Catalytic Transformations of Vinylthiiranes by Tungsten Carbonyl Complexes. A New Route to 3,6-Dihydro-1,2-dithiins

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Abstract: $W(CO)_5(NCMe)$ (**1**) has been found to transform vinylthiirane and a series of methyl-substituted vinylthiiranes into a series of 3,6-dihydro-1,2-dithiin compounds. Two equivalents of the vinylthiirane are required, and 1 equiv of a butadiene is formed by the transfer of its sulfur atom to the second vinythiirane, which is then transformed into the dihydrodithiin. The formation of 3,6-dihydro-1,2-dithiin (**9**) proceeds at 15 turnovers/h at 25 °C using vinylthiirane (**4**) and **1** as the catalyst. The catalyst is long-lived (up to 2000 turnovers have been obtained without loss of activity) and relatively insensitive to air. Methyl substitutents on the vinyl group increase the rate of reaction while methyl substituents on the thiirane ring slow it considerably. The introduction of phosphine ligands to the catalyst also leads to significant increases in the rate of reaction. The dithiin complex $W(CO)_5(\overline{SSCH_2CH{=}CHCH_2})$ (**13**) was isolated from the catalytic reactions and was structurally characterized. The dihydrodithiin is coordinated to the tungsten atom through one of its two sulfur atoms. Compound **13** was shown to be a species in the catalytic cycle. A mechanism involving a vinylthiirane intermediate that undergoes spontaneous ring opening, followed by addition of a second vinylthiirane to the terminal carbon of the chain, elimination of 1 equiv of butadiene, and formation of a sulfur–sulfur bond leading to **13** is proposed. The vinylthiirane intermediate is regenerated by ligand substitution which releases the dihydrodithiin product. Compound **9** readily polymerizes when its pure form is exposed to visible light. If the polymerization is interrupted at an early stage, 1,2,7,8-tetrathiacyclododeca-4,10-diene (**14**), a dimer of **9**, can be isolated. Compound **14** was obtained in 5.6% yield and was structurally characterized crystallographically.

Introduction

The cleavage of carbon–sulfur bonds in cyclic thioethers is central to the processes relating to the hydrodesulfurization of petroleum feedstocks.[1–3] We have recently been investigating ring-opening reactions of the strained cyclic thioethers, thietanes, and thiiranes, which are promoted by coordination of the sulfur atom to transition metal atoms of certain metal carbonyl complexes.[4–6] For the thietanes, we have even been able to

develop catalytic processes that lead to the formation of polythioether macrocycles catalytically by ring-opening cyclooligomerization processes involving three or more thietane molecules, e.g. eq 1.[5]

(1)
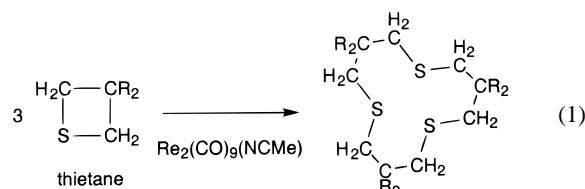
Thiiranes possess ring strain that has been estimated to be ≈19 kcal/mol in the parent molecule.[7] They are readily

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polymerized when treated with Lewis acids and Lewis bases.[8] They also eliminate sulfur to yield elemental sulfur and the corresponding olefin when heated.[8b−d,9] The desulfurization of thiiranes is promoted by complexation to transition metal atoms and adsorption onto metal surfaces.[10,11]

There have been a few reports of transition metal complexes containing thiiranes as ligands, and some of these have been characterized structurally by X-ray crystallographic methods.[6,12] We have found that the thiiranetungsten pentacarbonyl complex $W(CO)_5(SC_2H_4)$ reacts with thiiranes catalytically to yield a series of cyclic disulfides with release of 1 equiv of olefin for each disulfide unit that is formed (eq 2).[6]

$$2n \quad \xrightarrow[\text{-n } C_2H_4]{25°C} \quad + \quad \text{etc.} \quad (2)$$

$$W(CO)_5(SC_2H_4)$$
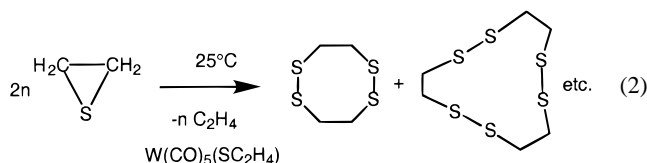
In this report, our studies of the transformations of a series of vinylthiiranes by $W(CO)_5(NCMe)$ (**1**) and its two phosphine derivatives, $W(CO)_4(PPh_3)(NCMe)$ (**2**) and $W(CO)_4(PMe_2Ph)-(NCMe)$ (**3**), are described. We have found that these reactions lead to the formation of 3,6-dihydrodithiins **A** and butadiene, catalytically. Dihydrodithiins **A** and **B** are a family of naturally occurring compounds that have been found to exhibit a range of antiviral, antifungal, and antibiotic properties.[13] A preliminary report of this work has been published.[14]

A   **B**
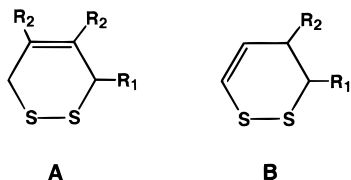
Experimental Section

General Data. Reagent grade solvents were stored over 4 Å molecular sieves. Infrared spectra were recorded on a Nicolet 5DXB FTIR spectrophotometer. ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra

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were recorded on a Varian Mercury 400 spectrometer operating at 100.59, 125.76, and 161.94 MHz, respectively. ^{31}P NMR spectra were referenced against H_3PO_4. Mass spectra were obtained using electron impact ionization. Elemental analyses were performed by Oneida Research Services (Whitesboro, NY). 3,4-Epoxy-1-butene was supplied by Eastman and was used without further purification. 2-Methyl-2-vinyloxirane was purchased from Aldrich and was used without further purification. The remaining epoxides were prepared by following procedure reported for the synthesis of 3,4-epoxy-2-methyl-1-butene.[15] $W(CO)_5(NCMe)$[16] (**1**), $W(CO)_5(PPh_3)$,[17] and $W(CO)_5(PMe_2Ph)$[17] were prepared according to the published procedures. [13]CO-enriched tungsten complexes (labeled with * herein) were prepared in the same manner as the unenriched complexes starting with [13]CO-enriched $W(CO)_6$.[5g] Product separations were performed by TLC in air on Analtech 0.25 and 0.50 mm silica gel 60 Å F_{254} glass plates. Plots of the kinetic data were fitted using Cricket Graph version 1.3 of Cricket Software on a Macintosh Power PC.

Synthesis of the Vinylthiiranes. All vinylthiiranes were prepared according to the published procedure for the synthesis of thiirane from the ethylene oxide.[18] Spectral data for vinylthiirane (**4**): ^{1}H NMR (δ in CDCl$_3$): 5.55 (m, 2H), 5.17 (m, 1H), 3.44 (m, 1H), 2.64 (dd, $^2J_{H−H}$ = 6.3 Hz, $^3J_{H−H}$ = 1.6 Hz, 1H), 2.32 (dd, $^2J_{H−H}$ = 5.5 Hz, $^3J_{H−H}$ = 1.6 Hz, 1H). ^{13}C NMR (δ in CDCl$_3$): 138.9 (1C), 117.6 (1C), 36.7 (1C), 25.3 (1C).[19] The mass spectrum shows the parent ion at 86 m/e, as well as additional ions with weights of 85, 71, and 64 m^+/e. Spectral data for 3,4-epithia-2-methyl-1-butene (**5**): ^{1}H NMR (δ in CDCl$_3$): 5.18 (br s, 1H), 4.97 (br s, 1H), 3.55 (t, J = 6.1 Hz, 1H), 2.51 (dd, $^2J_{H−H}$ = 6.5 Hz, $^3J_{H−H}$ = 1.6 Hz, 1H), 2.43 (dd, $^2J_{H−H}$ = 5.8 Hz, $^3J_{H−H}$ = 1.6 Hz, 1H), 1.62 (br s, 3H). ^{13}C NMR (δ in CDCl$_3$): 142.5 (1C), 114.9 (1C), 39.8 (1C), 23.0 (1C), 16.6 (1C). The mass spectrum shows the parent ion at 100 m/e, as well as additional ions with weights of 99, 85, and 65 m^+/e. Spectral data for 4,5-epithia-2-pentene (**6**): ^{1}H NMR (δ in CDCl$_3$): 5.84 (m, 1H), 5.02 (m, 1H), 3.39 (m, 1H), 2.55 (dd, $^2J_{H−H}$ = 6.6 Hz, $^3J_{H−H}$ = 1.2 Hz, 1H), 2.24 (dd, $^2J_{H−H}$ = 5.6 Hz, $^3J_{H−H}$ = 1.2 Hz, 1H), 1.65 (dd, $^2J_{H−H}$ = 6.8 Hz, $^3J_{H−H}$ = 1.6 Hz, 3H). ^{13}C NMR (δ in CDCl$_3$): 131.7 (1C), 129.4 (1C), 37.0 (1C), 25.3 (1C), 17.9 (1C). The mass spectrum shows the parent ion at 100 m/e, as well as additional ions with weights of 85, 67, and 65 m^+/e. Spectral data for 4,5-epithia-3-methyl-2-pentene (**7**): ^{1}H NMR (δ in CDCl$_3$): 5.73 (q, J = 6.8 Hz, 1H), 3.56 (t, J = 6.2 Hz, 1H), 2.47 (dd, $^2J_{H−H}$ = 6.5 Hz, $^3J_{H−H}$ = 1.6 Hz, 1H), 2.42 (dd, $^2J_{H−H}$ = 5.9 Hz, $^3J_{H−H}$ = 1.6 Hz, 1H), 1.64 (d, J = 6.8 Hz, 3H), 1.46 (br s, 3H). ^{13}C NMR (δ in CDCl$_3$): 132.6 (1C), 124.6 (1C), 42.5 (1C), 22.7 (1C), 14.1 (1C), 10.4 (1C). The mass spectrum shows the parent ion at 114 m/e, as well as additional ions with weights of 99, 79, and 67 m^+/e. Spectral data for 3,4-epithia-3-methyl-1-butene (**8**): ^{1}H NMR (δ in CDCl$_3$): 5.65 (dd, $^2J_{H−H}$ = 17.3 Hz, $^3J_{H−H}$ = 10.5 Hz, 1H), 5.33 (dd, $^2J_{H−H}$ = 17.2 Hz, $^3J_{H−H}$ = 0.7 Hz, 1H), 5.16 (dd, $^2J_{H−H}$ = 10.4 Hz, $^3J_{H−H}$ = 0.7 Hz, 1H), 2.58 (d, J = 1.5 Hz, 1H), 2.52 (d, J = 1.1 Hz, 1H), 1.74 (s, 3H). ^{13}C NMR (δ in CDCl$_3$): 142.8 (1C), 114.3 (1C), 45.0 (1C), 34.4 (1C), 23.3 (1C). The mass spectrum shows the parent ion at 100 m/e, as well as additional ions with weights of 99, 85, and 65 m^+/e.

Synthesis of $W(CO)_4L(NCMe)$ (L = PPh$_3$ and PMe$_2$Ph). A 100.0 mg amount of $W(CO)_5(PPh_3)$ (0.171 mmol) was dissolved in a mixture of 15 mL of methylene chloride and 15 mL of acetonitrile in a 50 mL three-neck round-bottomed flask equipped with a stir bar, 10 mL dropper addition funnel, and nitrogen inlet. The system was purged with nitrogen and 1.1 equiv (14.1 mg, 0.188 mmol) of Me$_3$NO dissolved in 10 mL of acetonitrile was added dropwise over 30 min. The solution was stirred for 4 h, and then the volatiles were removed in vacuo. The product was separated by TLC using a hexane/methylene chloride (4/ 1) solvent mixture to yield 64.4 mg (62%) of $W(CO)_4(PPh_3)(NCMe)$ (**2**) as light yellow needles and 29.8 mg of unreacted $W(CO)_5(PPh_3)$.

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Spectral data for **2**: IR ν_{CO} (cm^{-1} in CH$_2$Cl$_2$): 2018 (m), 1899 (vs), 1854 (s). ^{1}H NMR (δ in CD$_2$Cl$_2$): 7.53−7.30 (m, 15H), 1.56 (s, 3H). ^{13}C NMR (δ in CD$_2$Cl$_2$): 206.97 (d, $^2J_{^{31}P-^{13}C}$ = 5.2 Hz, $^1J_{^{183}W-^{13}C}$ = 159.9 Hz, 1C), 206.34 (d, $^2J_{^{31}P-^{13}C}$ = 31.0 Hz, $^1J_{^{183}W-^{13}C}$ = 154.2 Hz, 1C), 202.20 (d, $^2J_{^{31}P-^{13}C}$ = 7.1 Hz, $^1J_{^{183}W-^{13}C}$ = 130.3 Hz, 2C), 134.84 (d, $^1J_{^{31}P-^{13}C}$ = 37.4 Hz, 3C), 133.71 (d, $^2J_{^{31}P-^{13}C}$ = 11.5 Hz, 6C), 130.05 (d, $^4J_{^{31}P-^{13}C}$ = 2.3 Hz, 3C), 128.60 (d, $^3J_{^{31}P-^{13}C}$ = 9.2 Hz, 6C), 122.99 (s, 1C), 3.48 (s, 1C). ^{31}P NMR (δ in CD$_2$Cl$_2$): 29.1 ($^1J_{^{183}W-^{31}P}$ = 238 Hz, 1P). Analysis for **2** (C$_{24}$H$_{18}$O$_4$NPW): calcd C 48.10%, H 3.03%, N 2.34%; found C 47.63%, H 2.78%, N 2.28%. W(CO)$_4$(PMe$_2$Ph)-(NCMe) (**3**) was prepared similarly (68% yield) as a light yellow oil that can be obtained in a solid form by precipitation from a minimal amount of methylene chloride and hexane at −78 °C. Spectral data for **3**: IR ν_{CO} (cm^{-1} in CH$_2$Cl$_2$): 2016 (m), 1894 (vs), 1850 (s). ^{1}H NMR (δ in CD$_2$Cl$_2$): 7.55−7.36 (m, 5H), 1.91 (d, $^2J_{^{31}P-^1H}$ = 7.1 Hz, 6H), 1.87 (d, $^5J_{^{31}P-^1H}$ = 1.7 Hz, 3H). ^{13}C NMR (δ in CD$_2$Cl$_2$): 207.55 (d, $^2J_{^{31}P-^{13}C}$ = 29.3 Hz, $^1J_{^{183}W-^{13}C}$ = 155.8 Hz, 1C), 206.81 (d, $^2J_{^{31}P-^{13}C}$ = 4.5 Hz, $^1J_{^{183}W-^{13}C}$ = 155.8 Hz, 1C), 202.07 (d, $^2J_{^{31}P-^{13}C}$ = 7.5 Hz, $^1J_{^{183}W-^{13}C}$ = 129.4 Hz, 2C), 137.64 (d, $^1J_{^{31}P-^{13}C}$ = 33.9 Hz, 1C), 129.79 (d, $^2J_{^{31}P-^{13}C}$ = 10.6 Hz, 2C), 129.24 (d, $^4J_{^{31}P-^{13}C}$ = 2.3 Hz, 1C), 128.76 (d, $^3J_{^{31}P-^{13}C}$ = 9.1 Hz, 2C), 122.72 (s, 1C), 18.61 (d, $^1J_{^{31}P-^{13}C}$ = 27.1 Hz, 2C), 3.53 (s, 1C). ^{31}P NMR (δ in CD$_2$Cl$_2$): −14.7 ($^1J_{^{183}W-^{31}P}$ = 230 Hz, 1P). Analysis for **3** (C$_{14}$H$_{14}$O$_4$NPW): calcd C 35.39%, H 2.97%, N 2.95%; found C 35.56%, H 2.65%, N 2.77%.

Catalytic Transformations of Vinylthiirane and its Derivatives by W(CO)$_5$(NCMe) (1). A typical reaction is as follows: A 5.0 mg amount (0.014 mmol) of **1** was placed into an NMR tube with 0.50 mL of the corresponding thiirane and 0.50 mL of CD$_2$Cl$_2$. C$_6$Me$_6$ (10.0 mg) was added to serve as a quantitative reference. The solution was shaken and monitored by ^{1}H NMR at 25 °C for 24 h. During this time the formation of the corresponding dithiin and diene was observed. The yield appears to be quantitative as determined by ^{1}H NMR spectroscopy. The volatile products and solvent were then separated from the catalyst by trap-to-trap vacuum distillation with heating to 40 °C. The solvent and corresponding diene were then vacuum-distilled off at 0 to −10 °C to yield pure dithiin. Spectral data for 3,6-dihydro-1,2-dithiin (**9**): ^{1}H NMR (δ in CDCl$_3$): 5.97 (t, J = 2.1 Hz, 2H), 3.26 (d, J = 2.2 Hz, 4H). ^{13}C NMR (δ in CDCl$_3$): 125.5 (2C), 28.2 (2C).[20] The mass spectrum shows the parent ion at 118 m/e, as well as additional ions with weights of 103, 85, and 64 m^+/e. This reaction can be done in the open air as described above, but under these conditions, there is discoloration of the solution that is attributed to partial decomposition of the tungsten complex. When done under nitrogen the discoloration is significantly less, but the product yields and rates of reaction are not significantly different. The vinylthiiranes **5**−**8** were treated with **1** in a similar fashion to yield the following 3,6-dihydro-1,2-dithiin derivatives. 3,6-Dihydro-4-methyl-1,2-dithiin (**10**): ^{1}H NMR (δ in CDCl$_3$): 5.73 (m, 1H), 3.28 (m, 2H), 3.13 (m, 2H), 1.76 (br s, 3H). ^{13}C NMR (δ in CDCl$_3$): 132.7 (1C), 119.6 (1C), 32.2 (1C), 29.5 (1C), 26.0 (1C). The mass spectrum shows the parent ion at 132 m/e, as well as additional ions with weights of 117, 99, 85, and 67 m^+/e. 3,6-Dihydro-3-methyl-1,2-dithiin (**11**): ^{1}H NMR (δ in CDCl$_3$): 5.82 (m, 2H), 3.38 (m, 1H), 3.13 (m, 2H), 1.35 (d, J = 7.1 Hz, 3H). ^{13}C NMR (δ in CDCl$_3$): 132.3 (1C), 124.7 (1C), 35.3 (1C), 28.1 (1C), 20.8 (1C). The mass spectrum shows the parent ion at 132 m/e, as well as additional ions with weights of 99, 84, and 67 m^+/e. 3,6-Dihydro-3,4-dimethyl-1,2-dithiin (**12**): ^{1}H NMR (δ in CDCl$_3$): 5.65 (m, 1H), 3.49 (m, 1H), 3.01 (q, J = 6.8 Hz, 1H), 2.93 (m, 1H), 1.77 (br s, 3H), 1.58 (d, J = 7.0 Hz, 3H). ^{13}C NMR (δ in CDCl$_3$): 137.5 (1C), 119.6 (1C), 38.0 (1C), 29.8 (1C), 25.1 (1C), 20.0 (1C). The mass spectrum shows the parent ion at 146 m/e, as well as additional ions with weights of 113, 82, and 67 m^+/e.

Preparation of W(CO)$_5$(SSCH$_2$CH=CHCH$_2$) (13). A 50.0 mg amount of **1** (0.137 mmol) was dissolved in 5 mL of methylene chloride in a 10 mL three-neck round-bottom flask equipped with a stir bar, reflux condenser, and nitrogen inlet. Under a nitrogen atmosphere, 0.17 mL of vinylthiirane (2.74 mmol) was added and the resulting solution was stirred for 24 h. The volatiles were removed in vacuo, and the product was isolated by TLC (in air on Analtech 0.25 mm silica gel

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60 Å F_{254} plates) using a hexane/methylene chloride (3/1) solvent mixture to yield 29.1 mg (48%) of W(CO)$_5$(SSCH$_2$CH=CHCH$_2$) (**13**) and 5.1 mg of unreacted **1**. Spectral data for **13**: IR ν_{CO} (cm^{-1} in hexane): 2078 (w), 1986 (w), 1949 (vs), 1939 (m). ^{1}H NMR (δ in CDCl$_3$): 6.08 (m, 1H), 6.00 (m, 1H), 3.62 (m, 2H), 3.43 (m, 2H). ^{13}C NMR (δ in CD$_2$Cl$_2$): 199.80 ($^1J_{^{183}W-^{13}C}$ = 157.1 Hz, 1C), 196.80 ($^1J_{^{183}W-^{13}C}$ = 128.9 Hz, 4C), 125.28 (1C), 125.23 (1C), 41.98 (1C), 31.37 (1C). Analysis for **13**: (C$_9$H$_6$O$_5$S$_2$W) calcd C 24.45, H 1.37; found C 24.12, H 1.47.

Catalytic Transformation of Vinylthiirane by W(CO)$_4$(PPhR$_2$)-(NCMe) (R = Ph, 2; R = Me, 3). Synthesis of 3,6-Dihydro-1,2-dithiin. A typical reaction is as follows: A 0.014 mmol amount of catalyst was placed into an NMR tube with 0.50 mL of **4** and 0.50 mL of CD$_2$Cl$_2$. C$_6$H$_6$ (10.0 mg) was added to serve as a quantitative reference. The solution was shaken and the formation of **9** and butadiene was monitored hourly by ^{1}H NMR spectroscopy for 24 h at 25 °C.

Catalytic Transformation of 4 by 1 (Long Term). A 10.0 mg (0.0274 mmol) amount of **1** was dissolved in 10.8 mL of methylene chloride in a 25 mL three-neck round-bottom flask equipped with a stir bar, reflux condenser, and nitrogen inlet. C$_6$Me$_6$ (100.0 mg) was added to serve as an internal standard. **4** (11.54 g, 134 mmol) was then added, and the resulting solution was degassed and filled with nitrogen twice to remove traces of oxygen. The flask was then wrapped in aluminum foil and placed into a 25 °C water bath in the absence of light. Small aliquots of the reaction mixture were removed and analyzed by ^{1}H NMR every 24 h. Some CD$_2$Cl$_2$ was added to these samples for the purpose of the NMR frequency lock. After 5 days, the reaction was at 2040 turnovers and 93% conversion (ratio of **9** to **4**). The volatiles were removed in vacuo, and an additional 2.0 mL each of **4** and methylene chloride were added to the residue. The production of **9** resumed and was followed for an additional 24 h by ^{1}H NMR, demonstrating that the catalyst was still active.

**General Procedures for the Kinetic Studies.** All studies were conducted in clean 5 mm NMR tubes in CD$_2$Cl$_2$ solvent and were followed by ^{1}H NMR spectroscopy. A typical procedure is as follows. A 0.014 mmol amount of catalyst and 10.0 mg of C$_6$Me$_6$ (used as a quantitative internal reference) were placed in a clean, dry NMR tube. The tube was sealed with a rubber septum and was evacuated and filled with nitrogen three times. A 0.50 mL volume of CD$_2$Cl$_2$ was transferred to the sealed NMR tube via syringe, followed by a 0.50 mL volume of vinylthiirane. The tube was shaken to mix the reactants thoroughly and was then placed in a Varian Mercury 400 NMR spectrometer at 25.0 °C. All kinetic experiments were performed at least twice. The reaction rates were determined by measuring the disappearance of the vinylthiirane by integration of the alkenyl triplet and aliphatic doublet at 5.97 and 3.26 ppm, respectively, against the C$_6$Me$_6$ internal standard in a series of NMR spectra every 30 min.

Kinetics of the Transformation of 4 by W(CO)$_5$(SSCH$_2$CH=CHCH$_2$) (13). (a) Varying amounts (2, 4, 6, 8, and 10 mg) of **13** and 10.0 mg of C$_6$Me$_6$ were placed into separate NMR tubes with 0.50 mL of the vinylthiirane and 0.50 mL of CD$_2$Cl$_2$ each. The solutions were shaken and monitored by ^{1}H NMR at 25 °C for 4 h. During this time the formation of 3,6-dihydro-1,2-dithiin (**9**) and butadiene was observed. The spectra were recorded at the end of 4 h and the TONs were calculated. Figure 4 shows a plot of the results.

(b) A 0.014 mmol amount of **13** and 10.0 mg of C$_6$Me$_6$ was placed into an NMR tube with 0.50 mL of the vinylthiirane and 0.50 mL of CD$_2$Cl$_2$. The solution was shaken and monitored every 30 min by ^{1}H NMR at 25 °C for 24 h. During this time the formation of 3,6-dihydro-1,2-dithiin (**9**) and butadiene was observed. The yield appears to be quantitative as determined by ^{1}H NMR spectroscopy. The volatile products and solvent were then separated from the catalyst by trap-to-trap vacuum distillation with heating to 40 °C. The solvent and butadiene were then vacuum distilled off at 0 to −10 °C to yield pure **9**. The recovery of the catalyst was 50%. Figure 5 shows a plot of the results as a function of time.

Preparation of ^{13}CO-Enriched Complexes. All ^{13}CO-enriched complexes were prepared in the same manner as the unenriched complexes starting with ^{13}CO-enriched W(CO)$_6$.[5g] The ^{13}CO-enriched
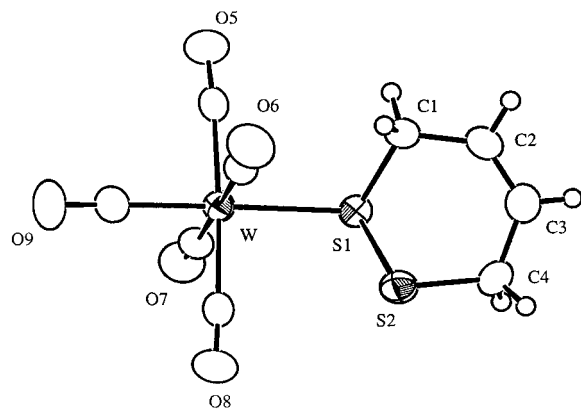
Figure 1. ORTEP diagram of the molecular structure of W(CO)₅- (SSCH₂CH=CHCH₂) (**13**) showing 40% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg) are as follows: W−S(1) = 2.549(2), S(1)−S(2) = 2.062(2), S(1)−C(1) = 1.820(7), S(2)−C(4) = 1.811(7), C(1)−C(2) = 1.487(9), C(2)−C(3) = 1.323-(8), C(3)−C(4) = 1.49(1); W−S(1)−C(1) = 109.8(2), W−S(1)−S(2) = 105.32(8), S(2)−S(1)−C(1) = 97.7(2), S(1)−S(2)−C(4) = 98.4-(2); torsion angle C(1)−S(1)−S(2)−C(4) = 63.6(3)°.
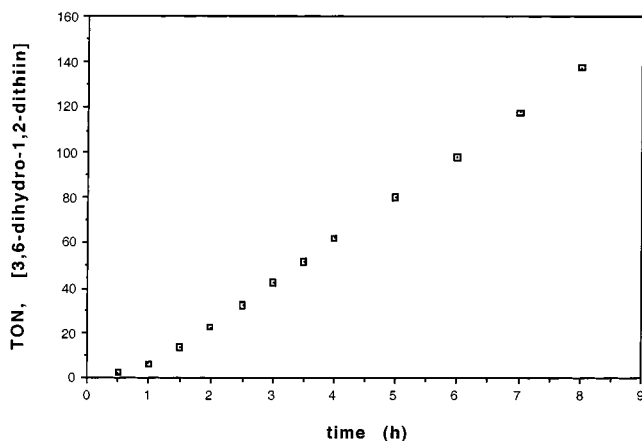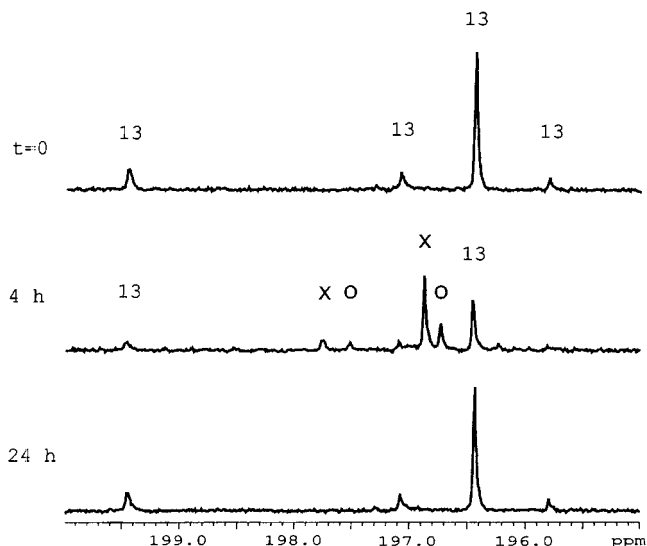

Figure 2. Plot of the formation of **9** from **4** as a function of time using the catalyst **1**.

Figure 3. ^{13}C NMR spectra in the CO region of the spectrum of a catalytic transformation of **4** in **9** by **13***. The resonances of **4** and **9** are not observed in this region. Two intermediates **X** and **O** form and then disappear when the reaction is completed.
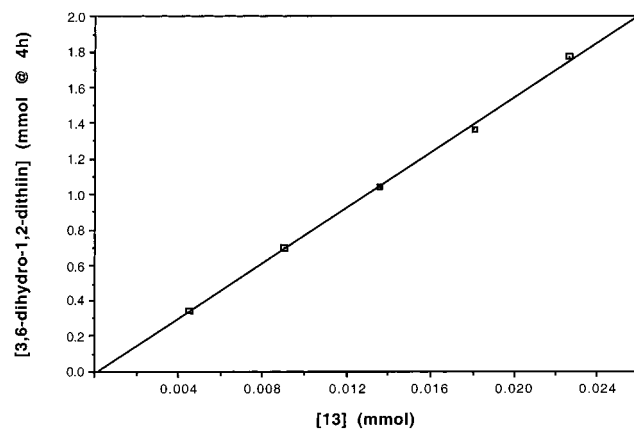
Figure 4. Plot of the formation of **9** as a function of the concentration of the catalyst **13**.

Figure 5. Plot of the disappearance of **4** as a function of time in catalysis by **13**.

complexes of W(CO)₅(NCMe) (**1***), W(CO)₅(SSCH₂CH=CHCH₂) (**13***), W(CO)₄(PPh₃)(NCMe) (**2***), and W(CO)₄(PMe₂Ph)(NCMe) (**3***) were then verified by ^{13}C NMR prior to use. Mass spectral analysis indicated the ^{13}CO enrichment was approximately 30%.

An NMR Analysis during Catalysis Using 13* as the Catalyst. Vinylthiirane (1.75 mL) and 1.75 mL of CD₂Cl₂ were vacuum degassed and placed in a 10 mm NMR tube with 25.0 mg of **13*** under nitrogen. The reaction was monitored hourly by ^{13}C NMR spectroscopy. This showed a decrease in concentration of **13*** and the formation of two W(CO)₅L intermediates during the catalysis. As the catalysis proceeded, the intermediates disappeared and **13*** reformed fully and was the only tungsten carbonyl complex in solution at the end of the time period. ^{13}C NMR spectra of the major intermediate (δ in CD₂Cl₂): 197.9 (1C), 197.0 (4C), 134.4 (1C), 122.1 (1C), 52.4 (1C), 37.7 (1C). ^{13}C NMR spectra of the minor intermediate: 197.7 (1C), 196.8 (4C), 135.6 (1C), 134.1 (1C), 44.1 (1C), 35.9 (1C). The ratio of major intermediate to the minor intermediate was approximately 2.5/1 when they were present in the largest amounts.

Control Experiments. (a) In the Absence of a Catalyst. Vinylthiirane (0.50 mL) and 0.50 mL of CD₂Cl₂ were placed in an NMR tube in the absence of any metal complexes. C₆Me₆ (10.0 mL) was added to serve as a quantitative reference. The solution was shaken and maintained at 25 °C for 24 h. During this time the formation of no more than trace amounts of **9** and butadiene (<1%) was observed.

(b) In the Presence of W(CO)₆. Vinylthiirane (0.50 mL), 0.50 mL of CD₂Cl₂, and 5.0 mg of W(CO)₆ (0.014 mmol) were placed in an

NMR tube. C₆Me₆ (10.0 mg) was added to serve as a quantitative reference. The solution was shaken and maintained at 25 °C for 24 h. During this time the formation of no more than trace amounts of **9** and butadiene (<1%) was observed.
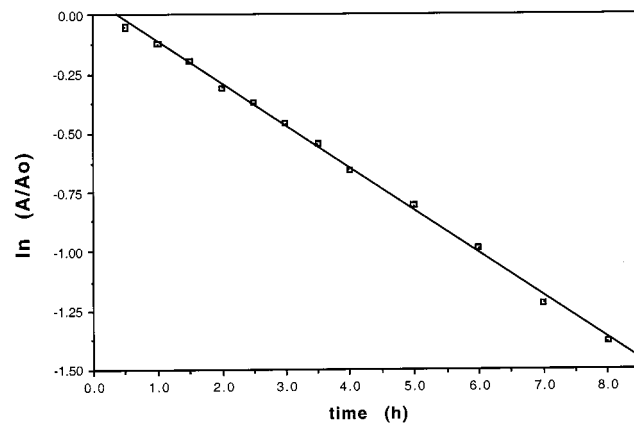
(c) Catalysis by 13* under a CO Atmosphere. Vinylthiirane (0.50 mL), 0.50 mL of CD₂Cl₂, and 5.0 mg of **13*** (0.014 mmol) were placed into an NMR tube. C₆Me₆ (10.0 mg) was added to serve as an internal

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Table 1. Results of Catalytic Transformations of Vinylthiirane to 3,6-Dihydro-1,2-dithiin

catalyst	atmosphere	% yield[a]	TON[b] (24 h)	TOF[c]
1	N_2	92	212	16
1	CO	91	208	16
1	air	86	212	15
13	air	91	220	19
2	air	93	228	47
3	air	96	222	53

[a] Yields based on eq 2 after 24 h. [b] TON = mol of dithiin/mol of catalyst. [c] TOF = mol of **9**/mol of catalyst·h (based on the amount of product formed after a 4 h reaction period).

standard. The solution was evacuated and filled with 1 atm of CO twice and then maintained at 25 °C for 24 h. The progress of the reaction was monitored hourly by ^{1}H NMR and ^{13}C NMR spectroscopy. There appeared to be no significant difference in rate of formation of **9** than under air or under a nitrogen atmosphere (see Table 1).

(d) Reaction of 1 with CO. A 10.0 mg amount of **1** was dissolved in 15 mL of methylene chloride in a 25 mL three-neck round-bottom flask equipped with a stir bar, gas inlet, and gas outlet. The solution was twice degassed and filled with 1 atm of CO, maintained at room temperature, and monitored by FTIR over a period of 4 days. After that time, the conversion of **1** to $W(CO)_6$ was approximately 50%.

Preparation of (SCH₂CH=CHCH₂SSCH₂CH=CHCH₂S) (14). A 125 mg (1.06 mmol) amount of **9** was added to a 5 mm NMR tube without solvent. The sample was purged with nitrogen and then irradiated for 10 min by using a 100 W soft white lamp placed 8 in. from the tube. As the mixture became viscous, the reaction was quenched by adding 0.75 mL of CD_2Cl_2. The formation of **14** was verified by ^{1}H and ^{13}C NMR spectroscopy. The product was separated from the unreacted **9** by TLC on silica gel using a hexane/methylene chloride (3/1) solvent mixture to yield 14.0 mg of **14** (5.6% yield), which elutes just behind the unreacted **9**. Spectral data for **14**: ^{1}H NMR (δ in $CDCl_3$): 5.73 (m, 4H), 3.46 (br d, $^3J_{H-H}$ = 5.1 Hz, 8H). ^{13}C NMR (δ in $CDCl_3$): 128.4 (4C), 35.4 (8C). The mass spectrum shows the parent ion at 236 m/e, as well as additional ions with weights of 150, 118, 103, and 85 m^+/e.

Crystallographic Analyses. Yellow crystals of **13** suitable for diffraction analysis were grown by slow evaporation of solvent from a solution in hexane at −17 °C. Colorless crystals of **14** suitable for diffraction analysis were grown by slow evaporation of solvent from a solution in hexane at 25 °C. The crystals used for the diffraction measurements were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer using graphite-monochromated Mo Kα radiation. The unit cell was determined and refined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table 2. All data processing was performed on a Silicon-Graphics INDIGO^2 workstation by using the TEXSAN motif structure solving program library obtained from the Molecular Structure Corp. (The Woodlands, TX). Neutral atom scattering factors were calculated by the standard procedures.[21a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[21b] Lorentz/polarization (Lp) and absorption corrections (DIFABS) were applied to the data. Full matrix least-squares refinements minimized the function: $\sum_{hkl}w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$.

Compound **13** crystallized in the orthorhombic crystal system. The space group *Pbca* was identified uniquely on the basis of the systematic absences observed during the collection of the intensity data. The structure was solved by a combination of direct methods (SIR2) and difference Fourier syntheses. All nonhydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms were located and refined.

(21) (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV, Table 2.2B, pp 99−101. (b) *Ibid.* Table 2.3.1, pp 149−150.

Table 2. Crystallographic Data for Compounds **13** and **14**

	13	**14**
formula	$WS_2O_5C_9H_6$	$S_4C_8H_{12}$
formula weight	442.11	236.42
crystal system	orthorhombic	monoclinic
lattice parameters		
a (Å)	15.688(2)	17.315(2)
b (Å)	17.534(3)	4.699(1)
c (Å)	9.305(1)	14.388(2)
α (deg)	90.0	90.0
β (deg)	90.0	110.20(1)
γ (deg)	90.0	90.0
V (Å^3)	2559.6(5)	1098.6(3)
space group	*Pbca* (no. 61)	*C2/c* (no. 15)
Z value	8	4
ρ_{calc} (g/cm^3)	2.29	1.43
μ(Mo Kα) (cm^{-1})	93.7	8.1
temperature (°C)	20	20
$2\theta_{max}$ (deg)	50	47
no. obsd ($I > 3\sigma(I)$)	1638	673
no. of variables	178	79
goodness of fit (GOF)[a]	1.38	2.29
max shift/error on final cycle	0.00	0.00
residuals:[a] R; R_w	0.022; 0.023	0.026; 0.030
abs corrn	DIFABS	DIFABS
transmn coeff, max/min	0.56−1.00	0.62−1.00
largest peak in final diff map (e$^-$/Å^3)	0.51	0.21

[a] $R = \sum_{hkl}(||F_{obs}| - |F_{calc}||)/\sum_{hkl}|F_{obs}|$; $R_w = [\sum_{hkl}w(|F_{obs}| - |F_{calc}|)^2/\sum_{hkl}wF_{obs}^2]^{1/2}$, $w = 1/\sigma^2(F_{obs})$; GOF $= [\sum_{hkl}w(|F_{obs}| - |F_{calc}|)^2/(n_{data} - n_{vari})]^{1/2}$.

Compound **14** crystallized in the monoclinic crystal system. The systematic absences in the data were consistent with either of the space groups *C2/c* or *Cc*. The former was selected and confirmed by the successful solution and refinement of the structure. The structure was solved by a combination of direct methods (SIR2) and difference Fourier syntheses. For the analysis of **14** all nonhydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were located and refined with isotropic thermal parameters.

Results

The vinylthiiranes **4−8** were readily converted into a 1/1 mixture of the 3,6-dihydro-1,2-dithiins **9−12** and the corresponding diene under unusually mild conditions in the presence of the catalyst $W(CO)_5(NCMe)$ (**1**) (eq 3). One equivalent of

4 $R_1=R_2=R_3=H$
5 $R_1=R_3=H,R_2=Me$
6 $R_1=Me,R_2=R_3=H$
7 $R_1=R_2=Me,R_3=H$
8 $R_1=R_2=H,R_3=Me$

9 $R_1=R_2=R_3=H$
10 $R_1=R_3=H,R_2=Me$
11 $R_1=Me,R_2=R_3=H$
12 $R_1=R_2=Me,R_3=H$
10 $R_1=R_2=H,R_3=Me$

(3)
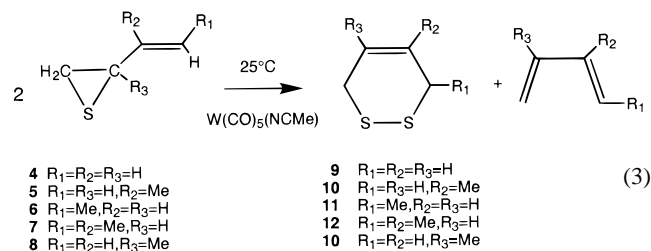
the corresponding butadiene was also formed. The yields and turnover frequencies (TOFs) for the various thiiranes are given in Table 3. The reaction is very sensitive to substituent effects, and the TOFs were found to range from a low of 2 h^{-1} when a methyl group is present on the thiirane ring to a high of 29 h^{-1} when a methyl group is located at the α-position of the vinyl group. The reaction rate of the parent **4** lies approximately midway between the two extremes at 15 turnovers/h. The reaction is relatively insensitive to the atmosphere and proceeds at essentially equivalent rates whether the reaction is performed in air, under nitrogen or even under CO; however, there was some discoloration of the solutions when they were conducted

Table 3. Results of Catalytic Transformations of Vinylthiiranes to Dihydrodithiins by Compound **1**

reagent	product	% yield[a]	TON[b] (24 h)	TOF[c]
4	**9**	86	212	15
5	**10**	84	141	29
6	**11**	86	149	24
7	**12**	80	146	19
8	**10**	34[d]	53	2

[a] Yields based on eq 2 at 24 h. [b] TON = mol of product/mol of catalyst (**1** = W(CO)$_5$NCMe). [c] TOF = mol of product/mol of catalyst·h. (based on the amount of product formed after 4 h). [d] 85% yield after 72 h.

under an atmosphere of air. This is attributed to partial decomposition of some of the catalyst. The decomposition was not extensive and the decomposition products could not be isolated or characterized. In the absence of catalyst or in the presence of W(CO)$_6$, only traces of the dithiin products (<1%) were formed under the same conditions.

Small amounts of a tungsten complex W(CO)$_5$(SSCH$_2$CH=CHCH$_2$) (**13**) were obtained from the catalytic reactions involving the substrate **4**. This product can be obtained in up to 48% yield when performed using larger quantities of the tungsten complex **1**. Compound **13** was characterized by a single-crystal X-ray diffraction analysis, and an ORTEP diagram of its molecular structure is shown in Figure 1. The molecule contains a W(CO)$_5$ grouping with a 3,6-dihydro-1,2-dithiin ligand coordinated to the tungsten atom through one of its two sulfur atoms, W−S(1) = 2.549(2) Å and S(1)−S(2) = 2.062-(2) Å. There is a double bond between the carbon atoms C(2) and C(3), C(2)−C(3) = 1.324(4) Å. The torsion angle at the sulfur−sulfur bond, C(1)−S(1)−S(2)−C(4), is 63.6(3)°. The minimum strain for torsion at the S−S bond is believed to occur at the angle of 90°.[22]

The catalytic activity of **13** for reaction 2 is slightly higher than that of **1**. This can be explained by that fact that **1** is only a precursor to the catalyst and **13** is actually a species in the catalytic cycle (see below). There is a noticeable induction period when **1** is used as the catalyst precursor. This induction period disappears when **13** is used as the catalyst. A plot of catalysis using **1** as the catalyst precursor is shown in Figure 2.

To learn more about the species involved in the catalysis, the progress of an active catalytic reaction was followed by ^{13}C NMR spectroscopy using ^{13}C-enriched **13** and unenriched **4**. These spectra showed that the concentration of **13** decreases as the reaction begins and two W(CO)$_5$-containing intermediates are formed. At the end of the catalysis, the intermediates disappear and **13** reforms fully and is the only detectable tungsten carbonyl complex in solution. Spectra in the CO region at the beginning, after 4 h and at the end of the reaction are shown in Figure 3. New resonances were also observed in the olefin and aliphatic region of the spectrum. The spectra of the major and minor intermediates are as follows: major intermediate: 197.9 (1C), 197.0 (4C), 134.4 (1C), 122.1 (1C), 52.4 (1C), 37.7 (1C); minor intermediate: 197.7 (1C), 196.8 (4C), 135.6 (1C), 134.1 (1C), 44.1 (1C), 35.9 (1C). The ratio of the major intermediate to the minor intermediate was approximately 2.5/1 when they were present in their greatest concentrations. From the relative intensities of the resonances in the CO region of the spectrum, it can be concluded that both intermediates contain W(CO)$_5$ groupings. The presence of two olefin and two aliphatic resonances for each isomer can be explained by the existence of two thiirane complexes of W(CO)$_5$. These are proposed to

differ by an exo or endo orientation of the vinyl group relative the W(CO)$_5$ group. This will depend on which of the two lone pairs of electrons on the sulfur atom is coordinated to the tungsten atom. Presumably, the less crowded exo isomer is the major isomer. Similar stereoisomerism was observed for the compound W(CO)$_5$[*cis*-(SC(H)MeC(H)Me)].[8c] Curiously, the

exo   endo
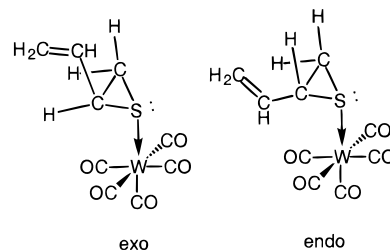
formation of free CO was also observed during the catalysis. To try to ascertain if this was mechanistically significant, the catalysis was conducted under an atmosphere of CO. Interestingly, the presence of a pure CO atmosphere had no effect on the rate of the catalytic reaction. Kinetic analysis showed that the reaction was first order in the concentration of the tungsten catalyst (see Figure 4) and that the disappearance of **4** was first order (see Figure 5). The catalysis is not affected by light. Similar results were obtained in room light and in the complete absence of light.

The PPh$_3$ and PMe$_2$Ph derivatives **2** and **3** of **1** were prepared, and their ability to produce the catalysis was investigated. The ^{13}C NMR spectra of these derivatives indicate that the phosphine ligand is positioned cis to the acetonitrile ligand. Interestingly, the catalytic activity of **2** and **3** is significantly higher than that of **1**, TOF = 47 for **2** and 53 for **3** for the substrate **4** (see Table 1).

The effects of methyl substituents on the thiirane on the rate of catalysis was also investigated. The catalysis was significantly increased when methyl groups were placed on the vinyl group but was significantly decreased when a methyl substitutent was placed on the thiirane ring.

Compound **9** has been prepared previously by the oxidation of the corresponding dithiol.[20,22] Calculations have indicated that it contains slight strain energy.[22] It is stable in solution at room temperature for extended periods; however, in the pure form, it undergoes polymerization to a white insoluble solid at room temperature in the presence of light.[23] While the polymerization is extensive, we were able to separate small amounts of a dimer of **9** by interrupting the polymerization in its early stages. This dimer has been not been reported previously. It was characterized by us through a combination of NMR, mass spectrometry, and single-crystal X-ray diffraction analysis and was shown to be the compound 1,2,7,8-tetrathiacyclododeca-4,10-diene (**14**). Compound **14** crystallizes in the monoclinic space group $C2/c$ with four molecules in the unit cell. An ORTEP drawing of the molecular structure of **14** is shown in Figure 6. The molecule is a 12-membered heterocycle with two disulfide linkages at the 1,2 and 7,8 positions. The molecule contains a center of symmetry in the solid state. The S−S bond distance, S(1)−S(2*) = 2.025(1) Å, is slightly shorter than the S−S distance observed for **9** characterized as a ligand in **13** (see above). The shortest transannular nonbonding contact in **14** lies between the two equivalent sulfur atoms S(2) and S(2*), S(2)···S(2*) = 3.670(1) Å. There are two C−C double bonds at the 4,5 and 10,11 positions, C(2)−C(3) = 1.324(4) Å. The torsion angle at

(22) Burns, J. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1990**, *112*, 6296

(23) Lautenschlaeger, F.; Schnecko, H. *J. Polym. Sci.* **1970**, *8*, 2579.
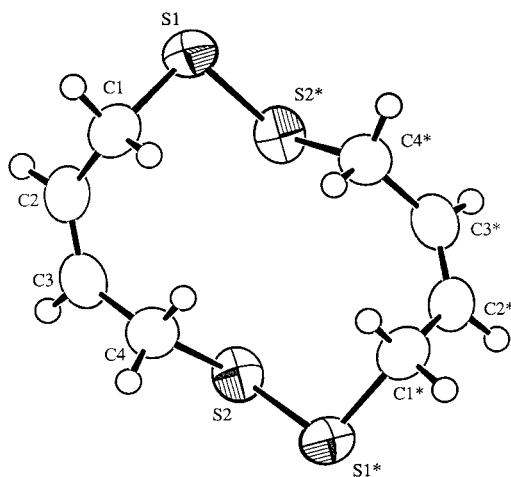
Figure 6. ORTEP diagram of the molecular structure of 1,2,7,8-tetrathiacyclododeca-4,10-diene (**14**) showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) as follows: S(1)−S(2*) = 2.025(1), S(1)−C(1) = 1.833(3), S(2)−C(4) = 1.827(3), C(1)−C(2) = 1.481(4), C(2)−C(3) = 1.324(4), C(3)−C(4) = 1.489(4), S(2)⋯S(2*) = 3.670(1), S(1*)−S(2)−C(1) = 104.4(1), S(2*)−S(1)−C(1) = 103.5(1).

the sulfur−sulfur bonds, C(1)−S(1)−S(2*)−C(4*), is 82.7(1)°, indicating that it should contain very little torsion strain.[20] After it is isolated, **14** is stable toward further polymerization; however, when it is present in solutions of **9** undergoing polymerization, it is consumed in the polymerization process. Thus, the isolation of **14** is dependent upon interrupting the polymerization of **9** by quenching the sample with solvent in the early stages of the process and then isolating by TLC. The yields are always low.

Discussion

In previous studies, we have shown that thiiranes will react with **1** to form stable complexes that can be isolated and crystallographically characterized. In these complexes the sulfur is coordinated to the tungsten atom. The complex W(CO)$_5$-(SC$_2$H$_4$) reacts with additional quantities of thiirane catalytically to yield a series of cyclic disulfides according to eq 2.[6] We believe that the reaction of **1** with the vinylthiiranes **4**−**8** proceeds by a similar process involving an initial coordination of the thiirane to the tungsten atom via the sulfur atom. However, these vinylthiirane complexes are more reactive than those of the simple thiiranes. We have not been able to isolate any vinylthiirane complexes of W(CO)$_5$, but spectra of the catalytically active solutions do show evidence for the formation of intermediates, and the spectra of these intermediates are consistent with that expected for vinylthiirane complexes, see above.

The catalytic formation of a 1/1 mixture of the 3,6-dihydro-1,2-dithiins **9**−**12** and the corresponding diene can be explained by Scheme 1, which begins with the formation of vinylthiirane complexes of W(CO)$_5$ **C** by displacement of the NCMe ligand from **1**, step a. The observation of an induction period when using **1** as the catalyst is consistent with a time-dependent conversion of **1** to the intermediates **C** and absence of an induction period when using **13** as the catalyst. It is also consistent with the absence of inhibition by free CO provided that free CO does not react readily with **1** or **13** to form W(CO)$_6$, which is catalytically inactive. The surprisingly slow reaction of **1** with CO was confirmed by an independent test (see the Experimental Section).

Scheme 1
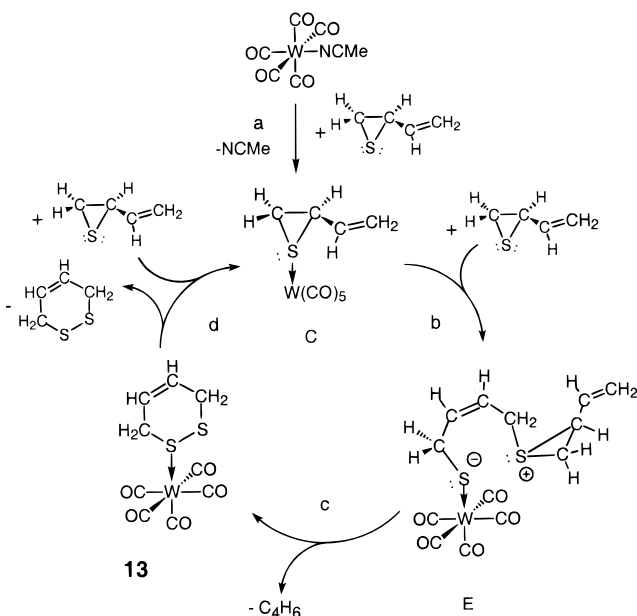
The mechanism of the ring opening of the thiirane ring could occur by either of two processes: (1) a unimolecular process leading to an allylium/thiolate intermediate such as **D**, followed
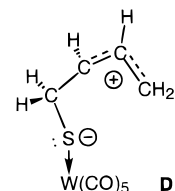
by a rapid addition of a second thiirane through its sulfur atom to the terminus of the carbon chain, or (2) a bimolecular nucleophilic addition mechanism in which the sulfur atom of a second thiirane adds to the β-carbon atom of the vinyl group of the thiirane ligand. The opening of the thiirane ring is concurrent with or follows this nucleophilic addition.

The unimolecular ring-opening process could provide an explanation for the increase in the rate of the reaction when methyl substitutents are placed on the vinyl group, namely the methyl groups provide a more stable form of the intermediate **D** and, presumably, a more facile route to it. The decrease in the reaction rate when the methyl group is placed on the thiirane ring can be attributed to the known stabilization of thiiranes by alkyl substituents on the ring. It is known that the introduction of methyl substitutents to thiirane stablizes it against ring-opening polymerization reactions.[8c] Lautenschlaeger et al. proposed unimolecular ring opening of vinylthiirane as a mechanism for its cation-induced polymerization.[23] Regardless of the ring-opening mechanism, the zwitterionic intermediate **E** can be anticipated, step b, upon the addition of the second equivalent of thiirane, and the C−C double bond is shifted to the position between the two CH groups. At this stage, the negatively charged thiolato sulfur atom and the positively charged thiiranium sulfur atom combine to neutralize one another with formation of a S−S bond and the elimination of butadiene, step c. This could occur either by S$^-$ attack on the S$^+$ atom, by spontaneous elimination of butadiene and self-neutralization, or perhaps by some electron-transfer mechanism. In any case, the complex **13** containing the 3,6-dihydro-1,2-dithiin ligand is formed. Complex **13** is observed spectroscopi-

cally, and it can even be isolated and structurally characterized (see above). The catalytic cycle is completed, step d, by substitution of the dithiin ligand by another 1 equiv of vinylthiirane to regenerate the vinythiiraneW(CO)$_5$ intermediate. This step would explain the observed first-order dependence of the reaction rate on the vinylthiirane concentration. Also, in view of the slowness of the reaction of **1** with CO, it can be concluded that this step must be *associative* in character and should enter into the rate equation. This would also be consistent with the unimolecular ring opening mechanism, whereas the bimolecular ring-opening mechanism might be expected to exhibit a second-order dependence on the vinylthiirane concentration if the ring-opening addition was the slow step of the reaction. Throughout the process only 1 equiv of W(CO)$_5$ is involved in the catalysis. This is consistent with the observed first-order rate dependence on the concentration of tungsten.

The enhancement of the rate of reaction by the introduction of phosphine ligands may be attributed either to steric effects or to electronic effects or a combination thereof. Increased steric crowding among the ancillary ligands on the tungsten atom would certainly favor transformations that lead to opening of the thiirane ring. However, the observation that the PMe$_2$Ph complex **3** is even more active than the PPh$_3$ complex **2** would indicate that the rate enhancement is probably more than a simple steric effect, since PMe$_2$Ph is less bulky than PPh$_3$. From an electronic perspective, if one replaces a CO ligand with a phosphine ligand, this would result in an increase in electron density on the metal because phosphines are poorer acceptors than CO. The increase in electron density on the metal atom would allow more π-bonding to the remaining ligands including the thioether. π-bonding between the d orbitals of metal atoms and the S$-$C σ^* bonds of thioethers is believed to produce significant weakening of the S$-$C bonds.[24] In the case of thiiranes, this should promote opening of the thiirane rings.

Dihydrodithiins have been prepared by the oxidation of dithiols[20,22] and the addition of "S$_2$" to 1,3-dienes.[25] The new method described herein utilizes readily accessible reagents and is catalytic with long-term activity. In one instance, we obtained 2040 turnovers over a 5 day period and the catalyst was still very active at the end of the reaction period.

Supporting Information Available: Tables of final atomic positional parameters, bond distances, bond angles, and anisotropic thermal parameters for the structural analyses of **13** and **14** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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