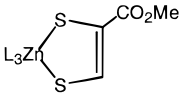
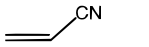
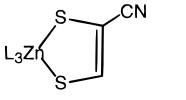
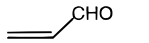
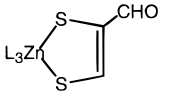
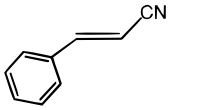
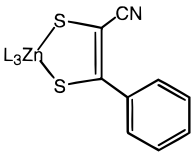
Table 1. Reaction Conditions for Synthesis of Dithiolenes from Alkenes

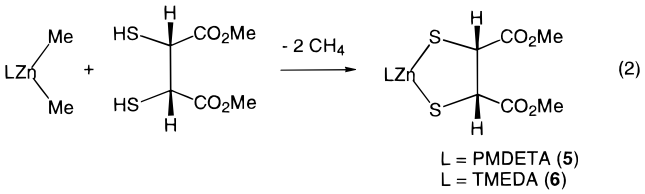
olefin	reaction conditions	product	yield (%)
	30 equiv olefin reflux MeCN 16 h		89
	30 equiv olefin reflux MeCN 16 h		86
	30 equiv olefin reflux MeCN 16 h		90
	30 equiv olefin reflux MeCN 16 h		95
	6 equiv olefin reflux MeCN 40 h		~30
	neat olefin 110 °C 40 h		75

of **1** and 10 equiv of dimethyl maleate consumed ca. 3.4 equiv of the alkene. Another ~2 equiv are assumed to react with the H_2S byproduct.[11]

Other common electrophilic alkenes react with **1** to give dithiolenes, including methyl acrylate, acrylonitrile, and cinnamonitrile (PhCH═CHCN). Typically, the reactions were conducted in refluxing MeCN solution using an excess of the alkene (Table 1). The reaction involving *trans*-PhCH═CHCN was slow and was therefore conducted in neat alkene to give Zn[S_2C_2(Ph)(CN)](PMDETA) (**3d**). The products were isolated as analytically pure off-white solids, which were further characterized by ^{1}H NMR and IR spectroscopies. The IR spectra show loss of ν_{ss} and appearance of ν_{CO} and ν_{CN} bands for the ester- and nitrile-containing products, respectively.

Other alkenes that are less electrophilic than those discussed above react with **1** to give dithiolenes, e.g., 2-pentenenitrile, 2-butenenitrile (crotononitrile), and acrolein (CH_2═CHCHO). The success of these attempts was indicated by the upfield shift of the ^{1}H NMR signals at ~δ2.3 for the methyl groups of PMDETA. The IR spectra show loss of ν_{ss} and appearance of ν_{CO} and ν_{CN} bands for the acrolein and nitrile derivatives, respectively. The acrolein reaction is complicated, we suspect, due to the competing formation of the acrolein dimer.[12] Acrylamide and styrene do not appear to react with **1** or **2**.

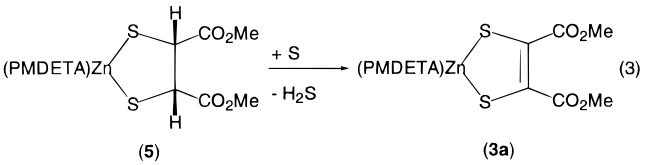
Synthesis of Alkanedithiolates. Alkanedithiolates are likely intermediates in the pathway leading to dithiolenes from alkenes. To test this idea we examined the reactivity of complexes of dimethyl *meso*-dimercaptosuccinate,[13,14] a chelating alkanedithiol formally derived by the formal addition of HS−SH across the C═C bond in dimethyl maleate. Complexes of this dithiolate were prepared by treatment of $ZnMe_2$(TMEDA) and $ZnMe_2$-(PMDETA) with the dithiol (eq 2).



(2)

The complexes Zn[$S_2C_2H_2(CO_2Me)_2$](PMDETA) (**5**) and Zn-[$S_2C_2H_2(CO_2Me)_2$](TMEDA) (**6**) were obtained as colorless solids, which exhibited good solubility in polar organic solvents. The NMR data shows that **6** exists as a single isomer. Ionization of the α-CH would be expected to give the *d*,*l*-isomer of the dithiolate, but we observed no evidence for this, even in the presence of Et_3N. In fact, were the α-CH bonds moderately acidic, we would expect some deprotonation in the synthesis of **6** by the dimethylzinc. The ^{1}H NMR properties are temperature dependent reflecting the fluxional character of this family of complexes. For example, at room temperature the four methyl (NMe_2) groups in **5** appear equivalent. This averaging could arise if the dithiolate ligand rotates or if an amine group dissociates. At lower temperatures more complex spectra emerge, consistent with the C_s and eventual C_1 symmetry expected for this complex (Figure 1). Complex **6** exhibits similiar behavior (Figure 2).

Dehydrogenation of $ZnS_2C_2H_2(CO_2Me)_2$ Complexes. Treatment of **5** with 4 equiv of S immediately resulted in the rapid formation of **1**. The fate of the dithiolate ligand is uncertain, but several unidentified ^{1}H NMR signals are observed in the −CO_2*Me* region (δ 3.6−3.8). Upon heating at 95 °C, this solution afforded **3a** in ~85% yield (eq 3). The addition of dimethyl maleate did not affect the rate or the efficiency of the transformation. Thus the alkene does not serve as the hydrogen acceptor in the dehydrogenation process.



(3)

Treatment of **6** with S_8 resulted in the formation of hexasulfide **2**, together with smaller (equilibrium) quantities of the corresponding ZnS_5 and ZnS_4 derivatives.[10] As in the case of **5**, the dithiolate is oxidatively removed from the Zn center, presumably concomitant with the formation of an organo-

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(12) Jenner, G.; Rimmelin, J.; Libs, S.; Antoni, F. *Tetrahedron* **1976**, *32*, 1107−1111.

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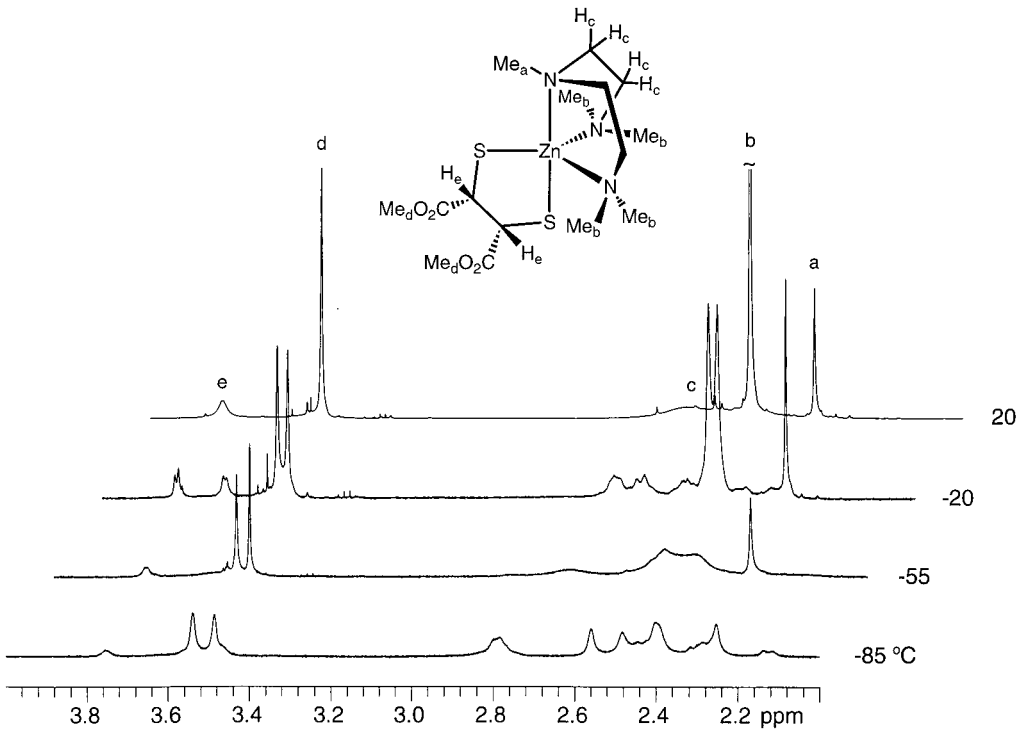


Figure 1. 500 MHz ^{1}H NMR spectra of Zn[$S_2C_2H_2(CO_2Me)_2$](PMDETA) (**5**) (CD_2Cl_2 solvent) recorded at various temperatures. Labels a−e refer to signal assignments for the room temperature spectrum.

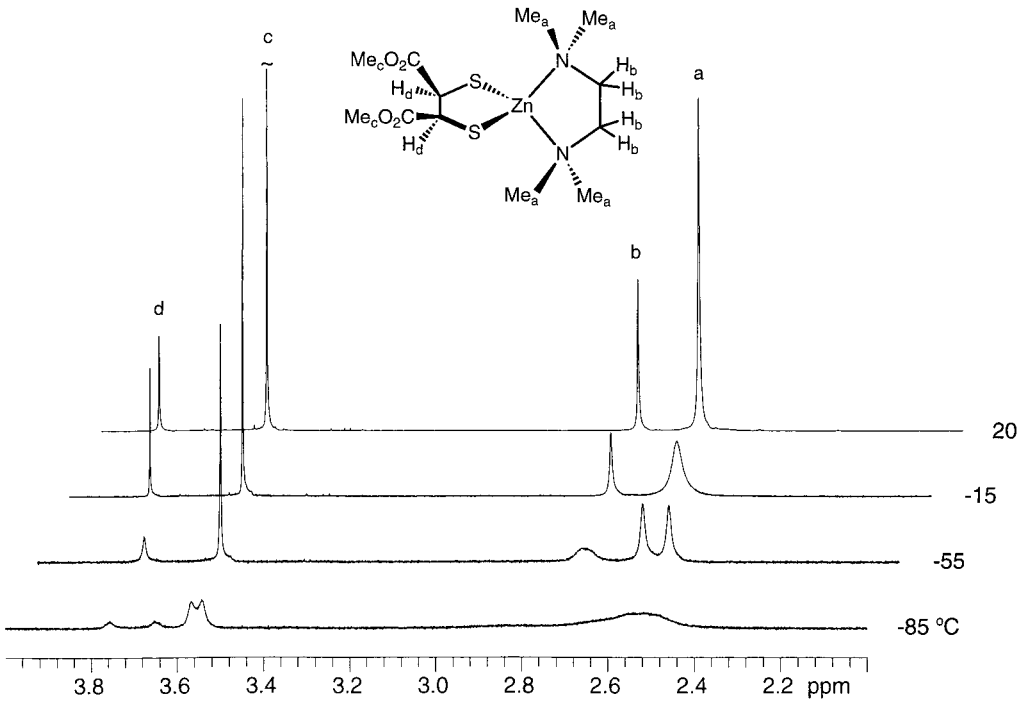


Figure 2. 500 MHz ^{1}H NMR spectra of Zn[$S_2C_2H_2(CO_2Me)_2$](TMEDA) (**6**) (CD_2Cl_2 solvent) recorded at various temperatures. Labels a−d refer to signal assignments for the room temperature spectrum.

polysulfide.[15] Further heating of this solution gave the dithiolene **4a** at a rate very similar to that for the conversion of **5** to **3a** (Figure 3). Solutions of the dithiolenes **3a** and **4a** are unreactive toward S_8.

We were interested to find that **5** and **6** are thermally unstable, because this is not typical for zinc thiolates. In refluxing MeCN solution, **6** decomposes over the course of several hours to give dimethyl fumarate and the dithiolene **4a**, both in ca. 20% yield, together with insoluble material, which we assume is ZnS (eq 4). It is probable that these species arise via the initial fragmentation of **6** into ZnS, S, and alkene. The elemental sulfur thus formed promotes the dehydrogenation of **6** to **4a**, as detailed

(15) Coucouvanis, D.; Patil, P. R.; Kanatzidis, M. G.; Detering, B.; Baenziger, N. C. *Inorg. Chem.* **1985**, *24*, 24−31.

(16) Osakada, K.; Yamamoto, T. *Inorg. Chem.* **1991**, *30*, 2328−2332.

(17) Cheon, J.; Zink, J. I. *J. Am. Chem. Soc.* **1997**, *119*, 3838−3839.

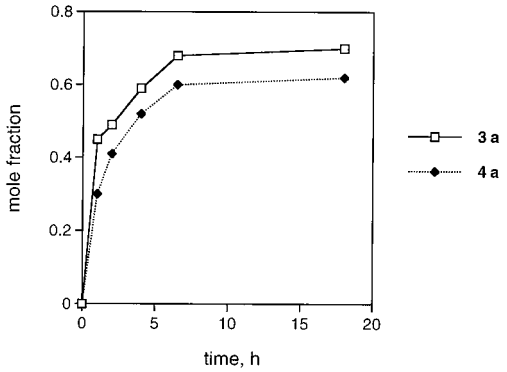
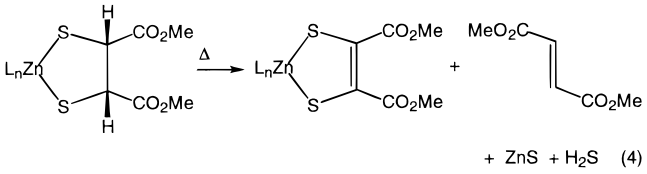


Figure 3. Time course of the formation of **3a** and **4a** from the reaction of **5** and **6** (1.4×10^{-2} M) with S_8 (0.5 equiv) in MeCN-d_3 (95 °C).

above. In no case do we observe free alkene in the reactions of **5** or **6** with sulfur (eg., eq 3).



The decomposition of zinc thiolates into ZnS has been previously demonstrated, but usually under more vigorous conditions.[16,17]

Metal Sulfide-Catalyzed Alkene Isomerization. The reactions of **1** and dimethyl maleate and crotononitrile were accompanied by significant isomerization of the alkene. In the synthesis of **3a** from dimethyl maleate, alkene isomerization is ~3 times faster than dithiolene formation (Figure 4).

Compared to **1**, dithiolene **3a** is a ~100× poorer catalyst for the isomerization of dimethyl maleate. The decreased nucleophilicity of **3a** does not arise for steric reasons, because the corresponding alkane dithiolate **5**, which has similar steric properties to **3a**, is a relatively efficient isomerization catalyst. The ability of these complexes to catalyze the isomerization of dimethyl maleate follows the order ZnS_4(PMDETA) > ZnS_6-(TMEDA) ≫ $Zn[S_2C_2(CO_2Me)_2]$(PMDETA).

Studies on $ZnS_4(Me_3TACN)$. In an effort to gain further insights into the new dehydrogenative route to dithiolenes, we examined a new analogue of **1**, $ZnS_4(Me_3TACN)$, where Me_3-TACN is *N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane.[18] This new complex was prepared in good yield by reaction of the triamine with **2** (eq 5).

$$ZnS_6(TMEDA) + Me_3TACN \rightarrow \underset{(\mathbf{2})}{} \quad \underset{(\mathbf{7})}{ZnS_4(Me_3TACN)} + TMEDA + 2\,S \quad (5)$$

Variable-temperature ^{1}H NMR spectra show that **7** is stereochemically nonrigid, with a time-averaged C_{3v} structure even at − 85 °C. The triamine does not dissociate from Zn because the two protons on the methylene groups remain diastereotopic. In solution **7** exists exclusively as the tetrasulfido complex; in contrast **1** exists in equilibrium with a higher (probably penta-) polysulfide.[10]

The results of a single-crystal X-ray diffraction study (Table 2) show that the Zn is pentacoordinate, like **1**. The zinc center

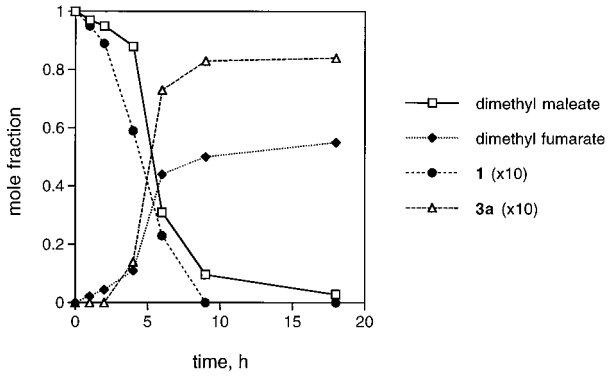


Figure 4. Time course of the components in the reaction of **1** (7.2×10^{-3} M) and dimethyl maleate (10 equiv) in MeCN-d_3 (95 °C).

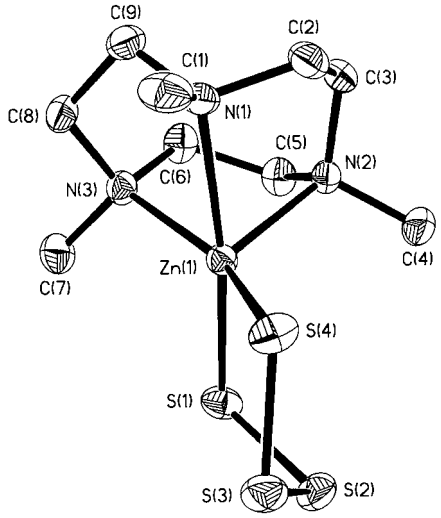


Figure 5. Structure of $ZnS_4(Me_3TACN)$ (**7**) with thermal ellipsoids set at the 50% (hydrogen atoms omitted for clarity).

Table 2. Bond Lengths (Å) and Angles (°) for **7**

Zn(1)−N(2)	2.143(2)	Zn(1)−N(3)	2.183(2)
Zn(1)−N(1)	2.359(2)	Zn(1)−S(1)	2.4580(6)
Zn(1)−S(4)	2.3316(6)	S(1)−S(2)	2.0589(9)
S(2)−S(3)	2.0513(10)	S(3)−S(4)	2.0523(9)
N(2)−Zn(1)−N(3)	83.43(7)	N(2)−Zn(1)−N(1)	80.24(7)
N(3)−Zn(1)−N(1)	78.23(7)	N(2)−Zn(1)−S(4)	117.78(5)
N(3)−Zn(1)−S(4)	152.52(5)	S(4)−Zn(1)−N(1)	87.94(5)
N(2)−Zn(1)−S(1)	100.95(5)	N(3)−Zn(1)−S(1)	93.81(5)
S(4)−Zn(1)−S(1)	98.52(2)	N(1)−Zn(1)−S(1)	171.81(5)
S(2)−S(1)−Zn(1)	98.50(3)	S(3)−S(2)−S(1)	103.58(4)
S(2)−S(3)−S(4)	104.14(4)	S(3)−S(4)−Zn(1)	103.66(3)

can be described as a distorted trigonal bipyramidal species with one amine and one sulfur atom occupying the axial positions (Figure 5). In **1**, the N−Zn linkage approximately trans (166°) to S is elongated (2.31 Å) vs the other two Zn−N bonds (2.17 and 2.19 Å). A similar elongation is seen in **7** ($\Delta r_{Zn-N} \approx 0.2$ Å), which was unexpected because the cyclic triamines is more highly constrained. One difference between **1** and **7** is that the latter adopts a more square pyramidal structure with the base of the square being defined by two sulfur and two nitrogen atoms. By virtue of the distortion, the polysulfido chelate in **7** is more exposed than in **1** (Figure 6).

We expected that **7**, with three highly constrained amine donors, would be more nucleophilic than **1**. Consistent with its high nucleophilicity, solid samples of **7**, which is bright yellow, readily (minutes) air-oxidize to the colorless thiosulfato derivative $ZnS_2O_3(Me_3TACN)$.[14] This behavior is similar to but much faster than the previously prepared ZnS_2O_3(PMDETA). Solu-

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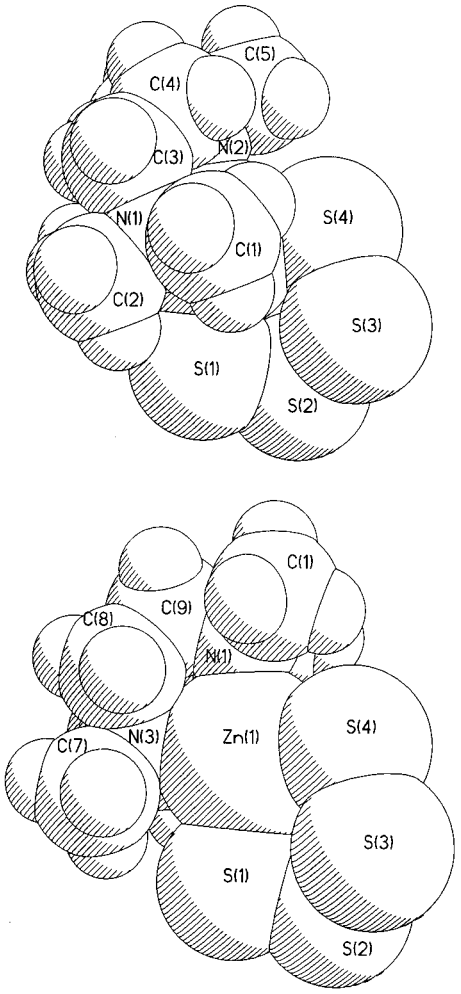
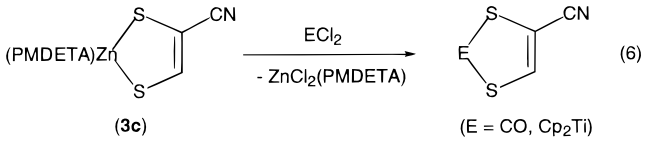


Figure 6. Space-filling models of ZnS_4(PMDETA) (**1**, top) and $ZnS_4(Me_3TACN)$ (**7**, bottom) highlighting the more exposed S_4 ligand in the Me_3TACN complex.

tions of **7** are significantly more reactive toward alkenes than are **1** and **2**: in refluxing MeCN, **7** converts dimethyl maleate to the dithiolene **8a** at a rate that is ~3 times that for **1**. Qualitatively, **7** is also better than **1** as a catalyst isomerization of dimethyl maleate to dimethyl fumarate.

Removal of Dithiolenes from Zn Centers. Given that the new dithiolene synthesis enjoys significant scope, we wanted to demonstrate that the organosulfur ligand could be removed from the zinc center. The zinc PMDETA dithiolenes **3a**−**d** were shown spectroscopically to react readily with the phosgene trimer in MeCN-d_3 to form their corresponding dithiocarbonates in quantitative yields. The transformations are signaled by the bleaching of the pale yellow color of the dithiolene. A preparative scale reaction of **3c** and $(COCl_2)_3$ produced the desired dithiocarbonate in 90% yield (eq 6).



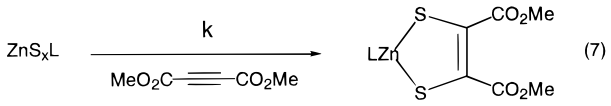
(3c) (E = CO, Cp_2Ti) (6)

In a similar manner, **3c** was found to react with Cp_2TiCl_2 in MeCN solution to give $Cp_2TiS_2C_2(CN)H$, obtained as green crystals in 84% yield. Using this methodology, Zn[S_2C_2-(CHO)H](PMDETA), which we could only obtain in impure form, was converted to $OCS_2C_2(CN)H$, which was readily purified.

Discussion

The chemistry of zinc thiolato complexes is a topical theme,[19] with particular recent interest focusing on the nucleophilic character of the thiolato ligands.[20−24] As we have shown in this and the previous paper,[10] one can prepare polysulfido complexes which are quite analogous to the known thiolato species but are promising reagents for the preparation of organosulfur compounds.

This and a previous paper[10] summarize our studies on the pentacoordinate zinc polysulfido centers, which are more nucleophilic than the corresponding tetracoordinated derivatives. The nucleophilic character of ZnS_4(PMDETA)[10] is demonstrated by its competition with ZnS_6(TMEDA) for the electrophilic alkyne dimethylacetylene dicarboxylate (DMAD)[26] (eq 7).



(7)

k(PMDETA) / k(TMEDA) ~ 100 (25 °C), see ref 10
k(Me_3TACN) / k(PMDETA) ~ 5 (25 °C)

The enhanced nucleophilicity of the pentacoordinate zinc polysulfido complexes led us to investigate electrophilic alkenes as substrates. A revealing finding was that the reaction of **1** with cis and trans alkenes (dimethyl maleate and dimethyl fumarate) produced the same product. The explanation for this initially surprising finding is that these reactions afford dithiolenes, thus the stereochemistry of the alkene is inconsequential. Further experiments showed that the reaction enjoys some generality in the case of electrophilic alkenes, which are otherwise known to be reactive toward sulfur nucleophiles.[26]

The conversion of dimethyl maleate (and dimethyl fumarate) to dithiolenes, while mechanistically informative, is not immediately useful because these dithiolenes can be prepared from DMAD, which is readily available. Similarly, the dithiolene $S_2C_2H(CO_2Me)^{2-}$ is more readily obtained from the corresponding alkyne.[25] The cyano-substituted dithiolenes Zn[$S_2C_2R(CN)$]-(PMEDTA) (R = H, Me, Et, Ph) are, however, of preparative interest.

We propose that the first step in the conversion of the alkene to a dithiolene involves the reversible formation of a dipolar intermediate, as indicated by the observation that the dithiolene synthesis is accompanied by significant isomerization of dimethyl maleate to dimethyl fumarate (Scheme 1). Nucleophiles such as PPh_3 are known to catalyze alkene[27] isomerization but the use of metal sulfido complexes is apparently novel.[28] In the dipolar species, rotation about the C−C bond is subject to only a small barrier.

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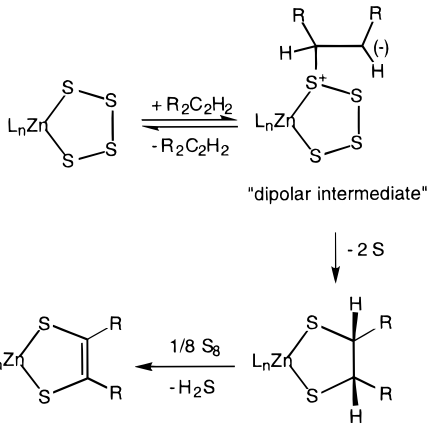
Scheme 1

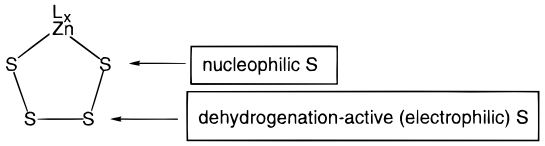


The relative rates of alkene isomerization vs dithiolene formation is a measure of the relative efficiencies of C−S scission vs ring closure to the alkanedithiolate for the dipolar intermediate. While the catalytic efficiency for isomerization differs for **1**, **2**, and **7**, the values of $k_{isom}/k_{dithiolene}$ are similar for the three complexes, being about 10. Ring closure of the dipolar intermediate, and elimination of elemental sulfur, would produce an alkanedithiolato complex. Such species were, however, not observed in any reaction involving alkene and the polysulfido complexes. We showed that such alkenedithiolato complexes, which were independently prepared, react with S_8 to produce dithiolenes. Furthermore the reactivity of the alkanedithiolates such as $Zn[S_2C_2H_2(CO_2Me)_2](PMDETA)$ is fully consistent with their *nonobservability*. Thus the alkanedithiolato complexes react with sulfur to give dithiolenes faster than the polysulfido complexes convert to dithiolenes.

The detailed pathway for the reaction of S_8 with the alkanedithiolate to give the dithiolene remains unclear. The addition of S_8 initially displaces the organosulfur ligand from the zinc forming $ZnS_4(PMDETA)$. It is already known that other thiolato complexes react with S_8 to give polysulfido complexes.[15] By implication, sulfidation of the dithiolato complex releases $S_xC_2H_2(CO_2Me)_2$. This species undergoes dehydrogenation, perhaps without involvement of the metal, to give a species that then reattaches to Zn to give the final dithiolene products. The noninvolvement of the metal in the dehydrogenation step is consistent with the finding that the rate of conversion of the alkanedithiolates to the dithiolene is independent of the coligands on zinc (TMEDA vs PMDETA).

Whereas sulfidation of $Zn[S_2C_2H_2(CO_2Me)_2](PMDETA)$ produces $ZnS_4(PMDETA)$, the corresponding dithiolene $Zn[S_2C_2(CO_2Me)_2](PMDETA)$ is unreactive toward S_8. This contrasting reactivity suggests that the S atoms in the dithiolene are less basic. This decreased basicity is also consistent with the diminished ability of the dithiolenes to catalyze the cis−trans isomerization of alkenes. It is likely that the rates of alkene isomerization could prove useful in assessing the nucleophilicity of other metal sulfido complexes.

Overall it can be seen that the sulfur atoms in the polysulfido ligand effect two transformations: nucleophilic addition to the electrophilic alkene and dehydrogenation of the alkanedithiolate. These two functions are effected, in a formal sense, by two different parts of the polysulfido chelate ring as shown below:



This picture is consistent with the finding that the triamine adducts of the zinc polysulfide are the best olefin isomerization. These species are the best nucleophiles because the triamine renders the Zn center especially electropositive which results in enhanced negative charge on the coordinated sulfur atoms. The electrophilic (noncoordinated) S atoms are poised to capture the incipient carbanion to give the alkanedithiolato complex (Scheme 1). In a formal sense, this same pool of noncoordinated S atoms is responsible for the oxidative dehydrogenation in the subsequent step. Of course, the pool of coordinated and uncoordinated sulfur atoms are subject to rapid exchange.

This conversion of dithiolates into dithiolene, e.g., **5** into **3a**, involves oxidation of a thiolate to an enethiolate. As such the dehydrogenation of the $ZnS_2C_2H_2R_2$ ring is reminiscent of the dehydrogenation of the $ZnOCH_2R$ moiety by liver alcohol dehydrogenase (LADH).[29−32] In LADH, the pyridinium cation $NAPD^+$ serves as the hydride acceptor whereas in the reactions described in this paper, elemental sulfur serves the role as hydride acceptor. The dehydrogenation activity of sulfur is well-known,[33,34] although its use in the dehydrogenation of metal complexes appears to be unprecedented.

Experimental Section

Synthetic operations were performed under a dinitrogen atmosphere using standard Schlenk-line techniques, unless mentioned otherwise. All chemicals were purchased from Aldrich and used without further purification. $ZnS_4(PMDETA)$,[10] dimercaptosuccinic acid dimethyl ester (DMSADME),[13] *N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane (Me_3-TACN),[18,35] and $ZnMe_2(TMEDA)$[36] were prepared by literature methods.

The following instruments were employed: Mattson Galaxy Series 3000 FTIR spectrometer and a Rigaku D-Max powder X-ray diffractometer with Cu target (X-ray diffraction). Solution NMR spectra were recorded with Varian NMR U400 and U500 spectrometers operating at 400 and 500 MHz, respectively. Chemical shifts are reported in ppm vs TMS (δ scale). Microanalyses were performed by the School of Chemical Sciences Microanalytical Laboratory.

$Zn[S_2C_2(CO_2Me)_2](PMDETA)$ (3a). A solution of 0.250 g (0.681 mmol) of $ZnS_4(PMDETA)$ in 50 mL of MeCN was treated with 2.95 g (20.4 mmol) of dimethyl fumarate or dimethyl maleate. The reaction solution was refluxed for 16 h. Upon cooling to room temperature, the solution was filtered. The filtrate was concentrated to 10 mL and then diluted with 50 mL of Et_2O to give an off-white powder. Yield: 0.261 g (86%). The product was identified by spectroscopic comparison with samples prepared previously from DMAD and $ZnS_4(PMDETA)$.[10]

$Zn[S_2C_2(H)CO_2Me](PMDETA)$ (3b). A solution of 0.261 g (0.711 mmol) of $ZnS_4(PMDETA)$ in 50 mL of MeCN was treated with 3.20 mL (3.08 g, 21.3 mmol) of methyl acrylate. The reaction solution was refluxed for 16 h. Upon cooling to room temperature, the solution was filtered, and the filtrate was concentrated to 10 mL and then diluted with 50 mL of Et_2O to give an off-white powder. Yield: 0.248 g (90%).

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The ^{1}H NMR spectrum of the product was identical to that for samples prepared previously from methyl propiolate and ZnS_4(PMDETA).[10]

Zn[S_2C_2(H)CN](PMDETA) (3c). A solution of 0.290 g (0.790 mmol) of ZnS_4(PMDETA) in 50 mL of MeCN was treated with 1.60 mL (1.29 g, 24.3 mmol) of acrylonitrile. The reaction solution was refluxed for 16 h. Upon cooling to room temperature, the solution was filtered, and the filtrate was concentrated to 10 mL and then diluted with 50 mL of Et_2O to give a tan powder. Yield: 0.238 g (85%). ^{1}H NMR (CD_3CN): δ 7.35 (bs, 1H, C*H*), 2.77 (m, 2H, CH_2), 2.66 (m, 4H, CH_2), 2.56 (m, 2H, CH_2), 2.34 (s, 15H, NCH_3). IR (KBr): 2187 cm^{-1} ($\nu_{C\equiv N}$). Anal. Calcd for $C_{12}H_{24}N_4S_2Zn$: C, 40.73; H, 6.84; N, 15.83; S, 18.12; Zn, 18.48. Found: C, 40.85; H, 6.76; N, 15.71; S, 17.78; Zn, 18.56.

Zn[S_2C_2(Ph)CN](PMDETA) (3d). A solution of 0.256 g (0.698 mmol) of ZnS_4(PMDETA) in 10.0 mL (10.3 g, 79.6 mmol) of *trans*-cinnamonitrile was refluxed for 72 h. Upon cooling to room temperature, the solution was diluted with 75 mL of Et_2O to give a pale orange powder. Yield: 0.225 g (75%). ^{1}H NMR (CD_3CN): δ 7.38 (m, 2H, C*H*), 7.26 (m, 2H, C*H*), 7.20 (m, 1H, C*H*), 2.78 (m, 2H, CH_2), 2.68 (m, 4H, CH_2), 2.58 (m, 2H, CH_2), 2.42 (s, 12H, NCH_3), 2.37 (s, 3H, NCH_3). IR (KBr): 2184 cm^{-1} ($\nu_{C\equiv N}$). Anal. Calcd for $C_{18}H_{28}N_4S_2Zn$: C, 50.28; H, 6.56; N, 13.03; S, 14.92; Zn, 15.21. Found: C, 50.68; H, 6.53; N, 12.63.

Zn[S_2C_2(Me)CN](PMDETA) (3e). A solution of 0.248 g (0.676 mmol) of ZnS_4(PMDETA) in 10.0 mL (8.24 g, 123 mmol) of crotononitrile was refluxed for 72 h. Upon cooling to room temperature, the solution was diluted with 75 mL of Et_2O to give a dark brown solid. The crude product was extracted with 30 mL of MeCN. The solution volume was reduced to 5 mL and then diluted with 60 mL of Et_2O to give a light brown powder. Yield: 0.150 g (~60%). This species was not isolated in analytical purity, but was characterized on the basis of spectroscopic data. ^{1}H NMR (CD_3CN): δ 2.77 (m, 2H, CH_2), 2.66 (m, 4H, CH_2), 2.56 (m, 2H, CH_2), 2.42 (s, 12H, NCH_3), 2.36 (s, 3H, NCH_3), 2.25 (s, 3H, CH_3). IR (KBr): 2178 cm^{-1} ($\nu_{C\equiv N}$).

Zn[S_2C_2(H)CHO](PMDETA) (3f). A solution of 0.240 g (0.654 mmol) of ZnS_4(PMDETA) in 50 mL of MeCN was treated with 450 μL (378 mg, 6.73 mmol) of acrolein. The reaction solution was refluxed for 48 h. Upon cooling to room temperature, the solution was filtered, and the filtrate was concentrated to 5 mL and then diluted with 50 mL of Et_2O to give a light brown powder. Yield: 0.238 g (85%). This species was not isolated in analytical purity, but was characterized on the basis of spectroscopic data as well as its conversion to the dithiocarbonate OCS_2C_2(CHO)H (see below). ^{1}H NMR (CD_3CN): δ 9.23 (s, 1H, C*H*O), 7.88 (bs, 1H, C*H*), 2.77 (m, 2H, CH_2), 2.66 (m, 4H, CH_2), 2.55 (m, 2H, CH_2), 2.40 (s, 3H, NCH_3), 2.34 (s, 12H, NCH_3). IR (KBr): 1626 cm^{-1} ($\nu_{C=O}$).

Zn[$S_2C_2(CO_2Me)_2$](TMEDA) (4a) from Dimethyl Fumarate. A suspension of 0.245 g (0.655 mmol) of ZnS_6(TMEDA) in 50 mL of MeCN was treated with 2.82 g (19.6 mmol) of dimethyl fumarate. The reaction solution was refluxed for 40 h. Upon cooling to room temperature, the solution was filtered, and the filtrate was concentrated to 10 mL and then diluted with 50 mL of Et_2O to give a light yellow powder. Yield: 0.208 g (82%). The product was identified by comparison of its ^{1}H NMR spectrum with that for samples prepared previously.[26]

Zn[S_2C_2(H)CN](TMEDA) (4b). A suspension of 0.256 g (0.698 mmol) of ZnS_6(TMEDA) in 10.0 mL (10.3 g, 79.6 mmol) of acrylonitrile was refluxed for 40 h. Upon cooling to room temperature, the solution was diluted with 70 mL of Et_2O to give a light orange powder. Yield: 0.225 g (75%). ^{1}H NMR (CD_3CN): δ 7.31 (s, 1H, CH), 2.83 (s, 4H, CH_2), 2.52 (s, 12H, NCH_3). IR (KBr): 2192 cm^{-1} ($\nu_{C\equiv N}$). Anal. Calcd for $C_9H_{17}N_3S_2Zn$: C, 36.42; H, 5.77; N, 14.46. Found: C, 36.31; H, 5.41; N, 13.80.

Zn[$S_2C_2(CO_2Me)_2H_2$](PMDETA) (5). A solution of 0.502 g (1.29 mmol) of **6** in 50 mL of CH_2Cl_2 was treated with 275 μL (0.228 g, 1.32 mmol) of PMDETA. The reaction was stirred for 15 min, and then the solution volume was reduced to 5 mL. The solution was then diluted with 60 mL of Et_2O to give a pale-yellow powder. Yield: 0.533 g (92%). ^{1}H NMR (CD_3CN): δ 3.69 (s, 2H, CH), 3.51 (s, 6H, OCH_3), 2.62 (bs, 8H, CH_2), 2.47 (s, 12H, NCH_3), 2.29 (s, 3H, NCH_3). IR (KBr): 1745 ($\nu_{C=O}$), 1714 cm^{-1} ($\nu_{C=O}$). Anal. Calcd for $C_{15}H_{31}N_3O_4S_2Zn$: C, 40.31; H, 6.99; N, 9.40. Found: C, 39.53; H, 6.65; N, 9.23.

Table 3. Crystal Data and Structure Refinement for **7**

empirical formula	$C_9H_{21}N_3S_4Zn$
formula wt	364.90
temp	198(2) K
wavelength	0.71073 Å
cryst syst, space group	monoclinic, *C*2/*c*
unit cell dimens (Å)	$a = 27.7112(2)$; $b = 7.83480(10)$; $c = 15.276$
(5747 reflns with $4 = \Theta = 28$)	$\alpha = \gamma = 90°$; $\beta = 116.0470(10)°$
vol, *Z*	2979.71(4) Å^3, 8
density (calcd)	1.627 Mg/m^3
abs coeff	2.192 mm^{-1}
cryst size	0.19 × 0.16 × 0.09 mm
cryst color/morph	yellow/prism
Θ range for data collection	1.64 to 28.28°
index ranges	$-36 \le h \le 28$, $-10 \le k \le 10$, $-20 \le l \le 19$
collection method	0.25° ω scans for 0.25 min/scan
reflns collected	9455 [$R_{int} = 0.0336$]
indep reflns	3587 [3022 obsd, $I > 2\sigma(I)$]
abs cor	ψ scan
max and min transmission	0.996 and 0.838
refinement (shift/err = 0.000)	full-matrix least-squares on F^2
data/restraints/parameters	3583/0/154
GOF on F^2	1.125
final *R* indices (obsd data)[a]	$R_1 = 0.0308$, $wR_2 = 0.0648$
R indices (all data)[a]	$R_1 = 0.0428$, $wR_2 = 0.0730$
largest diff peak and hole	0.355 and −0.390 e A^{-3}

[a] $w = 1/[\sigma^2(F_o^2) + (0.0211P)^2 + 5.0561P]$ where $P = (F_o^2 + 2F_c^2)/3$.

Thermolysis of Zn[$S_2C_2(CO_2Me)_2H_2$](PMDETA) to 3a. A solution of 5.7 mg (1.3×10^{-2} mmol) of **5** in 1 mL of MeCN-d_3 was treated with 1.0 mg (6.2×10^{-3} mmol) of methyl 4-cyanobenzoate as an internal standard. The reaction solution was refluxed for 18 h. ^{1}H NMR data showed a 15% conversion of **5** to **3a** and 10% formation of dimethyl fumarate.

Zn[$S_2C_2(CO_2Me)_2H_2$](TMEDA) (6). A solution of 0.867 g (4.09 mmol) of $ZnMe_2$(TMEDA) in 60 mL of CH_2Cl_2 was treated dropwise with a solution of 0.863 g (4.10 mmol) of $(HS)_2C_2(CO_2Me)_2H_2$ in 40 mL of CH_2Cl_2. The rate of addition was ~1 drop/s over 3 h. Upon completion, a small amount of precipitate was filtered off, and the solution volume was reduced to ~5 mL. The solution was then diluted with 50 mL of Et_2O to give a white powder. Yield: 1.39 g (87%). ^{1}H NMR (CD_2Cl_2): δ 3.75 (s, 2H, CH), 3.56 (s, 6H, OCH_3), 2.77 (s, 4H, CH_2), 2.54 (s, 12H, NCH_3). IR (KBr): 1733 ($\nu_{C=O}$), 1712 cm^{-1} ($\nu_{C=O}$). Anal. Calcd for $C_{12}H_{24}N_2O_4S_2Zn$: C, 36.76; H, 6.19; N, 6.96. Found: C, 36.97; H, 6.21; N, 7.19.

Thermolysis of Zn[$S_2C_2(CO_2Me)_2H_2$](TMEDA) to 4a. A solution of 5.0 mg (1.3×10^{-2} mmol) of **6** in 1 mL of MeCN-d_3 was treated with 1.0 mg (6.2×10^{-3} mmol) of methyl 4-cyanobenzoate as an internal standard. The reaction solution was refluxed for 18 h. ^{1}H NMR data showed a 20% conversion of **6** to **4a** and 15% formation of dimethyl fumarate.

Isomerization of Dimethyl Maleate by 1 and 2. In a typical experiment, a solution of 7.2×10^{-3} mmol of **1** or **2** in 1 mL MeCN-d_3 was treated with 9.0 μL (10 mg, 7.2×10^{-2} mmol) of dimethyl maleate. Approximately, 0.5 mg (3×10^{-3} mmol) of methyl 4-cyanobenzoate was added as an internal standard. The solution was refluxed for various times, and the ^{1}H NMR spectra were obtained. The mole fractions of olefin isomers and dithiolenes are presented in Figure 4.

Dehydrogenation of Zn[$S_2C_2(CO_2Me)_2H_2$]L_n (L = TMEDA, PMDETA) with S_8. In a typical experiment, a solution of 1.4×10^{-2}

mmol of **5** or **6** in 1 mL of MeCN-d_3 was treated with 1.8 mg (5.6×10^{-2} mmol) of S_8. Approximately 1 mg (6×10^{-3} mmol) of methyl 4-cyanobenzoate was added as an internal standard. The solution was refluxed for various times, and the ^{1}H NMR spectra were obtained. The mole fractions of dithiolenes are presented in Figure 3.

$ZnS_4(Me_3TACN)$ (7). A suspension of 1.92 g (5.13 mmol) of **2** in 50 mL of MeCN was treated with 1.10 mL (0.972 g, 5.68 mmol) of Me_3TACN. Immediately, a white flocculent precipitate (sulfur) is formed. After 15 min stirring, the solution was filtered, and the filtrate was concentrated to ~5 mL. A yellow microcrystalline solid was precipitated. Upon dilution of the solution with 50 mL of Et_2O, complete precipitation occurred. Yield: 1.51 g (80%). ^{1}H NMR (CD_3CN): δ 2.78 (m, 12H, CH_2), 2.59 (s, 9H, CH_3). IR (KBr): 492 cm^{-1} (ν_{ss}). Anal. Calcd for $C_9H_{21}N_3S_4Zn$: C, 29.62; H, 5.80; N, 11.51. Found: C, 29.76; H, 5.76; N, 11.33.

$Zn[S_2C_2(CO_2Me)_2](Me_3TACN)$ (8a). A solution of 0.245 g (0.671 mmol) of **7** in 50 mL of MeCN was treated with 2.50 mL (2.88 g, 20.0 mmol) of dimethyl maleate. The reaction solution was refluxed for 16 h. Upon cooling to room temperature, the solution was filtered. The filtrate was concentrated to 5 mL and then diluted with 75 mL of Et_2O to give an off-white powder. Yield: 0.265 g (89%). The same compound was prepared by treatment of 0.505 g (1.38 mmol) of **7** in 50 mL of MeCN with 200 μL (0.231 g, 1.63 mmol) of DMAD. After 1 h, the reaction mixture was filtered, and the filtrate was concentrated to 10 mL and then diluted with 60 mL of Et_2O to give a pale orange powder. Yield: 0.548 g (90%). The filtrate was cooled to −20 °C for 1 week. Pale orange single crystals were obtained (used for X-ray crystallographic analysis). ^{1}H NMR (CD_3CN): δ 3.59 (s, 6H, OCH_3), 2.75 (m, 12H, CH_2), 2.53 (s, 9H, CH_3). IR (KBr): 1708 and 1677 cm^{-1} ($\nu_{C=O}$). Anal. Calcd for $C_{15}H_{27}N_3O_4S_2Zn$: C, 40.68; H, 6.14; N, 9.49. Found: C, 40.39; H, 6.01; N, 9.62.

$OCS_2C_2(H)R$ (R = CN, CHO). In a representative reaction, a solution of 0.505 g (1.43 mmol) of **3c** in 50 mL of THF was treated with 0.145 g (0.489 mmol) of $(Cl_3CO)_2CO$. After 18 h, the clear yellow solution was concentrated to give a yellow residue which was extracted into 50 mL of $CHCl_3$, which was washed twice with 50 mL of H_2O, and dried with $MgSO_4$. Removal of the solvent gave a yellow solid. Yield: 0.184 g (90%). ^{1}H NMR (CD_2Cl_2): δ 7.98 (s, 1H, CH), 6.08 (bs, 10H, CH). IR (KBr): 2235 ($\nu_{C\equiv N}$), 1638 cm^{-1} ($\nu_{C=O}$). Anal. Calcd for C_4HNOS_2: C, 33.55; H, 0.70; N, 9.78. Found: C, 33.49; H, 0.93; N, 9.57. The corresponding formyl derivative $OCS_2C_2(H)CHO$[38] was prepared analogously and identified by ^{1}H NMR spectroscopy (CD_3CN): δ 9.53 (s, 1H, COH), 8.14 (s, 1H, CH).

$Cp_2TiS_2C_2(H)CN$. A solution of 0.275 g (0.777 mmol) of **3c** in 50 mL of MeCN was treated with 0.200 g (0.803 mmol) of Cp_2TiCl_2. After 3 h, the green solution was concentrated to dryness. An extract of the green residue in ~25 mL of CH_2Cl_2 was filtered through ~30 g of silica gel, and the solvent was evaporated. The green residue was recrystallized from 5 mL of CH_2Cl_2 by the addition of 45 mL of hexanes. Yield: 0.198 g (84%). ^{1}H NMR (CD_2Cl_2): δ 7.98 (s, 1 H, CH), 6.08 (bs, 10 H, CH). IR (KBr): 2195 cm^{-1} ($\nu_{C\equiv N}$). Anal. Calcd for $C_{13}H_{11}NS_2Ti$: C, 53.25; H, 3.78; N, 4.75. Found: C, 53.15; H, 3.87; N, 4.69.

Crystal Preparation and Structure Refinement Summary for 7. Crystals were grown from layering Et_2O/MeCN. The data crystal, with the size 0.19, 0.16, and 0.09 mm, was mounted using Paratone-N (Exxon) on to a thin glass fiber. The crystal was bound by faces (1, 0−1), (−2, 0, 3), (−1, 0, 0), (1, 0, 0), (−1, 1, 0), and (−1, −1, 1). Distances from the crystal center to those facial boundaries were 0.04, 0.045, 0.095, 0.095, 0.09, and 0.08 mm, respectively. Systematic conditions suggested the space group *C*2/*c* (Table 3). The structure was solved by Direct Methods.[37] The space group choice was confirmed by successful convergence of the full-matrix least-squares refinement on F^2. The highest peaks in the final difference Fourier map were 0.335 e/Å^3; the final map had no other significant features. A final analysis of variance between observed and calculated structure factors showed no dependence on amplitude or resolution.

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Supporting Information Available: Atomic coordinates and anisotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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