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(60/40) solution, and subsequent recrystallization from the same solvent yielded 0.2 g (10%) of (η^5-C_5H_5)W(CO)$_2$(PPh$_3$)CPM, mp 135–137 °C.

Kinetic Analysis. Kinetic studies on the rate of the reaction between Mo–CPM and PPh$_3$ were performed in THF under pseudo-first-order conditions, monitoring the rate of disappearance of the CO stretching frequency at 2012 cm^{-1}. All spectroscopic analysis was performed by using a Perkin-Elmer 580B infrared instrument and CaF$_2$ cells. The reaction was found to be first order with respect to the Mo complex and zero order with respect to PPh$_3$. The various rate constants are recorded in Table IV, and the resulting activation parameters are $\Delta H = 11.2$ kcal/mol and $\Delta S = -28.0$ eu.

Acknowledgment. This research was supported by the Robert A. Welch Foundation, Houston, TX, the donors, the Petroleum Research Fund, administered by the American Chemical Society, and by the NIH Division of Research Resources (RR-08012). The infrared spectrophotometer was purchased with funds awarded by the NSF.

Supplementary Material Available: Tables of atomic coordinates, temperature factor expressions, and complete bond lengths and bond angles for the Fe–COCPM structure (6 pages); a listing of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

Chemistry of $(RC_5H_4)_2TiS_5$. New Information on Its Reactions with Nucleophiles, Syntheses and Reactions of 1,4-$[(RC_5H_4)_2Ti]_2S_4$, and a Second Isomer of $(RC_5H_4)_2TiS_2C_2(CO_2Me)_2$

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Received August 28, 1986

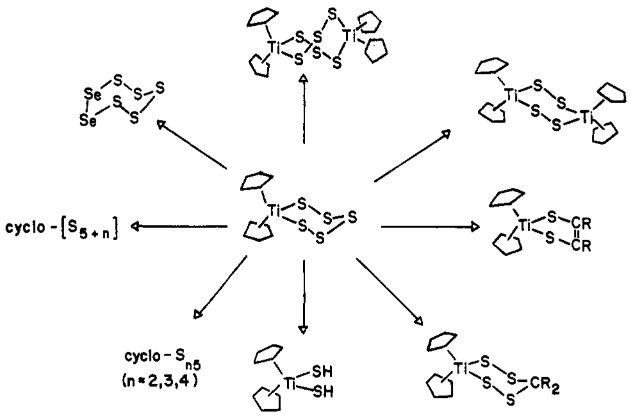
Described are a series of reactions of $[(RC_5H_4)_2TiS_x]_n$ (R = H, CH$_3$, *i*-Pr; x = 5 (**1**, n = 1), 3 (**2**, n = 2), 2 (**3**, n = 2)). The reactions of **1** with organophosphines in the presence of acetylenes gives the dithiolenes $(RC_5H_4)_2TiS_2C_2R_2$. In the absence of acetylenes desulfurization of **1** gives the dimers $[(RC_5H_4)_2Ti]_2S_x$ (x = 4, 6). These dimers could not be prepared from $(RC_5H_4)_2TiCl_2$ and Li_2S_x; however, reaction of $(RC_5H_4)_2TiCl_2$ and Li_2S_2 in the presence of CS$_2$ gives high yields of **3**. The oxidation of $(RC_5H_4)_2Ti(SH)_2$ also gives **3**. The mechanisms of these reactions are discussed in light of corresponding work on 1,2-$C_6H_4(SR)_2$ (R = H, S$_x$). The structure of 1,4-$[(i\text{-}PrC_5H_4)_2Ti]_2S_4$ (**3c**) was determined by X-ray crystallography. It crystallizes in the monoclinic space group $C2/c$ with a = 35.481 (10) Å, b = 10.976 (3) Å, c = 23.553 (6) Å, β = 130.74 (3)°, V = 6950 (3) Å^3, and Z = 4 and refined to R = 0.052 and $R(w)$ = 0.074. The analysis confirms the structure as an 1,4-M$_2$S$_4$ ring in the chair conformation. Whereas **1** reacts with electrophilic acetylenes to give dithiolenes, the corresponding ambient temperature reaction of **3** with dialkyl acetylenedicarboxylates (DEAD or DMAD) gives vinyl disulfides. The structure of the vinyl disulfide complex $(CH_3C_5H_4)_2TiS_2C_2(CO_2CH_2CH_3)_2$ (**4**) was confirmed by X-ray diffraction (monoclinic, $P2_1/n$; a = 9.772 (2) Å, b = 14.573 (2) Å, c = 11.756 (2) Å, β = 100.25 (1)°, V = 1647.4 (5) Å^3, and Z = 4; refinement to R = 0.0387 and $R(w)$ = 0.0411). The TiSSCC ring adopts an envelope conformation. The formation of **4** from **3** occurs via a bimolecular pathway according to the following equation $d[4]/dt = (4.2 \times 10^{-3}\ M^{-1}\ s^{-1})[3][DMAD]$. Compound **4** easily rearranges to give the dithiolene. Labeling studies (C$_5$H$_5$ vs. CH$_3$C$_5$H$_4$; DMAD vs. DEAD; ^{32}S vs. ^{34}S) demonstrate the intramolecularity of this rearrangement. These findings suggest that other acetylene–metal sulfide reactions may proceed via this unexpected pathway.

Introduction

There is presently great interest in the coordination chemistry of main-group atoms, chains, and clusters. Considerable information is already available concerning the structural chemistry of transition metal derivatives of "naked" metalloids. Relatively little is however known about the *reactivity* of these simple main-group ligands.

In recent years our interests have focused on inorganic sulfur ligands. Molecular metal sulfides, disulfides, and polysulfides are well-known. Binary metal sulfido anions and the neutral metal carbonyl and cyclopentadienyl sulfides have received the greatest attention. The metal sulfido anions are attractive because of their relative simplicity, and studies on such compounds are relevant to important transformations underlying various industrial,[1] biological,[2] and mineralogical[3] processes. The organometallic sulfides are of special interest because, in our opinion, their reaction chemistry presently exceeds in scope

Scheme I



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that of the binary sulfides. An additional attraction for the organometallic sulfides is their good kinetic behavior and their solubility in nonpolar solvents, both are useful in mechanistic studies.

In a series of papers we have described different aspects of the chemistry of $(RC_5H_4)_2TiS_5$ (Scheme I). The present report concerns several new mechanistic and structural results some of which expand considerably on points made in some earlier papers. We have performed several experiments that shed light on reactive intermediates formed from $(RC_5H_4)_2TiS_5$. There is presently little information available on highly reactive intermediates in metal sulfide chemistry. It was through these studies that we developed an interest in 1,4-$[(RC_5H_4)_2Ti]_2S_4$ which is more reactive than the pentasulfide. Of great interest is the finding that the reaction of this Ti_2S_4 cycle with acetylenes gives the dithiolene product via an isolable vinyl disulfide intermediate. The formation and rearrangement of the vinyl disulfide has been studied by kinetic and labeling experiments.

Results and Discussion

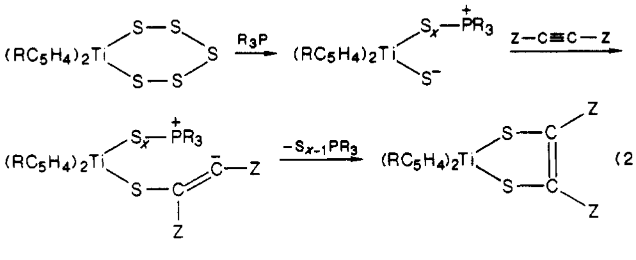
Reactions of $(RC_5H_4)_2TiS_5$ with Tertiary Phosphines. We have previously reported that the reaction of $(RC_5H_4)_2TiS_5$ (1) and tertiary phosphines affords six- and eight-membered rings of the general formula $[(RC_5H_4)_2Ti]_2S_x$ (x = 4 and 6) in yields ranging from 30 to 50% (eq 1).[4,5] The product distribution that results

$$\underset{\mathbf{1a-c}}{2(RC_5H_4)_2TiS_5} \xrightarrow[-R_3PS]{+R_3P} \underset{\substack{\mathbf{2a-c}\ (x = 6)\\ \mathbf{3a-c}\ (x = 4)}}{[(RC_5H_4)_2Ti]_2S_x} \qquad (1)$$

a, R = H; **b**, R = CH_3; **c**, R = i-Pr

from sulfur abstraction from 1 has been shown to be primarily a function of the nucleophilicity of the phosphines.[6] Separate experiments show the Ti_2S_6 rings are not precursors to the Ti_2S_4 rings. These desulfurizations are closely related to reaction of elemental sulfur with phosphines with the important exception that ring contraction products, e.g., S_x ($x \neq 8$), are *not* isolable in the PR_3–S_8 reaction.[9] The low reactivity of 3 and 1,4-$[(RC_5H_4)_2Ti]S_4CH_2$[7] toward phosphines implies that it is the S(β)–S(γ) linkage in 1 which is attacked by the phosphine.

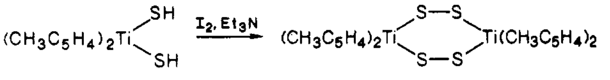
The formation of ionic intermediates[9-11] in the reaction of 1 with phosphines is evidenced by the rapid formation of the dithiolene $(RC_5H_4)_2TiS_2C_2(CO_2CH_3)_2$ when this desulfurization is conducted in the presence dimethyl acetylenedicarboxylate (DMAD), even at −20 °C (eq 2). For comparison, the reaction of $(RC_5H_4)_2TiS_5$ and DMAD in the absence of $(n\text{-}C_4H_9)_3P$ requires temperatures in excess of 110 °C.[8]



(2)

Nucleophiles other than phosphines react with $(RC_5H_4)_2TiS_5$. The reaction of $(RC_5H_4)_2TiS_5$ with aqueous ammonium sulfide in the presence of ketones of CH_2Br_2 produces the 1,4-$[(RC_5H_4)_2Ti]S_4CR_2$ complexes.[7]

Alternative Syntheses of 1,4-$[(RC_5H_4)_2Ti]_2S_4$. We found that $(CH_3C_5H_4)_2Ti(SH)_2$[12,13] undergoes oxidation by iodine in the presence of base to give a 40–50% yield of the tetrasulfide **3b** (eq 3). There is precedent for the intermolecular coupling of metal thiols such as the conversion of $[Cr(H_2O)_5SH]^{2+}$ to $(\mu\text{-}S_2)[Cr(H_2O)_5]_2{}^{4+}$.[14,15]



(3)

3b

Köpf and Shaver had previously reported that only $(RC_5H_4)_2TiS_5$, is formed from $(RC_5H_4)_2TiCl_2$ and solutions of $S_x{}^{2-}$ (x = 1–7).[16-18] We have reconfirmed this result. In contrast, we find that the addition of CS_2 to a solution of Li_2S_2,[19] *prior* to its addition to a THF slurry of $(RC_5H_4)_2TiCl_2$, afforded a high yield of 3. These experiments were originally conducted in an effort to prepare the perthiocarbonato complex, and the formation of 3 under these conditions is interpreted in terms of the ejection of CS_2 from an unstable perthiocarbonate intermediate (eq 4). Such elimination pathways have been

$$(RC_5H_4)_2TiCl_2 \xrightarrow[-2LiCl]{+Li_2CS_4} (RC_5H_4)_2TiCS_4 \xrightarrow{-CS_2} \underset{\mathbf{3b}}{{}^1/_2 1,4\text{-}[(RC_5H_4)_2Ti]_2S_4} \qquad (4)$$

demonstrated recently by Coucouvanis and co-workers, who found, inter alia, that the dimeric complex bis(perthiocarbonate) complex $[Mo_2S_4(CS_4)_2]^{2-}$ could be reversibly converted to $[Mo_2S_8]^{2-}$.[20,21]

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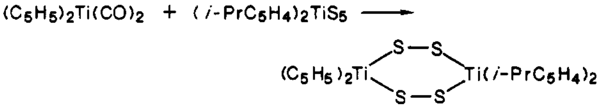
Table I. Bond Distances (Å) and Angles (deg) for 1,4-$(RC_5H_4)_2TiS_4X$

parameter	X = S; R = H[a]	X = $(i\text{-}PrC_5H_4)_2Ti$; R = *i*-Pr (**3c**)	X = CH_2; R = *i*-Pr[b]
	Bond Distances		
Ti–S(1)	2.448 (1)	2.441 (1)	2.438 (1)
Ti–S(2)	2.422 (1)	2.420 (1)	2.420 (1)
S(1)–S(3)	2.059 (2)	2.061 (2)	2.055 (1)
S(2)–S(4)	2.059 (2)	2.061 (2)	2.051 (2)
Ti–CNT1[c]	2.071	2.082	2.073
Ti–CNT2	2.066	2.069	2.063
S(1)···S(2)	3.58	3.510	3.489
	Bond Angles		
Ti–S(1)–S(2)	107.41 (6)	108.21 (7)	107.4 (1)
Ti–S(5)–S(4)	108.58 (5)	113.89 (6)	109.4 (1)
S–Ti–S	94.59 (4)	92.47 (5)	91.6 (1)
Cp_a–Ti–Cp_b	133.7	131.6	130.1
	Dihedral Angles		
S–Ti–S/S(1)S(2)S-(3)S(4)	58.1	58.7	56.1
S–X–S/S(1)S(2)S-(3)S(4)	71.6		73.2

[a] Reference 24. [b] Reference 7. [c] CNT1 = centroid for C(1)–C(5); CNT2 = centroid for C(9)–C(13).

Attempts to promote the redistribution of **3b** and **3c** led primarily to decomposition and gave only small amounts of the unsymmetrical dimers. On the other hand, the reaction of $(C_5H_5)_2Ti(CO)_2$ and pentasulfide **1c** gave ca. 55% of the unsymmetrical tetrasulfide shown in eq 5. Reaction 5 did not afford any of the symmetrical **3c**, $(C_5H_5)_2TiS_5$, or Ti_2S_5 cycles.



$$(C_5H_5)_2Ti(CO)_2 + (i\text{-}PrC_5H_4)_2TiS_5 \longrightarrow (C_5H_5)_2Ti(S_4)Ti(i\text{-}PrC_5H_4)_2 \quad (5)$$

The Structure of 1,4-[(*i*-PrC$_5$H$_4$)$_2$Ti]$_2$S$_4$ (3c). The asymmetric unit consists of two independent half molecules of the dimer and a partial occupancy of CH_2Cl_2. The two independent molecules are structurally similar; the nondisordered molecule was used for comparison to other $(RC_5H_4)_2Ti$–S systems (Table I). The disulfide distances in **3**, orthorhombic sulfur,[22] and **1**[23] are all within 0.01 Å of 2.06 Å. The environment about the titanium centers is very similar to that observed in other $(RC_5H_4)_2Ti$–S compounds.[7] The cyclo-M_2S_4 unit is not common in metal sulfide chemistry.[24]

The apparent instability of the titanocene di- (and tri-) sulfide monomers, with respect to the dimers, begs the more general questions as to why some ME_x ring sizes are preferred over others. Although $(RC_5H_4)_2TiS_2$ is not stable, the analogous molybdenum complex $(C_5H_5)_2MoS_2$ has been reported as well as $(C_5H_5)_2MoS_4$.[26,27] The structure of $(C_5H_5)_2Mo(S_2)$ is supported by Green's $(C_5H_5)_2Mo(P_2H_2)$ which has been characterized by X-ray diffraction.[28] The stability of $Cp^*_2MS_x$ ($Cp^* = C_5(CH_3)_5$), where $x = 3$ for M = Ti[29] and $x = 2$ for M = V,[30] indicates that steric effects dictate the stabilities of these MS_x rings. The existence of these small-ring compounds also lends credence to our proposal that intermediates of the type $(RC_5H_4)_2TiS_x$ (x = 3, 2) are formed in the desulfurizations of **1**. Variations in polychalcogenide–metal ring size have also been observed in non-metallocene systems. The compound $[Ir(dmpe)_2]Cl$ (dmpe = 1,2-$(Me_2P)_2C_2H_4$) reacts with Se_8 to give $[Ir(Se_4)(dmpe)_2]^+$ which upon treatment with $(C_6H_5)_3P$ affords $[Ir(Se_2)(dmpe)_2]^+$.[31]

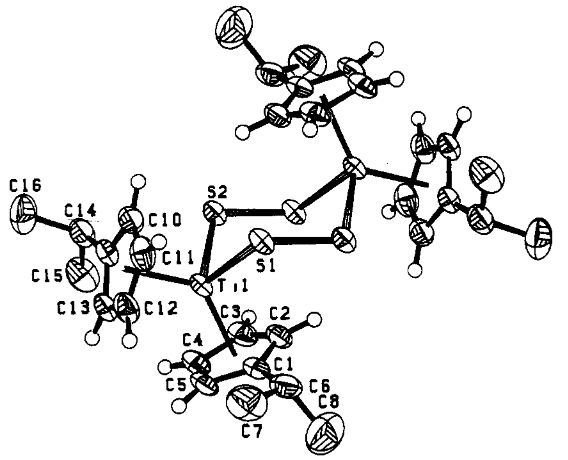


Figure 1. ORTEP drawing of 1,4-[(*i*-PrC$_5$H$_4$)$_2$Ti]$_2$S$_4$ (**3c**) (30% thermal ellipsoids).

Reactivity of *cyclo*-Titanium Sulfides toward Acetylenes. We have previously reported[8] that $(RC_5H_4)_2TiE_5$ (R = H and CH_3 and E = S and Se) reacts with DMAD to afford alkenedichalcogenide complexes. Similar syntheses involving methylpropiolate ($CH_3O_2CC{\equiv}CH$) and $CH_3CH_2O_2CC{\equiv}CCO_2CH_2CH_3$ (DEAD) are also viable. The alkylidene bis(persulfido) complex 1,4-$(RC_5H_4)_2TiS_4C(CH_3)_2$[7] reacts much more rapidly with these acetylenes than does $(RC_5H_4)_2TiS_5$. The rate of acetylene addition to the S_4CR_2 complexes is comparable in rate to that for $(RC_5H_4)_2TiSe_5$ and is approximately eight times faster than that for $(RC_5H_4)_2TiS_5$. Interestingly, 1,4-$((CH_3)_2C)_2S_4$ is unreactive toward DMAD even after several days at 145 °C. These observations indicate that *it is the sulfur atoms adjacent to titanium which initially bind to the acetylene.* The nonreactivity of 1,4-$((CH_3)_2C)_2S_4$ is also in accord with the new mechanistic information described below which reveals the direct involvement of the metal in the binding of the acetylene.

The practically insoluble **3a** was found to dissolve in the presence of DMAD to give a quantitative yield (by NMR) of the green crystalline vinyl disulfide complex $(C_5H_5)_2TiS_2{\cdot}C_2(CO_2CH_3)_2$ (**4**) (eq 6). Similarly, the addition of DMAD to solutions of the Ti_2S_4 cycles **3b** and **3c** with DMAD cleanly gave the corresponding vinyl disulfides which were isolated as viscous green oils. The ^1H NMR spectrum (toluene-d_8) of **4** consists of three singlets, even

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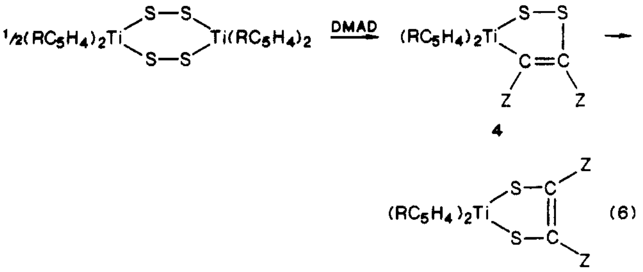

(6)

at −95 °C, in the ratio 10:3:3 assigned to the C_5H_5 groups and two different methyl ester groups. While the dithiolene complex has a facile ring flipping (T_c = −34 °C at 90 MHz and $\Delta G^{\ddagger}$ = 11.9 kcal/mol),[8,32] 4 is far more dynamic with broadening of the C_5H_5 resonance occurring only at −95 °C (200 MHz). Attempts to prepare 4 from the reaction of DMAD and $(RC_5H_4)_2TiS_5$ or $(RC_5H_4)_2TiS_4CR_2$, at temperatures below 90 °C, have not been successful. Vinyl disulfides had not previously been observed in the reaction of DMAD with $(RC_5H_4)_2TiS_5$ due to the high activation energy associated with the addition of DMAD to the poorly nucleophilic pentasulfide (Figure 6).

The rate of the reaction of **3b** and DMAD in CH_2Cl_2 solution was determined spectrophotometrically to be first order in both reagents. Representative data and numerical results are collected in Figures 2 and 3 and Table II. Our results indicate the rate-limiting step in the synthesis of 4 involves a polar species formed in a bimolecular process (Figure 4). In comparison with the $(RC_5H_4)_2TiSe_5$–DMAD system,[8] the reaction of 4 shows a more negative $\Delta S^{\ddagger}$ and a stronger solvent dependence. Many of the reactions of DMAD appear to proceed via dipolar intermediates on the basis of trapping experiments.[33,34] Coucouvanis has proposed that similar reactions proceed via a concerted cycloaddition.[35]

The Structure of β-$(C_5H_5)_2TiS_2C_2(CO_2CH_3)_2$. The structural analysis verified the monomeric and unsymmetric nature of 4 (Table III and Figure 5). The $(C_5H_5)_2Ti$ moiety structurally resembles that in the dithiolene complexes,[8] $(C_5H_5)_2TiC_4(C_6H_5)_4$,[36] and a several related compounds. The TiS_2C_2 rings in both 4 and the isomeric dithiolene are found in an envelope conformation. The Ti atom occupies the apex of the envelope flap in the dithiolene. However, in 4, the S(2) atom occupies this apical position and the Ti–C(2)–C(1)–S(1) atoms are essentially planar (±0.03 Å) with S(2) being 0.98 Å above this plane. The C–S bond length in 4 is close to the value normally assigned as a single bond.[37] Thus the puckering of S(2) probably arises from the lone pair–lone pair repulsions[38] between the sulfur atoms. Halbert and Stiefel's oxomolybdenum vinyl disulfide contains planar MoS_2C_2 rings.[39]

Table II. Kinetic Data for the Reaction of $[(CH_3C_5H_4)_2Ti]_2S_4$ and DMAD

a. k_{obsd} (M^{-1} s^{-1}) vs. $[DMAD]_0$ (24 °C in CH_2Cl_2)

$[Ti_2S_4]_0$[a]	$[DMAD]_0$	10^4k_{obsd}[b]	10^3k (= k_{obsd}/[DMAD]$)^b$
0.010	0.053	2.40	4.53
0.010	0.101	4.18	4.17
0.010	0.202	7.85	3.88

b. k (M^{-1} s^{-1}) vs. Temperature (CH_2Cl_2[c])

	13 °C	18 °C	24 °C	29 °C	34 °C
10^3k (= $k_{obsd}/[DMAD]_0$)	2.43	2.98	4.17	6.08	6.90

c. k (M^{-1} s^{-1}) vs. Solvent Polarity at 24 °C[c]

	benzene	CH_2Cl_2	CH_2Cl_2/ Me_2SO (1:1)
k (= $k_{obsd}/[DMAD]_0$)	1.33×10^{-3}	4.17×10^{-3}	1.33×10^{-2}

[a] Ti_2S_4 = 1,4-$[(CH_3C_5H_4)_2Ti]_2S_4$. [b] Average value of six runs at each initial concentration of both reagents. [c] $[Ti_2S_4]_0$ = 0.01 M; $[DMAD]_0$ = 0.101 M.

Table III. Selected Bond Distances and Angles for the Vinyl Disulfide $(C_5H_5)_2TiS_2C_2(CO_2CH_3)_2$ (4)

	(a) Bond Distances (Å)		
Ti–CNT1[a]	2.051 (3)	S(1)–S(2)	2.048 (1)
Ti–CNT2	2.061 (3)	S(1)–C(1)	1.780 (3)
Ti–S(2)	2.397 (1)	C(1)–C(2)	1.337 (4)
Ti–C(2)	2.194 (3)		
	(b) Bond Angles (deg)		
CNT1–Ti–CNT2	133.7 (2)	S(2)–S(1)–C(1)	100.5 (1)
CNT1–Ti–S(2)	103.8 (1)	S(1)–C(1)–C(2)	121.4 (2)
CNT1–Ti–C(2)	110.2 (2)	C(1)–C(2)–Ti	119.3 (2)
CNT2–Ti–S(2)	111.0 (1)	S(1)–C(1)–C(3)	115.2 (2)
CNT2–Ti–C(2)	103.7 (2)	C(2)–C(1)–C(3)	123.4 (3)
C(2)–Ti–S(2)	83.2 (0)	C(1)–C(2)–C(5)	118.9 (3)
Ti–S(2)–S(1)	98.2 (0)	Ti–C(2)–C(5)	121.6 (2)
	(c) Dihedral Angles (deg)		
C(1)–S(1)–S(2)–Ti	−37.4 (2)	S(2)–S(1)–C(1)–C(2)	24.5 (3)
S(1)–C(1)–C(2)–Ti	5.9 (2)	C(3)–C(1)–C(2)–C(5)	3.1 (4)

[a] CNT1 = centroid for atoms C(7)–C(11); CNT2 = centroid for atoms C(12)–C(16).

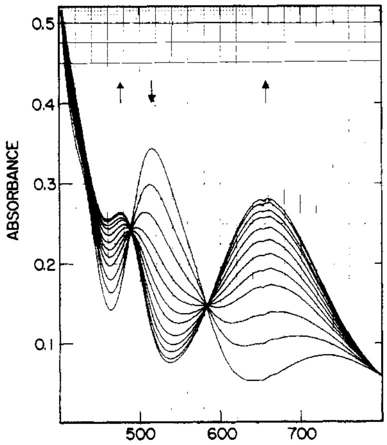

Figure 2. Electronic spectra at various stages of the reaction of 1,4-$[(CH_3C_5H_4)_2Ti]_2S_4$ and DMAD.

Rearrangement of β-$(RC_5H_4)_2TiS_2C_2(CO_2CH_3)_2$. The vinyl disulfide rearranges at 90 °C to give the dithiolene

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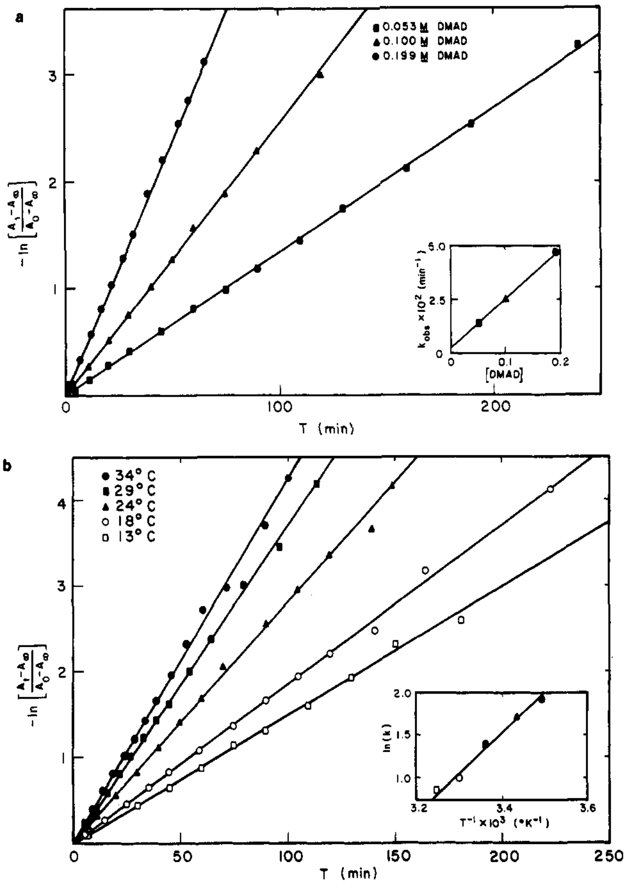

Figure 3. First-order plots for the reaction of 1,4-$[(CH_3C_5H_4)_2Ti]_2S_4$ and DMAD for various concentrations of DMAD (a) and various reactions temperatures (b).

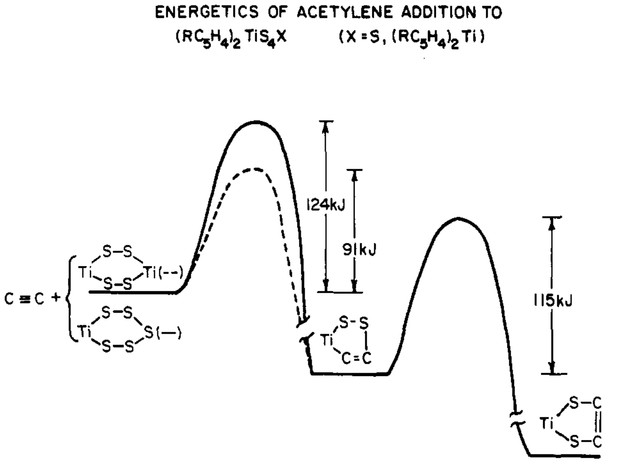

Figure 4. Qualitative reaction coordinate for the addition of acetylenes to $(RC_5H_4)_2TiS_4X$ (X = S or $(RC_5H_4)_2Ti$). The 124-kJ barrier was obtained from our previous study of DMAD + $(CH_3C_5H_4)_2TiSe_5$ and is underestimated since $(RC_5H_4)_2TiS_5$ is even less nucleophilic. The 115-kJ value was estimated from a preliminary kinetic study on the rearrangement of β-$(C_5H_5)_2TiS_2C_2(CO_2CH_3)_2$ to α-$(C_5H_5)_2TiS_2C_2(CO_2CH_3)_2$.

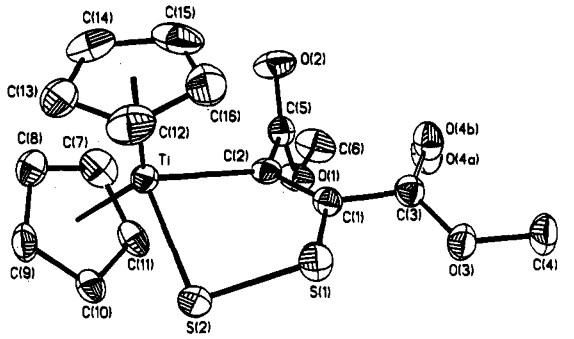

Figure 5. ORTEP drawing of the non-hydrogen atoms of the vinyl disulfide $(C_5H_5)_2TiS_2C_2(CO_2CH_3)_2$ (**4**) molecule (40% thermal ellipsoids). A second rotational orientation for one Cp ring (C7–11) is not shown; O(4) is disordered on two sites shown as O(4a) and O(4b).

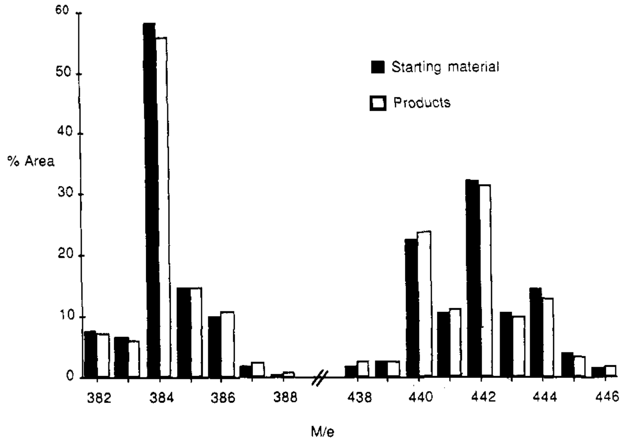

Figure 6. Signal-averaged field ionization mass spectral data for the reactants (vinyl disulfides) and products (1,2-dithiolenes) of the thermolysis (90 °C) of $(RC_5H_4)_2TiS_2C_2(CO_2R')_2$. The reactants consisted of a 1:1 mixture of β-$(C_5H_5)_2TiS_2C_2(CO_2CH_3)_2$ (mol wt 384 for ^{48}Ti and ^{32}S) and β-$(CH_3C_5H_4)_2TiS_2C_2(CO_2CH_2CH_3)_2$ (mol wt 442 for ^{48}Ti and ^{34}S), the latter enriched in ^{34}S.

in 50–60% yields (eq 6). This result strongly suggests that *a vinyl disulfide is an intermediate in the reactions of acetylene with* $(RC_5H_4)_2TiS_5$ *which give dithiolenes.* In a preliminary study of the rearrangement process, a mixture equimolar in the vinyl disulfides $(C_5H_5)_2TiS_2C_2(CO_2CH_3)_2$ and $(CH_3C_5H_4)_2TiS_2C_2(CO_2C_2H_5)_2$ was maintained at 90 °C for 24 h. After chromatographic removal of the unreacted vinyl disulfide complexes, the dithiolene products were assayed by field ionization mass spectroscopy (FI MS) which showed that only 5% ligand exchange had occurred. However, the control experiment, involving thermolysis of the corresponding dithiolenes, also revealed approximately 5% ligand exchange. To determine the possibility of sulfur exchange, a 1:1 mixture of **4** and ^{34}S-

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Table IV. Literature Examples of Transition Metal Promoted Dithiolene Syntheses

A. Reactions of Metal Sulfido Complexes with Acetylenes and Related Reactions

metal complex	acetylene[a]	product	ref
$(RC_5H_4)_2TiS_4X$ (X = S, CR_2, $Ti(RC_5H_4)_2$)	$ZC{\equiv}CZ$, $ZC{\equiv}CR$	$(RC_5H_4)_2TiS_2C_2Z$(R or Z)	this work, 8
$(RC_5H_4)_2V_2S_5$	$ZC{\equiv}CZ$	$(RC_5H_4)V(S_2C_2Z_2)_2$	41
$(RC_5H_4)_2V_2S_4$	$ZC{\equiv}CZ$	$(RC_5H_4)_2V_2(S)_2(S_2C_2Z_2)$	42
$[Mo(S)(S_4)_2]^{2-}$	$ZC{\equiv}CZ$	$[Mo(S_2C_2Z_2)_3]^{2-}$	43
$(R_nC_5H_{4-n})_2Mo_2S_4$	$RC{\equiv}CR$	$(R_nC_5H_{4-n})_2Mo_2(S_2C_2R_2)_2$	44
$(RC_5H_4)_2Mo_2S_2(S_2CH_2)$	$RC{\equiv}CR$	$(RC_5H_4)_2Mo_2(S_2C_2R_2)(S_2CH_2)$	45
$(RC_5H_4)_2W_2S_4$	$RC{\equiv}CR$	$(RC_5H_4)_2W_2(S)_2(S_2C_2R_2)_2$	46
$Fe_2(S_2)(CO)_6$	$ZC{\equiv}CZ^b$	$Fe_2(S_2C_2Z_2)(CO)_6$	47
$(C_5H_5)_2Fe_2S_4$	$ZC{\equiv}CZ$	$(C_5H_5)_2Fe_2(S_2C_2(CF_3)_2)_2$	48
$(EtC_5Me_4)_2Ru_2S_4$	$RC{\equiv}CR^c$	$(EtC_5Me_4)_4Ru_2S_2C_2R_2$	49
$[Ni(S_4)_2]^{2-}$	$ZC{\equiv}CZ$	$[Ni(S_2C_2Z_2)_2]^{2-}$	50
$Mo_2O_2(S)_2(S_2)_2{}^{2-}$	$ZC{\equiv}CZ$	$Mo_2O_2(S)_2(S_2C_2Z_2)_2{}^{2-}$	39

B. Related Dithiolene Syntheses

reactants	product	ref
$(RC_5H_4)_3Co_3(CR)_2 + S_8$	$(RC_5H_4)CoS_2C_2R_2$	51
$(RC_5H_4)_2ZrPh_2 + Se_8$	$(RC_5H_4)_2Zr(1,2\text{-}Se_2C_6H_4)$	52
$(C_5H_5)_2TiS_5$	$(C_5H_5)Ti(S_5C_5H_5)$	53
$(RC_5H_4)Co(CO)_2 + S_8 + R_2C_2$	$(RC_5H_4)CoS_2C_2R_2$ + thiophenes	54
$(C_5H_5)Co(CO)_2 + Se_8 + R_2C_2$	$(C_5H_5)CoSe_2C_2R_2$	55
$(C_5H_5)_2Rh(CO)_2 + S_8 + Z_2C_2$	$(C_5H_5)RhS_2(R_2C_2)_n$	56

[a] Z = CO_2CH_3 or CF_3; R = H, alkyl, or phenyl. [b] Photochemical reaction, also see ref 57. [c] Reaction proceeds in presence of PBu_3.

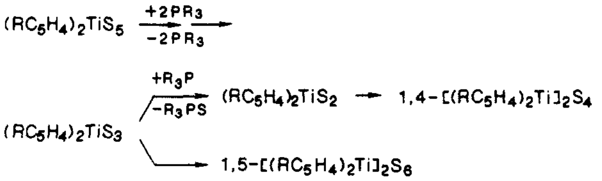
enriched vinyl disulfide $(CH_3C_5H_4)_2TiS_2C_2(CO_2Et)_2$ was converted to dithiolenes. Comparison of the FI MS spectrum of the starting materials with the products indicated no exchange had occurred (Figure 6). *The vinyl disulfide–dithiolene rearrangement is therefore intramolecular.*

Concluding Remarks

Reactions of Acetylenes with Metal Sulfides. There have been many studies of the formation of C–S bonds through the reaction of metal sulfides with unsaturated organic compounds, particularly acetylenes (Table IV). The earliest work in this area was the discovery of Schrauzer that nonstoichiometric nickel sulfide reacts with acetylenes to give $Ni(S_2C_2R_2)_2$.[40] The majority of di- and polysulfido complexes react with only very electrophilic acetylenes like DMAD and hexafluoro-2-butyne to give dithiolenes. Electrophilic acetylenes are well-known to react with elemental sulfur;[34,58] therefore, it is not very surprising that metal polysulfido complexes do also. However, it was not expected that these reactions would proceed via an insertion process. Certain metal sulfides react with unactivated acetylenes.[44–46,49] These reactions reveal exceptional reactivity for the sulfur ligands and are therefore of great interest.

Vinyl disulfides and their analogues have been observed or invoked previously. Clark observed an unsymmetrical intermediate in the conversion of $PtO_2(PPh_3)_2$ to the dioxalene $Pt(O_2C_2(CO_2Me)_2)(PPh_3)_2$.[59] Lindner has isolated $MSPC_2$ cycles from the reaction of η^2-SPR_2 complexes with DMAD.[60] Halbert and Stiefel synthesized the first vinyl disulfide by the addition of DMAD to a disulfidomolybdenum(V) complex; interestingly, this compound could not be induced to rearrange to a dithiolene.[39]

The Relationship of $(RC_5H_4)_2TiS_5$ to Organic and Inorganic Polysulfides. Our results indicate that reactive monotitanium intermediates are produced in the reaction of 1 with phosphines and that it is the coupling of these intermediates which give rise to 2 and 3. The Ti_2S_4/Ti_2S_6 product distribution, arising from the competition between the coupling of two $(RC_5H_4)_2TiS_3$ units and further desulfurization of $(RC_5H_4)_2TiS_3$, appears to be kinetically governed: the more nucleophilic phosphines affording a greater degree of desulfurization (eq 7). In light of such a mechanism it is not yet understood why $[(RC_5H_4)_2Ti]_2S_5$ has not been observed.[62]



(7)

The products that we observe for the $(RC_5H_4)_2TiS_x$–phosphine reactions are related to those obtained from the benzo polysulfides. The chief aspect of the similarity between the benzo and titanocene sulfides is the rigidity of the phenylene and titanocene templates. For example, neither system shows a tendency to form a stable monomeric disulfide. The oxidation of 1,2-benzenedithiol with iodine gives, in addition to oligomers, the C_4S_4 heterocycle dibenzotetrathiocin, an organosulfur analogue of 3.[63,64] Rasheed has reported the synthesis of derivatives of dibenzotetrathiocin by the abstraction of a sulfur atom from the corresponding benzotrithiole (eq 8).[65] The

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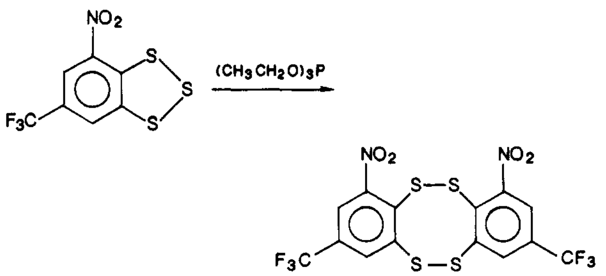
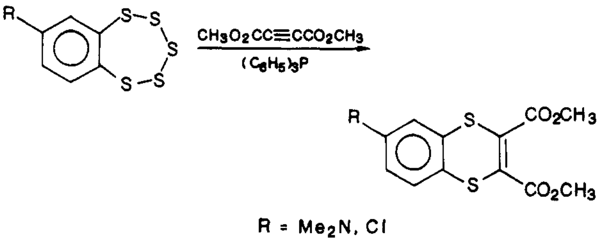


(8)

benzopentathiepins also resemble $(RC_5H_4)_2TiS_5$ in that desulfurization can lead to ionic intermediates that can be trapped. Chenard has reported that while 1,2-benzenepentathiepin reacts only sluggishly with DMAD at 140 °C to give 1,4-benzodithiins, the addition of $(C_6H_5)_3P$ to the reaction mixture gives the same product at room temperature in 51% yield (eq 9).[66]



(9)

The studies of Steudel[22] and others[67] have shown that many sulfur (and selenium) homocycles are stable and that some exist in facile equilibria with *cyclo*-S_8. Some of these studies provide evidence for the coupling of reactive *cyclo*-S_x intermediates.[68] The present work shows that very reactive metal sulfides, viz., $(RC_5H_4)_2TiS_x$ ($x = 2, 3$), can be generated from stable polysulfide complexes.[66] Other examples of reactive metal sulfides generated by desulfurizations are formed from $(RC_5H_4)_2V_2S_4$[69] and $(EtC_5(CH_3)_4)_2Ru_2S_4$.[49] The latter reactions appear to involve coordinatively unsaturated intermediates.

Experimental Section

Materials and Methods. All preparative reactions were performed under an atmosphere of nitrogen. Tetrahydrofuran (THF), benzene, and toluene were distilled from NaK alloy. Hexane was obtained as reagent grade and was distilled from sodium benzophenone ketyl. Dichloromethane and carbon disulfide were distilled from P_4O_{10}. Methylcyclopentadiene was purified by two redistillations. Cyclopentadiene dimer and 2-bromopropane were dried over 4-Å seives. Dimethyl and diethyl acetylenedicarboxylate (Aldrich) were redistilled; the fractions boiling at 47–49 °C (0.3 mmHg for DMAD) or 106–110 °C (11 mmHg for DEAD) were retained. $(C_5H_5)_2TiCl_2$ was purchased from Boulder Scientific and Pressure Chemical Co. Thin-layer chromatography was performed on Eastman 13181 silica gel plates; flash chromatography was performed with 2 × 15 cm of Woehm 32–63 silica gel that had been deactivated with 5% (w/w) water. Labeled elemental sulfur, 98% ^{34}S, was purchased from Monsanto (Miamisburg, OH).

The following instruments were used in this work: IR, Nicolet MX-5 FTIR spectrometer; UV–vis, Varian Cary 2300 spectrophotometer; ^1H NMR and ^{13}C NMR, Nicolet NT-360 (360 MHz, internal ^1H frequency lock) and Varian XL-200 (200 MHz, internal ^1H frequency lock) spectrometers. Field desorption (FD) and field ionization (FI) mass spectroscopy were measured on a Varian 731 spectrometer at the University of Illinois Mass Spectrometry Laboratory. All new organometallic compounds that were isolated as crystalline solids gave satisfactory analyses (University of Illinois Microanalytical Laboratory).

***i*-PrC$_5$H$_5$ (Isopropylcyclopentadiene Isomers).**[70] This synthesis was conducted on a 2-mol scale in ammonia (1.5 L). At dry ice/acetone temperature, 46 g of Na (2 mol) was added to the ammonia in gram portions. After being stirred for 30 min, the sodium/liquid ammonia solution was titrated with 204 g of freshly cracked cyclopentadiene monomer (3.09 mol), affording a colorless solution. Degassed 2-bromopropane, 354.8 g (2.9 mol), was then added dropwise, and the mixture was allowed to warm to room temperature. After extraction with ether and aqueous wash, distillation gave 196 g of the product (1.8 mol, 90% based on sodium), collected at 45 °C (50 mmHg).

(*i*-PrC$_5$H$_4$)$_2$TiCl$_2$. A 189-mL sample of 1.9 M solution of *n*-BuLi in hexanes was added to a solution of 37.6 g of $(CH_3)_2CHC_5H_5$ in 500 mL of THF, cooled by using a dry ice/acetone bath. The mixture was allowed to warm to room temperature, affording a homogeneous pale yellow solution. This was then added to a solution of 14 mL (130 mmol) of $TiCl_4$ in 250 mL of toluene. After being stirred for 2 h, the dark red slurry was washed three times with 100 mL of 3 M HCl. The organic layer was washed with 50-mL portions of water until the washings came through clear. Concentration to 150 mL and filtration afforded 18.4 g (55 mmol, 43% based on titanium) of bronze-red crystals. ^1H NMR: δ 6.34 (m, 4 H), 3.2 (sept, 1 H, 5.5 Hz), 1.2 (d, 6 H, 5.5 Hz).

(RC$_5$H$_4$)$_2$TiS$_5$. These compounds (R = H, CH_3, and $CH(CH_3)_2$) were prepared ca. 87% yield by the reaction of acetone solutions of $(RC_5H_4)_2TiCl_2$ and aqueous ammonium polysulfide, as described elsewhere.[68] In these syntheses care must be taken to *completely saturate the ammonium sulfide solution with sulfur* as yields are otherwise reduced due to the formation of 1,4-$[(RC_5H_4)_2Ti]S_4C(CH_3)_2$.

1,4-[(RC$_5$H$_4$)$_2$Ti]$_2$S$_4$. The procedures used to prepare the three compounds (R = H, CH_3, and $CH(CH_3)_2$) are similar in the quantities used and the yield of product. $(C_5H_5)_4Ti_2S_4$ is practically insoluble in all solvents but can be partially purified by washing with large amounts of CH_2Cl_2. For the $CH_3C_5H_4$ and *i*-PrC_5H_4 compounds, the products are easily purified by recrystallization from CH_2Cl_2/hexanes.

(1) A solution of 1.0 mL of $(n\text{-}C_4H_9)_3P$ in 10 mL of CH_2Cl_2 was added dropwise to a slurry of 0.5 g (1.48 mmol) of $(C_5H_5)_2TiS_5$ in 25 mL of CH_2Cl_2. After being stirred for 15 min, the mixture was filtered and washed with CH_2Cl_2 until the washings came through clear; 0.125 g (0.26 mmol, 35%) of red powder was obtained.

(2) To 1.03 g (32.2 mmol) of sulfur was added 16.1 mL of a 1 M solution of $LiBHEt_3$ in THF followed by 1.1 mL of CS_2. The resulting orange solution was stirred for 10 min before being added to a slurry of 4.0 g (16.1 mmol) of $(C_5H_5)_2TiCl_2$ in 30 mL of THF. Stirring for 1 h, filtration, and washing as above with CH_2Cl_2 afforded 2.8 g (5.8 mmol, 72%) of red powder. This procedure was used to prepare ^{34}S-enriched $[(CH_3C_5H_4)_2Ti]_2S_4$.

(3) To a solution of 0.272 g (1 mmol) of $(CH_3C_5H_4)_2Ti(SH)_2$ in 10 mL of THF was added dropwise a mixture of 0.504 g (2 mmol) of I_2 and 0.560 mL (4 mmol) of Et_3N in 20 mL of THF. The red solution rapidly became deep red-purple. The mixture was stirred at room temperature for 30 min. Filtration of the reaction solution, rinsing with toluene, afforded 0.21 g of white crystals. The volatiles were removed in vacuo, and the red oil was chromatographed on a 2 × 5 cm column of silica gel with CH_2Cl_2. After elution of a small amount of $(CH_3C_5H_4)_2TiS_5$, the slower moving red band was collected, diluted with hexanes, and concentrated to afford 0.120 g of purple crystals (0.22 mmol, 44%). ^1H NMR: δ 6.58 (m, 2 H), 6.36 (m, 2 H), 6.11 (m, 2 H), 5.91 (m, 2 H), 2.48 (s, 3 H), 1.87 (s, 3 H).

Reaction of (CH$_3$C$_5$H$_4$)$_2$TiS$_5$ with Tertiary Phosphines. (*n*-C$_4$H$_9$)$_3$P. To a slurry of 11.9 g (32.5 mmol) of **1b** in 100 mL

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of CH_2Cl_2 was added dropwise a solution of 30 mL (120 mmol) of $(n\text{-}C_4H_9)_3P$ in 40 mL of CH_2Cl_2. After the solution was stirred for 15 min, 40 mL of hexane was added. After being concentrated to 100 mL, the reaction solution was filtered. Recrystallization afforded 3.82 g (7.07 mmol, 43%) of red crystalline **3b**.

$(c\text{-}C_6H_{11})_3P$. This reaction is completely analogous to the $(n\text{-}C_4H_9)_3P$ reaction.

$(C_6H_5)_3P$. A solution of 0.732 g (2 mmol) of **1b** in 50 mL of CH_2Cl_2 was refluxed for 15 min; then a solution of 0.786 g (3 mmol) of $(C_6H_5)_3P$ in 15 mL of CH_2Cl_2 was added. After being refluxed for 30 min, the black reaction mixture was cooled to room temperature and 2 g of silica gel (deactivated with 10% (w/w) water) was added. Evaporation of the solvent in vacuo afforded a green-blue solid that was placed on a 2 × 10 cm column of deactivated silica gel. Elution with CH_2Cl_2 gave a glue band that was collected, diluted with acetone, and concentrated to the point of crystallization. Filtration afforded 0.059 g (0.11 mmol, 10%) of **2b**. The yields are actually higher (~40%) by ^1H NMR; however, attempts to recover more of the product gave samples impure with $(C_6H_5)_3PS$.

$(C_6H_5)_2CH_3P$. A solution of 1.0 g (2.7 mmol) of **1b** in 50 mL of CH_2Cl_2 was refluxed for 15 min, and then a solution of 1.4 mL (~7 mmol) of $P(C_6H_5)_2CH_3$ in 15 mL of CH_2Cl_2 was added dropwise. Reflux was continued for 5 min. After evaporation of the solvent, the brown oil was dissolved in a minimum of CH_2Cl_2 and chromatographed on a 2 × 10 cm column of silica gel eluting with CH_2Cl_2. The blue band was collected, diluted with hexanes, and concentrated to induce crystallization. Filtration afforded 0.176 g (0.31 mmol, 22%) of **2b**. A slower moving red band was collected worked up similarly giving 0.173 g (0.32 mmol, 23%) of **3b**.

Reaction of $(RC_5H_4)_2TiS_5$ and $(n\text{-}C_4H_9)_3P$ in the Presence of DMAD. A solution of 0.366 g (1 mmol) of **1b** in 15 mL of CH_2Cl_2 and 1 mL (8 mmol) of DMAD was cooled to −20 °C. A solution of 1.5 mL (6 mmol) of $(n\text{-}C_4H_9)_3P$ in 6 mL of CH_2Cl_2 was added dropwise, and the solution became a green-brown. The solution was stirred for ~1 h at −20 °C. After solvent evaporation, the resulting oil was dissolved in CH_2Cl_2 and chromatographed on a 2 × 10 cm column of silica gel eluting with CH_2Cl_2. Red and green bands were collected, diluted with CH_3OH, and concentrated to give 0.006 g (0.01 mmol, 1.5%) of **3b** and 0.13 g (0.39 mmol, 39%) of $(CH_3C_5H_4)_2TiS_2C_2(CO_2CH_3)_2$, respectively.

1,4-$[(CH_3C_5H_4)_2Ti][(C_5H_5)_2Ti]S_4$. A toluene solution of 0.220 g (1.13 mmol) of $(C_5H_5)_2Ti(CO)_2$ was added to a suspension of 0.386 g (1 mmol) of **1b** in 20 mL of toluene. After 1 h, the reaction solution was evaporated and the residue was chromatographed on a 2 × 5 cm column of silica gel eluting with CH_2Cl_2. The faster moving orange band was collected and crystallized with hexanes giving 0.056 g (0.15 mmol) of **3b**. The second red band was also crystallized similarly giving 0.215 g (0.42 mmol) of the desired compound as red crystals. A similar reaction involving 1 mmol each of **1b** and $(CH_3C_5H_4)_2Ti(CO)_2$ gave 0.37 mmol of **3b**.

$(C_5H_5)_2TiS_2C_2H(CO_2CH_3)$. A solution of 1.067 g (3.15 mmol) of **1a** and 1.5 mL (16 mmol) of $CH_3O_2CC{\equiv}CH$ in 20 mL of xylenes was refluxed for 4–5 h. After evaporation of the solvent, the green oil was dissolved in CH_2Cl_2, diluted with hexanes, concentrated, and filtered to give 0.345 g (1.1 mmol, 33%) of green crystals. ^1H NMR: δ 8.38 (s, 1 H), 6.00 (s, 10 H), 3.80 (s, 3 H).

1,4-$[(RC_5H_4)_2Ti]S_4C(CH_3)_2$. The procedures used to prepare the R = H, CH_3, and *i*-Pr derivatives are similar in terms of the quantities used and the yields. The products with R = H and CH_3 are very soluble in halogenated and aromatic solvents but far less so in alcohols and hexanes. The product containing R = $CH(CH_3)_2$ is soluble in alcohols and hexane.

Slow dropwise addition of 1 mL of $(NH_4)_2S$ to a slurry of 0.50 g (1.48 mmol) of **1a** in 30 mL of acetone gave of a deep red solution. After evaporation, the red oil was dissolved in a minimum of CH_2Cl_2 and chromatographed on a column of silica gel with 2:1 hexane–dichloromethane. The fast moving red band was collected and concentrated, giving 0.254 g (0.74 mmol, 50%) of black crystals. ^1H NMR: δ 6.33 (s, 5 H), 6.23 (s, 5 H), 1.77 (s, 3 H), 1.00 (s, 3 H).

Reaction of Acetylenes with $(C_5H_5)_2TiS_4C(CH_3)_2$. A solution of 0.12 g (0.34 mmol) of $(C_5H_5)_2TiS_4C(CH_3)_2$ and 0.8 mL (8.5 mmol) of $CH_3O_2CC{\equiv}CH$ (or an equivalent amount of DMAD) in 10 mL of xylenes was refluxed for 25 min. The yield was 36% (a 58% yield was obtained for the DMAD reaction).

β-$(C_5H_5)_2TiS_2C_2(CO_2CH_3)_2$ (4). A slurry of 0.80 g (1.65 mmol) of **3a** in 1.0 mL (8.13 mmol) of DMAD and 25 mL of CH_2Cl_2 was stirred at 25 °C for 72 h. The solvent was evaporated, and the resulting green oil was washed with 5–10-mL portions of cold (−25 °C) hexanes. The crude product was extracted into 10 mL of CH_2Cl_2, and this solution was diluted with hexane and concentrated to 15 mL, giving 1.22 g (3.17 mmol, 96%) of green crystals of the vinyl disulfide. ^1H NMR: δ 6.38 (s, 10 H), 3.70 (s, 6 H) (for toluene-d_8, δ 5.90 (s, 10 H), 3.49 (s, 3 H), 3.22 (s, 3 H)).

β-$(CH_3C_5H_4)_2TiS_2C_2(CO_2CH_2CH_3)_2$. A solution of 0.54 g (1.0 mmol) of **3b**, 0.4 mL (2.2 mmol) of DEAD, and 20 mL of CH_2Cl_2 was stirred at 25 °C for 8 h. Workup as described above gave 0.69 g (1.58 mmol, 79%) of green crystals. This procedure was used to prepare ^{34}S-enriched samples (see Figure 6).

Isomerization of β-$(C_5H_5)_2TiS_2C_2(CO_2CH_3)_2$. A solution of 0.10 g of **4** was dissolved in 50 mL of toluene and heated at 90 °C for 24 h. Removal of the solvent and recrystallization from CH_2Cl_2/hexanes afforded 0.065 g (65% yield) of green crystals. The product was identical with an authentic sample of the dithiolene $(C_5H_5)_2TiS_2C_2(CO_2CH_3)_2$ on the basis of ^1H NMR. In an analogous procedure, a 1:1 mixture of ^{34}S-enriched $(CH_3C_5H_4)_2TiS_2C_2(CO_2CH_2CH_3)_2$ and unenriched $(C_5H_5)_2TiS_2C_2(CO_2CH_3)_2$ were converted to the corresponding dithiolenes (see Figure 6).

Kinetic Study of the Reaction of 1,4-$[(CH_3C_5H_4)_2Ti]_2S_4$ and DMAD. These measurements were made by monitoring the disappearance of **3b** although good plots could be generated by monitoring the formation of the vinyl disulfide. All kinetic runs were performed in a 50-mL three-neck flask equipped with an N_2 inlet and two stoppers. In a typical experiment, the apparatus was flushed with N_2 for 15 min and placed in a water bath at 24.5 °C. The flask was charged with 20 mL of CH_2Cl_2 followed by 0.154 g of **3b**. The solution was stirred for 20 min before 175 μL of DMAD was added in one portion via syringe. The progress of the reaction was monitored by removing 1-mL aliquots that were diluted to 100 mL before recording their visible spectrum (400–800 nm). The reactions were monitored for at least 4 half-lives.

The rate constant, k_{obsd}, was calculated by linear least-squares regressive analysis for plots of $-\ln[(A_t - A_\infty)/(A_0 - A_\infty)]$ vs. t that included iterative fitting of A_∞. The absorbance at 540 nm was used for all calculations. The average correlation coefficient was 0.999. The calculated second-order rate constant, $k = k_{obsd}/[\mathrm{DMAD}]$, was the average of six runs. Activation parameters were determined by similar procedures at 13.0, 18.0, 24.5, 29.0, and 34.0 °C.

The average rate constants for the reactions in benzene and Me_2SO/CH_2Cl_2 ($[\mathrm{DMAD}]_0 = 7.1 \times 10^{-2}$ M and $[\mathbf{3c}]_0 = 1.4 \times 10^{-2}$ M) were 1.33×10^{-3} and 1.33×10^{-2} $M^{-1}\,s^{-1}$, respectively.

X-ray Crystallography of 3c. Deep red-violet, opaque single crystals were grown by slow diffusion of methanol into a CH_2Cl_2 solution of **3c** at −25 °C. A prismatic crystal (0.4 × 0.6 × 0.7 mm) was mounted to a glass fiber roughly normal to the $(3,\bar{2},\bar{3})$ planes. The crystals were monoclinic, space group $C2/c$—C_{2h}^6, with a = 35.481 (10) Å, b = 10.976 (3) Å, c = 23.553 (6) Å, β = 130.74 (2)°, Z = 8 (the asymmetric unit consists of two independent half molecules), V = 6950 (3) Å^3, ρ(calcd) = 1.329 g cm^{-3}, $F(000)$ = 2920, and μ(Mo Kα) = 7.84 cm^{-1}.

Intensity measurements were made on a Syntex P2$_1$ automated diffractometer using graphite-monochromated Mo Kα (λ = 0.710 69 Å) radiation. A total of 8017 independent reflections having $2\theta \leq 55°$ were measured in two concentric shells. Of these the 4463 reflections with $I > 2.58\sigma(I)$ were used for refinement. Three standard reflections measured every 100 reflections indicated deterioration of the crystal was occurring during the experiment (16% loss of intensity was attributed to the gradual loss of CH_2Cl_2 from the crystal lattice). The average valves and probability distribution of the normalized structure factors suggested the centric space group that was confirmed by a successful refinement. Prohibitively high correlation coefficients were obtained for an acentric refinement.

Positions for the titanium and sulfur atoms were deduced from an E map (MULTAN-80). A weighted difference Fourier synthesis incorporating these six atoms revealed the positions for an additional 19 carbon atoms. Subsequent least squares–difference

Table V. Atomic Coordinates ($\times 10^4$) for 3b

	x/a	y/b	z/c
Ti(1)	5585.9 (3)	-0227.0 (8)	-0176.6 (4)
Ti(2)	1956.9 (3)	2497.8 (7)	-1337.1 (4)
S(1)	4682.0 (4)	-0433 (1)	-1041.4 (6)
S(2)	5583.6 (4)	1263 (1)	0578.5 (7)
S(3)	2632.5 (4)	1106 (1)	-0453.6 (6)
S(4)	1806.1 (4)	2915 (1)	-0487.8 (6)
C(1)	5599 (2)	-2439 (4)	-0114 (3)
C(2)	5613 (2)	-1961 (5)	0458 (3)
C(3)	6057 (2)	-1313 (5)	0977 (3)
C(4)	6316 (2)	-1354 (5)	0710 (3)
C(5)	6039 (2)	-2050 (5)	0060 (3)
C(6)	5215 (2)	-3297 (5)	-0721 (3)
C(7)	5192 (3)	-3313 (6)	-1375 (4)
C(8)	5307 (3)	-4549 (7)	-0411 (5)
C(9)	5976 (2)	1537 (5)	-0254 (3)
C(10)	5453 (2)	1649 (5)	-0819 (3)
C(11)	5268 (2)	0675 (5)	-1331 (3)
C(12)	5676 (2)	-0042 (5)	-1077 (3)
C(13)	6101 (2)	0459 (5)	-0432 (3)
C(14)	6329 (2)	2466 (5)	0331 (3)
C(15)	6813 (2)	1911 (6)	1019 (3)
C(16)	6436 (2)	3437 (6)	-0026 (4)
C(17)	2008 (2)	4719 (4)	-1378 (3)
C(18)	1822 (2)	4239 (5)	-2068 (3)
C19)	2198 (2)	3494 (5)	-1946 (3)
C(20)	2612 (2)	3529 (4)	-1182 (3)
C(21)	2491 (2)	4266 (4)	-0825 (3)
C(22)	1756 (2)	5678 (4)	-1260 (3)
C(23)	2011 (3)	6902 (5)	-1119 (5)
C(24)	1209 (2)	5765 (6)	-1899 (3)
C	0	1830 (1)	2500
Cl	0444 (1)	1192 (3)	2582 (3)
C(25A)	1373 (2)	1766 (5)	-2609 (3)
C(27A)	1107 (2)	2257 (5)	-2403 (3)
C(28A)	1205 (2)	1517 (5)	-1825 (3)
C(29A)	1532 (2)	0569 (5)	-1673 (3)
C(25A)	1636 (2)	0723 (5)	-2158 (3)
C(30A)	1922 (4)	-0168 (9)	-2253 (6)
C(31A)	2219 (5)	0496 (10)	-2474 (7)
C(32A)	1524 (5)	-1070 (1)	-2860 (8)
C(26B)	1195 (2)	1931 (5)	-2525 (3)
C(27B)	1127 (2)	1793 (5)	-1997 (3)
C(28B)	1433 (2)	0817 (5)	-1511 (3)
C(29B)	1690 (2)	0351 (5)	-1738 (3)
C(25B)	1543 (2)	1040 (5)	-2365 (3)
C(30B)	1659 (4)	0743 (9)	-2876 (6)
C(31B)	1253 (5)	-0190 (1)	-3469 (8)
C(32B)	2160 (5)	0140 (1)	-2429 (8)

Fourier calculations gave the positions for remainin g non-hydrogen atoms including those partially occupied by the disordered cyclopentadienyl ring atoms. In the final cycle of least-squares refinement (SHELX), positions for all non-hydrogen atoms were independently refined with anisotropic thermal coefficients with the exception of the isopropyl carbon atoms on the disordered cyclopentadienyl ring which were refined with isotropic thermal coefficients and constrained to idealized bond lengths (1.54 Å); the disordered ring atoms which were constrained to idealized geometry (C–C = 1.42 Å) and refined as two groups (group "A" occupancy 0.507 (2)). The hydrogen atoms were fixed in idealized positions (0.95 Å, trigonal or tetrahedral) except for the alkyl hydrogens of the disordered isopropyl groups which were omitted owing to the uncertainty in the carbon positions. The final difference Fourier map had no significant features. The final cycle of least squares converged to $R = 0.052$ and $R(w) = 0.074$. Atomic coordinates are presented in Table V.

X-ray Crystallography of 4. A dark green conically shaped crystal (0.34-mm base diameter and 0.39-mm height) was grown by the slow diffusion of hexanes into a toluene solution of 4. The crystal was monoclinic, space group $P2_1/n$, with $a = 9.772$ (2) Å, $b = 14.573$ (2) Å, $b = 14.573$ (2) Å, $c = 11.756$ (2) Å, $\beta = 100.25$ (1)°, $Z = 4$, $V = 1647.4$ (5) Å^3, ρ(calcd) = 1.48 g cm^{-3}, and μ(Mo Kα) = 7.90 cm^{-1}.

Intensity measurements were made on a Nicolet R3 diffractometer using Mo Kα ($\lambda = 0.71073$ Å) radiation. A total of 2842 independent reflections having $4° < 2\theta < 50°$ were measured. Of these 2165 reflections had $F_o > 3\sigma(F_o)$. Three standard reflections measured every 197 reflections showed <1% variation.

Table VI. Atomic Coordinates ($\times 10^4$) for 4

	x	y	z
Ti	2700 (1)	7921 (1)	979 (1)
S(1)	4992 (1)	9412 (1)	2448 (1)
S(2)	3300 (1)	8705 (1)	2792 (1)
O(1)	6376 (2)	6613 (2)	1131 (2)
O(2)	5493 (3)	7171 (2)	-619 (2)
O(3)	7843 (2)	9261 (2)	2454 (2)
O(4A)	7945 (53)	8203 (29)	1037 (41)
O(4B)	7795 (37)	8417 (21)	894 (25)
C(1)	5732 (3)	8579 (2)	1631 (3)
C(2)	4960 (3)	7913 (2)	1055 (2)
C(3)	7243 (3)	8693 (2)	1623 (3)
C(4)	9302 (3)	9459 (3)	2492 (3)
C(5)	5639 (3)	7226 (2)	424 (3)
C(6)	7176 (4)	5964 (3)	598 (3)
C(7)	2534 (8)	6338 (3)	643 (5)
C(8)	1152	6665	569
C(9)	997	6981	1682
C(10)	2283	6849	2443
C(11)	3233	6452	1800
C(12)	1744 (3)	9391 (2)	356 (2)
C(13)	826	8693	-161
C(14)	1516	8184	-921
C(15)	2861	8569	-874
C(16)	3001	9315	-84
C(7′)	1765 (20)	6445 (9)	352 (6)
C(8′)	851	6875	1002
C(9′)	1565	6970	2158
C(10′)	2921	6600	2223
C(11′)	3044	6275	1107

The Ti and the two S atoms were located by direct methods, and the remaining non-hydrogen atoms were found in subsequent difference Fourier syntheses. The Cp(7–11) ring is rotationally disordered about the Ti–centroid axis; occupancies were refined for the two orientations: (7–11), 70%, and (7′–11′), 30%. The two orientations were ideally staggered. Additionally, one of the carbonyl oxygen atoms, O(4), was disordered in two positions, O(4a) and O(4b), in occupancies of 58% and 42%, respectively. Throughout refinement the Cp rings were constrained to rigid pentagons (d(C–C) = 1.42 Å).

All non-hydrogen atoms were refined with anisotropic temperature factors. Hydrogen atoms were incorporated as idealized, isotropic, updated contributions (d(C–H) = 0.96 Å). Computer programs used are contained in the SHELXTL library (Nicolet Corp.) and were executed on a Data General Eclipse S-30. The final difference Fourier map had no significant features. The final cycle of least squares converged to R = 0.0387 and $R(w) = 0.0411$. Atomic coordinates are presented in Table VI.

Acknowledgment. This research was supported by the National Science Foundation. We thank Professor Ralf Steudel for his timely comments.

Registry No. **1a**, 12116-82-4; **1b**, 78614-86-5; **1c**, 88510-17-2; **2b**, 78961-79-2; **3a**, 106162-08-7; **3b**, 106162-10-1; **3c**, 106162-09-8; **4** (R = H, Z = CO_2CH_3), 106162-15-6; **4** (R = HcH_3, Z = $CO_2CH_2CH_3$), 106162-16-7; $(i\text{-}PrC_5H_4)_2TiCl_2$, 12130-65-3; $(CH_3C_5H_4)_2Ti(SH)_2$, 79816-63-0; $(CH_3C_5H_4)_2TiSe_5$, 78614-88-7; 1,4-$[(CH_3C_5H_4)_2Ti]_2S_4$, 106191-39-3; 1,4-$[(i\text{-}PrC_5H_4)_2Ti]Se_4$, 106162-11-2; $(CH_3C_5H_4)_2TiCl_2$, 1282-40-2; $(CH_3C_5H_4)_2TiS_2C_2(CO_2CH_3)_2$, 82865-09-6; $(C_5H_5)_2Ti(CO)_2$, 12129-51-0; $(CH_3C_5H_4)_2Ti(CO)_2$, 90413-05-1; 1,4-$[(CH_3C_5H_4)_2Ti][(C_5H_5)_2Ti]S_4$, 106162-12-3; $(C_5H_5)_2TiS_2C_2H(CO_2CH_3)$, 106162-13-4; $(C_5H_5)_2TiSe_5$, 12307-22-1; $(C_5H_5)_2TiSe_2C_2H(CO_2CH_3)$, 106162-14-5; 1,4-$[(C_5H_5)_2Ti]S_4C(CH_3)_2$, 88510-18-3; 1,4-$[(CH_3C_5H_4)_2Ti]S_4C(CH_3)_2$, 88510-19-4; 1,4-$[(i\text{-}PrC_5H_4)_2Ti]S_4C(CH_3)_2$, 88510-20-7; $(C_5H_5)_2TiS_2C_2(CO_2CH_3)_2$, 78961-80-5; $(i\text{-}PrC_kH_4)_2TiSe_5$, 97732-75-7; C_5H_6, 542-92-7; $i\text{-}PrC_5H_5$, 27288-03-5; $TiCl_4$, 7550-45-0; $CH_3O_2CC{\equiv}CH$, 922-67-8; 2-bromopropane, 75-26-3.

Supplementary Material Available: Tables of thermal parameters for compounds **3c** and **4** and hydrogen coordinates for **4** (3 pages); listings of structure factors for **3c** and **4** (32 pages). Ordering information is given on any current masthead page.