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Synthesis of Trithiolanes and Tetrathianes from Thiiranes Catalyzed by Ruthenium Salen Nitrosyl Complexes

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Abstract: The compound [Ru(salen)(NO)(H_2O)](SbF_6) (**1**) (salen = *N*,*N*′-ethylene-bis-salicylidene aminate) reacts catalytically with thiiranes and converts them to olefins and 1,2,3,4-tetrathianes or 1,2,3-trithiolanes. The monosubstituted thiiranes styrene sulfide and propylene sulfide reacted to form the corresponding olefin and the 4-substituted 1,2,3-trithiolane in a 2:1 ratio in isolated yields in excess of 90%. The disubstituted thiirane *cis*-stilbene sulfide was converted to *cis*-stilbene and 5,6-*trans*-1,2,3,4-diphenyltetrathiane in a 3:1 ratio in the presence of a catalytic amount of **1** in CD_3NO_2. Coordination of *cis*-stilbene sulfide to the salen complex in a ligand substitution reaction was established by isolation of [Ru(salen)(NO)(*cis*-stilbene sulfide)](SbF_6) (**6**). ^{1}H NMR studies performed on **6** indicated that the salen macrocycle had rearranged upon thiirane coordination. A similar rearrangement was found to be stabilized by other ligands including tetramethylethylene sulfide, tetrahydrothiophene, and d_3-acetonitrile. The α-deuterio-*cis*-stilbene sulfide catalyst adduct (*d*-**6**) reacted with unlabeled *cis*-stilbene sulfide to form deuterium-labeled *trans*-diphenyltetrathiane and unlabeled *cis*-stilbene as shown by GCMS and ^{1}H NMR. Thus, the solution thiirane behaves as a sulfur donor and forms olefin, whereas the coordinated thiirane becomes the cyclic polysulfide. β-*cis*-Deuteriostyrene sulfide was used to show that ring closure to form cyclic polysulfide incorporated inversion of stereochemistry versus starting thiirane. A mechanism for catalysis consistent with experimental data is presented that requires coordination of thiirane to the metal complex followed by bimolecular attack of free thiirane on the coordinated thiirane.

Metal-catalyzed atom transfer reactions comprise a growing family of highly useful processes. Olefin epoxidation, cyclopropanations, and aziridinations, for example, have been applied to a wide variety of organic substrates and metal catalysts, often with exquisite control over selectivity and stereochemistry. Metal salen catalysts have been shown to be exceptionally versatile and stereoselective in epoxidation[1,2] and ring opening reactions.[3] The active discussion of the mechanistic principles of these reactions[4−6] led us to consider simple dative interactions of epoxides and thiiranes with metal complexes incorporating the salen ligand to probe for structural features that control selectivities in these reactions.[7] Well-characterized stable coordination compounds that include coordinated epoxides or thiiranes are few because of the inherent strain of the three-membered ring and the labilizing effect of the coodinating metal complex.[8]

Here we describe thiirane coordination and subsequent reactions of complexes derived from [Ru(salen)(NO)(H_2O)](SbF_6) (**1**) (Figure 1, where salen = *N*,*N*′-ethylene-bis-salicylidene aminate)[9] upon treatment with excess thiiranes. An unusual ruthenium-catalyzed sulfur transfer chemistry is observed, in which monosubstituted and disubstituted thiiranes are catalytically disproportionated to olefin and the corresponding 1,2,3-trithiolanes or 1,2,3,4-tetrathianes. These cyclic trisulfide

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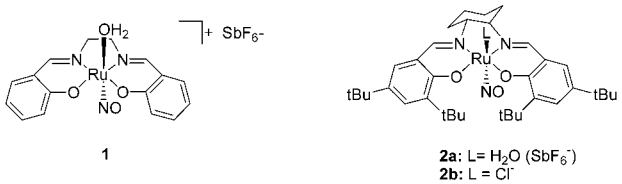

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Figure 1. Structures of ruthenium salen nitrosyl complexes.

and tetrasulfide products and their derivatives have a limited literature,[10] although cyclic and acyclic trisulfides and tetrasulfides are central motifs in a number of natural products including the calicheamicins,[11] lissoclinotoxin,[12] varacin,[13] and various compounds isolated from thermophilic bacteria.[14]

The reaction chemistry of ruthenium complexes and thiiranes that forms trithiolanes and tetrathianes has no available precedent in the literature and appears to define a new chemical pathway in the interaction of thiiranes with metal complexes. The overall reaction, coordination of thiirane to catalyst, conformational changes upon thiirane coordination, and the proposed mechanism of catalysis are presented in this paper.

Results

Synthesis and Characterization of Ruthenium Nitrosyl Catalysts. The ruthenium complex **1** depicted in Figure 1 has been shown by ^{1}H NMR to coordinate weak ligands such as aldehydes by ligand exchange for water in nonprotic solvent.[9a] This precedent suggested the potential of this complex to synthesize thiirane and/or epoxide complexes through analogous ligand exchange mechanisms. The reported synthesis of **1**,[9a] which works well to obtain gram quantities of the material, was applied to derive the more substituted salen derivative [Ru(L_1)(NO)(H_2O)](SbF_6) (**2**), where L_1 = *R*,*R*,-(−)-1,2-cyclohexanebis(3,5-di-tertbutyl)salicylidene aminate as shown in Figure 2. Complete characterization of **2** was obtained by IR, ^{1}H NMR, and FAB-MS (see Experimental Section). The direct precursor to **2**, the chloro complex Ru(L_1)(NO)(Cl) (**2b**), was identical in all respects to the complex reported previously.[15]

Catalytic Desulfurization of Thiiranes with Ruthenium Complexes. Treatment of **1** with excess monosubstituted or disubstituted thiiranes in nitromethane at room temperature caused desulfurization of the thiiranes to generate olefin and unidentified coproducts. Reactions could be spectroscopically monitored by mixing the reactants in an NMR tube in d_3-nitromethane at 0 °C and warming the tube in an NMR probe to ambient temperature to obtain ^{1}H NMR spectra. Olefin products were easily recognized by the appearance of vinyl proton resonances in ^{1}H NMR spectra of reaction mixtures, and confirmed by isolation in several cases. Olefin formation was

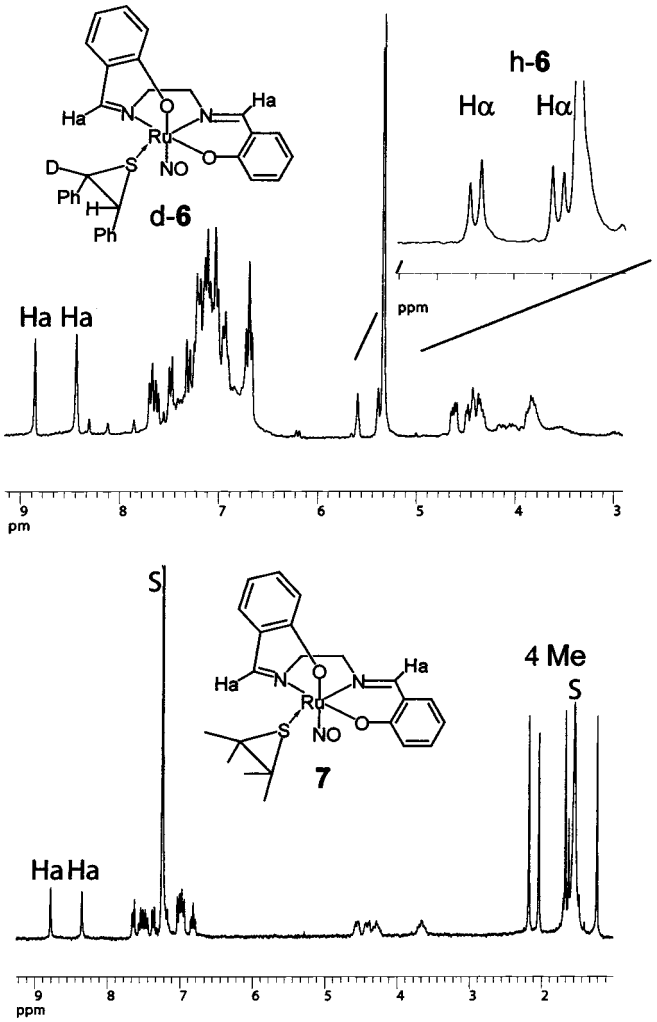

Figure 2. Top: ^{1}H NMR of α-deuterium-*cis*-stilbene sulfide complex **6** (*d*-**6**) in CD_2Cl_2. Inset: The resonances of the H_α protons of coordinated stilbene sulfide in all proteo **6**. Bottom: The ^{1}H NMR spectrum of the tetramethylethylene sulfide complex **7** in $CDCl_3$. The four methyl groups are correspondent to the four methyl groups of the tetramethylethylene sulfide ligand. S indicates residual water or $CHCl_3$.

observed using the following thiiranes: ethylene sulfide, propylene sulfide, cyclohexene sulfide, styrene sulfide, and *cis*- and *trans*-stilbene sulfide. Both ethylene and propylene were lost from NMR tubes by venting, and the subsequent spectra were shown to be depleted of the respective olefin resonances. Recovery and reuse of the complex **1** after reactions showed that it was the active catalyst of these reactions. Experimental details of these reactions are found in Table 1 and in the Experimental Section.

The reactions of styrene sulfide and *cis*-stilbene sulfide in the presence of **1** were studied in detail. Thus, treatment of **1** with a 30-fold excess of styrene sulfide resulted in the formation of a 63% yield of styrene versus starting thiirane (mol/mol). The styrene was readily isolated and analyzed by GCMS and ^{1}H NMR, and compared to a chemical standard to verify identity. A second product was also obtained and shown by MS, ^{1}H NMR to be the previously unreported 4-phenyl-1,2,3-trithiolane **3**. This compound was fully characterized by ^{1}H NMR, ^{13}C NMR, and MS. The ^3J coupling constants were fully consistent with a five-membered ring (see Experimental Section for full characterization). The trithiolane **3** was formed in a

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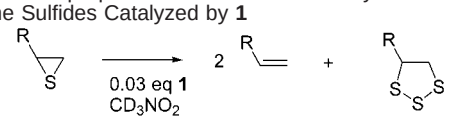
Table 1. Reactions of Thiranes and Ruthenium Nitrosyl Salen Catalysts[a]

substrate	catalyst[b]	olefin	sulfide product
styrene sulfide	**1**	styrene	4-phenyltrithiolane
propylene sulfide	**1**	propylene	4-methyltrithiolane
cis-stilbene sulfide	**1**	*cis*-stilbene	5,6-*trans*-diphenyl tetrathiane
styrene sulfide	**2**	styrene	4-phenyltrithiolane
styrene sulfide	**2**[c]	styrene	4-phenyltrithiolane < 5% e. e. unreacted styrene sulfide < 5% e. e.
propylene sulfide	**2**	propylene	4-methyltrithiolane
cis-stilbene sulfide	**2**	*cis*-stilbene	5,6-*trans*-diphenyl tetrathiane
trans-stilbene sulfide	**1**	*trans*-stilbene[d]	NI[e]
cyclohexene sulfide	**1**	cyclohexene[f]	NI[g]
ethylenesulfide	**1**	ethylene[h]	NI[i]
tetramethylethylene sulfide	**1**	ND	ND

[a] NI: product not identified, ND: no product detected. [b] Reactions with **1** were run in CD_3NO_2 and those with **2** were run in CD_2Cl_2. In each reaction, 0.1 mmol of substrate was added to 1 mL of solution containing 2.5 mM catalyst (2.5×10^{-3} mmol). [c] Reaction terminated at 30% conversion as determined by ^{1}H NMR, solvent flash evaporated, and sample redissolved in a 2:3 mixture of (*R*)-(−)-$CF_3CHOHPh$:CCl_4.[18] ^{1}H NMR spectrum of redissolved reaction mixture was used to measure enantiomeric excess (e.e.). [d] Isolated and compared to authentic *trans*-stilbene. [e] Product was produced in 1:3 ratio versus olefin, but was determined not to be *trans*-diphenyl-tetrathiane. Probable identity of product is *cis*-diphenyltetrathiane (unstable to isolation). [f] Isolated and compared to authentic cyclohexene. [g] Unstable. [h] ^{1}H NMR δ: 5.5, olefin was major product, and disappeared upon opening cap of NMR tube as determined by loss of corresponding resonance in ^{1}H NMR spectrum. [i] Multiple unstable products.

Scheme 1. Disproportionation Reactions of Styrene and Propylene Sulfides Catalyzed by **1**



R = Ph
R = Me

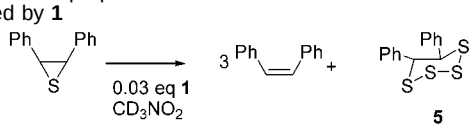
3: R = Ph
4: R = Me

isolated yield of 90% (based on theoretical). Integrations of ^{1}H NMR resonances of styrene and trithiolane in reaction mixtures showed that they were formed in 2:1 ratio, respectively, confirming an apparent disproportionation of thiirane to the two products in the ratio expected based upon the sulfur content in **3** (Scheme 1).

The behavior of propylene sulfide with **1** in CD_3NO_2 was analogous to that of styrene sulfide. Propylene was identified by ^{1}H NMR resonances at δ 5.8, 5.05, 4.95, and 1.95. These peaks disappeared after opening the NMR tube to air for several minutes indicating evaporation of propylene from the sample. Propylene was formed in a 2:1 ratio as determined by ^{1}H NMR versus a second product **4** identified as 4-methyl-1,2,3-trithiolane (91% yield). MS data in particular corresponded well to a prior literature report of this compound,[16] and ^3J coupling constants were completely consistent with the five-membered ring formulation (see Experimental Section for complete characterization).

In the second detailed case examined, excess *cis*-stilbene sulfide was added to a solution of **1** and converted over several hours to *cis*-stilbene. The identity of *cis*-stilbene was confirmed by GCMS and ^{1}H NMR and comparison with authentic *cis*-stilbene. A second compound **5** was isolated by silica gel chromatography and identified as *trans*-5,6-diphenyl-1,2,3,4-tetrathiane (73% isolated yield) by comparison to the authentic compound synthesized independently by a known method (see Scheme 2 for structure).[17] Previous X-ray characterization for this compound makes this structural assignment unambiguous.[17a] ^{1}H NMR spectra of **5** and authentic *trans*-5,6-diphenyl-1,2,3,4-tetrathiane were identical, and GCMS analysis decomposed both materials to *trans*-stilbene and S_6 and S_8. The ratio of *cis*-stilbene

Scheme 2. Disproportionation Reaction of *cis*-Stilbene Sulfide Catalyzed by **1**



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generated versus **5** was found to be 3:1 based on NMR integration of spectra of reaction mixtures. A disproportionation of the disubstituted stilbene sulfide was effected by **1** (Scheme 2) with an altered stoichiometry as compared with the styrene sulfide reaction with **1** (Scheme 1). The overall reaction of styrene sulfide was 6 times faster than that of *cis*-stilbene sulfide reaction under similar conditions.

The chiral complex **2** was effective in catalyzing the identical reactions as complex **1**. Like **1**, the complex could be isolated unchanged after reactions were completed and subsequently reused. Because of improved catalyst solubility, the reactions of **2** with thiiranes could be effected in CH_2Cl_2, with no apparent change in reaction outcome (Table 1). Use of special conditions to resolve thiirane and sulfide stereoisomers[18] (see Table 1 for details) showed that styrene sulfide reactions catalyzed by **2** did not enantiomerically enrich unreacted styrene sulfide in partially completed reactions and phenyltrithiolane was not produced in measurable enantiomeric excess (Table 1).

Coordination of *cis*-Stilbene Sulfide. The reaction of thiiranes with **1** begins with coordination of the thiirane to the ruthenium complex. Observations of the reaction of **1** with excess *cis*-stilbene sulfide in CD_3NO_2 by ^{1}H NMR showed changes in the catalyst structure as a consequence of the presence of thiirane. For example, the catalyst imine singlet at δ 8.7 disappeared, and two separate singlets at δ 9.05 and 8.65 with half intensity appeared. These changes were shown to be due to a thiirane adduct of *cis*-stilbene sulfide and catalyst by isolation and ^{1}H NMR and IR characterization of the complex.

The ^{1}H NMR spectrum of the adduct **6** showed that the symmetry of the complex was reduced upon thiirane coordination (Figure 2, inset and top panel). This observation is consistent with a reorganization of the complex to a lower symmetry form upon binding thiirane. The reorganization thought most probable is shown in Scheme 4. The proposed structure of the thiirane complex would place the two methine protons of the coordinated

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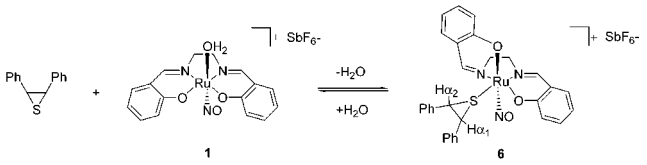
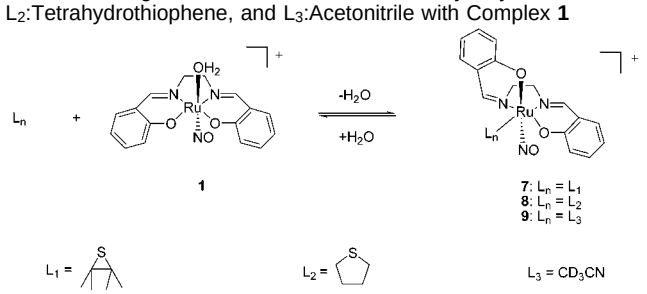
Scheme 3. Proposed Adduct Formation Due to Reaction of **1** with *cis*-Stilbene Sulfide



Scheme 4. Ligation Reactions of L_1:Tetramethylethylene Sulfide, L_2:Tetrahydrothiophene, and L_3:Acetonitrile with Complex **1**



cis-stilbene in different chemical environments, and in fact were found to be doublets at δ 5.85 and 5.55 in the ^{1}H NMR spectrum (inset, Figure 2, top panel). Deuterium incorporation at one α carbon (70% enrichment) of *cis*-stilbene sulfide caused these doublets to become singlets (Figure 2, top panel). The nitrosyl of the complex was shown to be intact with a strong peak at 1865 cm^{-1} in the IR spectrum. Upon long standing in solution, small amounts of free *cis*-stilbene and **1** could be recovered, in addition to *cis*-stilbene and *trans*-diphenyltetrathiane. This indicated that coordination to **1** without isomerization of the thiirane was reversible, and suggested the competency of the adduct to effect the desulfurization reaction.

Coordination of Hindered Thiiranes, Inert Sulfides, and Solvent to 1. A hindered thiirane that was inert to desulfurization and disproportionation was used to provide additional support for the geometry of coordinated thiirane complexes derived from **1**. The ^{1}H NMR spectrum of the tetramethylethylene sulfide adduct **7** in CD_2Cl_2 was similar to the spectrum of the *cis*-stilbene adduct, particularly for resonances of the salen ligand, indicating a nonsymmetrical complex (Figure 2, bottom panel). Four singlets for the methyl groups of tetramethylethylene sulfide ligand confirmed coordination to a low symmetry environment (Figure 2, bottom panel). In contrast, the free thiirane methyl groups were all equivalent by ^{1}H NMR.

The ligand tetrahydrothiophene in CD_3NO_2 was shown to form an adduct **8**, deduced to be ligand replacement of the tetrahydrothiophene for the water ligand with isomerization of the macrocycle to produce the twisted complex (Scheme 4). The ^{1}H NMR spectrum of the adduct (data not shown, see Experimental Section) was similar to the spectra of low symmetry complexes formed by reaction of thiiranes with **1**. For example, two imine proton resonances were observed at δ 8.85 and 8.45, and chemical shifts and couplings of proton resonances of the macrocycle were similar. An analogous structure **9** (Scheme 4) also arose from the dissolution of **1** into d_3-acetonitrile, where incubation of several hours was required to convert the initial symmetrical complex (Figure 3, top panel) to a twisted geometry (85% at equilibrium) in which coordinated acetonitrile is proposed to adopt a cis relationship to the NO ligand in the complex (Figure 3, bottom panel).

Bimolecular Reaction of Thiirane and Thiirane-Catalyst Adduct. The reaction of *cis*-stilbene sulfide with **1** produced

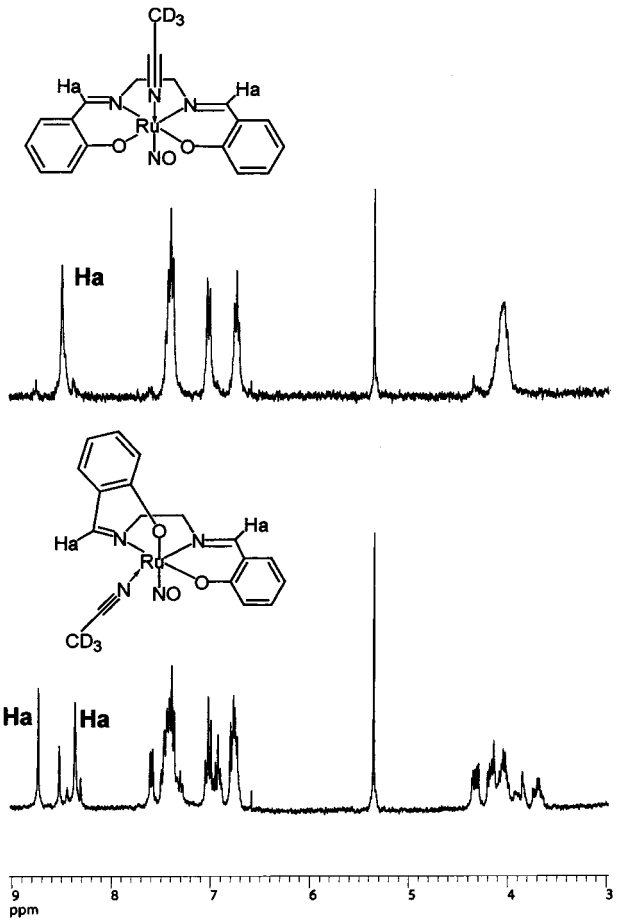


Figure 3. Top: ^{1}H NMR of **1** in acetonitrile-d_3 minutes after dissolution in acetonitrile. Bottom: ^{1}H NMR spectrum of the sample in top panel after 6 h of incubation at room temperature.

Table 2. Stilbene Formation as a Function of Concentration of Stilbene Sulfide and **6**[a]

[*cis*-stilbene sulfide] M	[**6**] M	rate M min^{-1}
1.0×10^{-2}	8.0×10^{-4}	1.8×10^{-5}
5.0×10^{-3}	8.0×10^{-4}	8.9×10^{-6}
2.5×10^{-3}	8.0×10^{-4}	3.7×10^{-6}
5.0×10^{-3}	5.0×10^{-4}	5.7×10^{-6}

[a] The rates obtained were determined by the initial rates method. The bimolecular rate constant k_2 determined from these data is $k_2 = 0.72 \pm 0.12$ M^{-1} min^{-1}.

olefin and tetrathiane, and a *cis*-stilbene sulfide coordinate adduct **6**. The thiirane adduct is the putative first intermediate in the catalytic cycle that disproportionates thiiranes to products. As stated previously, the adduct is stable in the absence of free thiirane for extended periods (4−6 h), but decomposed upon long standing. In the presence of excess *cis*-stilbene sulfide, the adduct rapidly reacted to form *cis*-stilbene and diphenyltetrathiane. Varying the amount of both adduct and thiirane established the rate law for production of olefin and tetrathiane (Table 2). The rate law is first order in adduct and thiirane; that is, k[adduct][thiirane] = d[olefin]/3 dt, where k is the second-order rate constant. The value of k was found to be 0.72 $\pm$ 0.12 M^{-1} min^{-1} at 298 K.

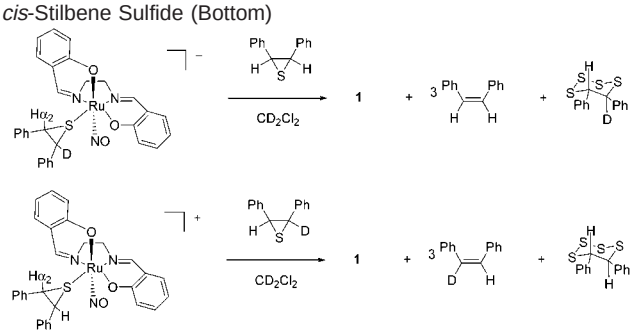
Coordinated Thiirane Is the Sulfur Acceptor: Free Thiirane Is the Sulfur Donor. Treatment of the deuterio-complex [Ru(salen)(NO)(α-deuterio-*cis*-stilbene-sulfide)](SbF$_6$) (*d*-**6**) in CD_2Cl_2 with 3 equiv of unlabeled *cis*-stilbene sulfide

Table 3. GCMS Analyses of Stilbenes from Reactions of *h*-**6** and *d*-**6** with Stilbene Sulfides and Controls[a]

sample	180 (%)	181 (%)	182 (%)
d-**6**, *cis*-stilbene sulfide	100	12.9	1.0
cis-stilbene	100	14.2	1.1
h-**6**, α-*d*-*cis*-stilbene sulfide	100	87.8	14.5
d-*cis*-stilbene	100	85.7	12.0

[a] Rows 1 and 3 represent samples obtained from reactions of the listed components dissolved in CD_2Cl_2. The identities of *d*-**6** and *h*-**6** are shown in Figure 2 top panel, and are coordinated α-deuterio-*cis*-stilbene sulfide: catalyst adduct and all-proteo *cis*-stilbene sulfide adduct, respectively. Reactions were run in a molar ratio of 3:1 free *cis*-stilbene sulfide:adduct, and are single turnover reactions as explained in the text. Reactions were evaporated, triturated with pentane, concentrated, and purified by filtration through 1 mL of silica to remove tetrathiane, and analyzed by GCMS. Rows 2 and 4 represent GCMS analysis of unlabeled and labeled *cis*-stilbenes used to synthesize the respective unlabeled and labeled *cis*-stilbene sulfides.

Scheme 5. Reaction of Deuterium-Labeled *cis*-Stilbene Sulfide Adduct with Unlabeled cis-Stilbene Sulfide (Top) and Reaction of Unlabeled *cis*-Stilbene Sulfide Adduct with Deuterium-Labeled *cis*-Stilbene Sulfide (Bottom)



formed stilbene and diphenytetrathiane and a precipitate identified as the starting catalyst **1** as determined by ^{1}H NMR. GCMS analysis of isolated *cis*-stilbene confirmed that the *cis*-stilbene produced did not contain deuterium (Table 3), whereas ^{1}H NMR spectra (data not shown) indicated that deuterium label was concentrated in the tetrathiane product (Scheme 5; top panel). Conversely, treatment of the proteo complex, Ru(salen)(NO)(*cis*-stilbene-sulfide)](SbF$_6$) (*h*-**6**), with deuterium-labeled stilbene sulfide generated deuterium-labeled *cis*-stilbene with 100% *d*-content based upon a fully labeled control (Table 3). ^{1}H NMR spectra (data not shown) corroborated that the deuterium label was concentrated in the stilbene product (Scheme 5; bottom panel). This labeling pattern is consistent with free thiirane desulfurization to form olefin. Accordingly, it is the coordinated thiirane that accepts sulfur to become *trans*-diphenyltetrathiane. Moreover, ligand exchange of thiiranes must be slow relative to the rate of product formation, since no scrambling of label was observed.

Inversion at Carbon in Formation of Trithiolane. The molecule *cis*-2-deuterio-styrene sulfide (95% deuterium incorporation) was used to probe for stereochemical changes occurring at either the α or the *β* carbon along the reaction coordinate that forms olefin and 4-phenyl-trithiolane in the reaction of styrene sulfide catalyzed by **1**. Ten equivalents of *cis*-2-deuterio-styrene sulfide treated with a single equivalent of **1** in CD_3NO_2 yielded deuterium-labeled styrene and deuterium-labeled phenyltrithiolane. The deuterium stereochemistry in styrene was determined by ^{1}H NMR to be Z, identical to the starting thiirane. Conversely, the deuterium stereochemistry in phenyltrithiolane was determined to be *β*-*trans*, indicating an inversion in relative stereochemistry of the deuterium versus starting thiirane (Scheme 6). The absence of a peak at *δ* 3.7 in the spectrum assignable to the trans proton of phenyltrithiolane indicated deuterium enrichment at this position (Figure 4). The two remaining α and *β* proton resonances (*δ* 4.9 and 3.5, respectively) of phenyltrithiolane were doublets. The stereochemical assignment of deuterium was aided by the NOESY spectrum of **5** which provided clear determination of *β*-*cis* and *β*-*trans* proton resonances of the ^{1}H NMR spectrum of phenyltrithiolane (see Experimental Section for NOE data and assignments).

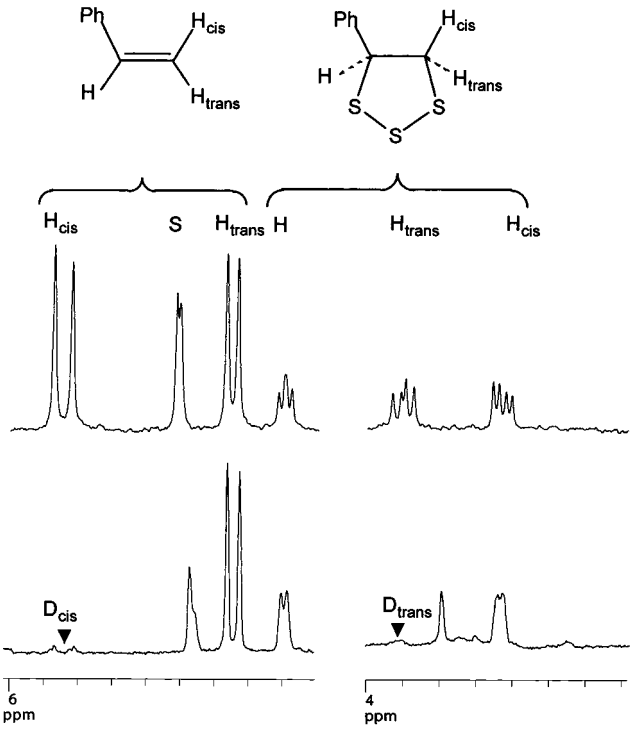
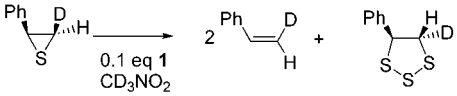


Figure 4. Reaction of styrene sulfide and *cis*-2-deuteriostyrene sulfide after treatment with **1** in CD_3NO_2. The top spectrum is the reaction of styrene sulfide, showing styrene and phenyltrithiolane resonances. The bottom spectrum is the corresponding reaction of the deuterium-labeled styrene sulfide. The styrene formed shows a retention of the initial cis-stereochemistry of the thiirane. The deuterium stereochemistry is inverted to the trans-geometry in the phenyl-trithiolane product.

Scheme 6. Reaction of *cis*-2-Deuterio-styrene Sulfide Catalyzed by **1**



Discussion

The stable coordination of thiiranes to metal centers is intrinsically difficult, because thiiranes are reactive to reducing metal centers by sulfur transfer,[8,19] or react by polymerization in the presence of Lewis acid metal catalysts.[8] Additional modes of reaction have been reported. For example, metal-catalyzed S−S bond formation between free thiiranes and metal-coordinated thiiranes leading to desulfurization and olefin formation from free thiirane has been observed in the presence of the electrophilic tungsten complex W(CO)$_5$(thiirane).[20] In our attempts to coordinate thiiranes to complex **1**, we observed an apparent analogue of this latter reaction mode, and observed

(19) For an exceptional example of terminal metallo-sulfide formation upon thiirane coordination to a metal complex, see: Proulx, G.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 7953.

formation of olefin and trithiolane or tetrathiane products. The products contain multiple consecutive S−S bonds contained in five- or six-membered rings representing ring expansions of the initial thiirane by sulfur atom additions.

The reactions described here are disproportionation reactions of monosubstituted and disubstituted thiiranes. For example, propylene and styrene sulfide both reacted in the presence of **1** to form the corresponding olefin and the 4-alkyltrithiolane in a 2:1 ratio. *cis*-Stilbene sulfide reacted to form *cis*-stilbene and *trans*-diphenyltetrathiane in a 3:1 ratio. These reactions are very efficient with yields in the range 70−90% and occur at room temperature within several hours. The reaction is catalytic in the metal complex as shown by recovery of the intact complex after reactions, and by mechanistic studies that clearly show the involvement of the complex in activation of thiirane. These reactions occurred in CD_3NO_2, and CD_2Cl_2, although in CD_2Cl_2 insolubility of **1** restricted experiments to single turnover reactions derived from a soluble thiirane coordinate adduct **6**. Enantioselectivity derived from the macrocycle in **2** could not be addressed fully in this very limited investigation. In the one instance examined carefully, styrene sulfide was not enantiomerically enriched by catalysis by **2**, and phenyl-trithiolane was not formed in enantiomeric excess.[21]

A *cis*-stilbene sulfide adduct was isolated by precipitation in reaction mixtures containing **1** and excess stilbene sulfide. The adduct could be partially decomposed to *cis*-stilbene sulfide and **1** upon standing in CD_2Cl_2, and a ^{1}H NMR spectrum of the adduct in this solvent included obvious thiirane resonances, including two methine doublets. These methine doublets were confirmed to be thiirane in origin by deuterium labeling of the methine position of *cis*-stilbene sulfide at one carbon, whereupon the doublets became singlets. The dispersion observed for these peaks and their couplings shows that the thiirane coordination environment lacks 2-fold symmetry. A reorganization of the salen macrocycle of **1** upon thiirane binding is proposed to explain this observation (Scheme 3). Similar macrocycle rearrangements were observed for coordinate adducts of tetramethylethylene sulfide, which is unreactive to desulfurization chemistry, tetrahydrothiophene, and upon dissolution of **1** in acetonitrile (Scheme 4).

Geometries of ruthenium nitrosyl salen complexes have been structurally characterized only where the salen ligand adopts the planar symmetrical geometry and includes the structure of **1**,[9a] the structrure of **2b**,[15] and the structure of an *O*-nitritoruthenium salen nitrosyl complex obtained by Wilkinson and co-workers.[22] Nevertheless, Wilkinson and co-workers[23] as well as Leung et al.[15] report that the Ru(salen)$(CO)_2$ adopts the twisted geometry analogous to the geometry proposed in this study. Re(V)-oxo salen-type complexes also exhibit a tendancy to form twisted geometries.[24] ^{1}H NMR spectroscopy of these complexes[24,25] showed that the observed chemical shift splitting of the imines ($\Delta\delta$ 0.25−0.5)[24,25] is similar to the splittings determined for the Ru complexes derived from reaction of thiiranes, tetrahydrothiophene, and acetonitrile with **1**. Thiirane coordinate adducts to ruthenium have some precedent as well; stable coordination of thiiranes and epoxides has been reported in several low valent ruthenium complexes.[26,27]

Kinetic studies conducted by ^{1}H NMR in CD_2Cl_2 with **6** in the presence of free *cis*-stilbene sulfide showed that the formation of olefin and tetrathiane is tightly coupled; moreover, these studies showed that reactant disappearance rates (**6** and *cis*-stilbene sulfide) and product appearance rates (tetrathiane and *cis*-stilbene) were matched. Studies of the rate of product formation as a function of reactant concentration established that the rate law is first order in adduct and free thiirane. This result is consistent with bimolecular attack of thiirane with coordinated thiirane as the likely rate-limiting step in the overall catalytic cycle for reaction of *cis*-stilbene sulfude with **1**, since under catalytic conditions the adduct is observed as the major form of the complex during reaction. The bimolecular reaction step was shown by labeling studies to generate olefin from solution thiirane and tetrathiane from the coordinated thiirane. Labeling studies upon styrene sulfide indicate that trithiolane is formed with net stereochemical inversion at carbon. This was shown by reaction of *cis*-2-deuterio-styrene sulfide, which reacted with **1** to form *trans*-5-deuterio-4-phenyl-1,2,3-trithiolane. This stereochemical result parallels the formation of *trans*-diphenyltetrathiane from *cis*-stilbene sulfide in reaction with **1**, and the apparent nonformation of *trans*-diphenyltetrathiane from reaction of *trans*-stilbene sulfide with **1** (Table 1).

The mechanism shown in Scheme 7 accounts for all of the data obtained on the reaction of **1** with thiiranes. After coordination of thiirane, nucleophilic attack of free thiirane on the carbon of coordinated thiirane leads to inversion at carbon of the coordinated thiirane. The attack is proposed to be at the less substituted carbon of the coordinated thiirane, since styrene sulfide reacted significantly faster than *cis*-stilbene sulfide. Moreover, steric hindrance obtained by placement of four methyl substituents, as in the case of tetramethylethylene sulfide, prevented reaction of the thiirane beyond coordination with the catalyst presumably because of steric prevention of nucleophilic attack at the substituted carbons. The nucleophilic attack at carbon of the coordinated thiirane introduces inversion at one carbon of the coordinated species and is consistent with results from deuterium labeling of styrene sulfide which established that inversion is integral to the mechanism that generates cyclic trithiolane. The proposed mechanism is similar to that of the tungsten carbonyl thiirane reactions that generate olefin and form S−S bonds from thiiranes.[20] Investigations of these reactions indicate that initial bimolecular reaction occurs by attack of free thiirane at the carbon of the coordinated thiirane to generate inversion prior to olefin formation.[20]

The process of olefin formation yields a putative metal ligated-dithietane, first proposed by Adams and co-workers for the reaction of thiiranes with tungsten carbonyls.[20] The extrusion of olefin itself is likely to be concerted and nonradical in nature,

(20) (a) Adams, R. D. *Acc. Chem. Res*. **2000**, *33*, 171. (b) Adams, R. D.; Perrin, J. L. *J. Am. Chem. Soc*. **1999**, *121*, 3984. (c) Adams, R. D.; Yamamoto, J. H.; Holmes, A.; Baker, B. J. *Organometallics* **1997**, *16*, 1430. (d) Adams, R. D.; Queisser, J. A.; Yamamoto, J. H. *J. Am. Chem. Soc*. **1996**, *118*, 10674.

(21) Treatment of chiral catalyst **2** with tetrahydrothiophene at high concentrations produced a saturable ratio of twisted and flat forms of the complex. NMR spectra indicated that only one of two possible diasteromers was formed in the twisted form.

(22) Wilkinson, G. *Inorg. Chim. Acta* **1977**, *24*, L95.

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(24) Herrmann, W. A.; Rauch, M. U.; Artus, G. R. *Inorg. Chem*. **1996**, *35*, 1988.

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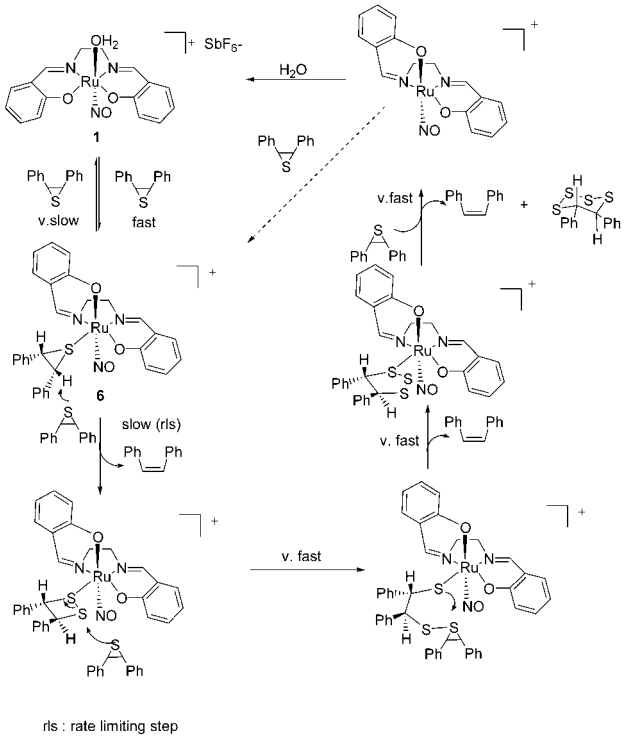
(27) (a) Groves, J. T.; Han, Y.; Engen, D. V. *J. Chem. Soc., Chem. Commun.* **1990**, 436. (b) Han, Y. Ph.D. Thesis, Department of Chemistry, Princeton University, 1992.

Scheme 7. Proposed Mechanism for Desulfurization of *cis*-Stilbene Sulfide Catalyzed by **1**



because stilbene sulfide and styrene sulfide stereochemistry (from *cis*-deuterio-styrene sulfide) is unchanged in the product olefin. This result is in contrast to the predominant loss of initial stereochemistry seen for the trialkyltin radical desulfurization of *cis*-thiiranes.[28] The dithietane intermediate was not observed in our studies, and has not been characterized to our knowledge in any metal complex. This intermediate acts as a reactive entity which by ring strain, and electrophilic activation, is able to react further with free thiirane to complete the catalytic mechanism. The metal ligated-dithietane and intermediates downstream of it were not observed in reaction mixtures, suggesting they are transiently formed and rapidly turned over under reaction conditions.

Further experimental work to establish the complete reaction coordinate is still required, but the mechanism presented accounts for the data and adopts existing precedents and proposed reaction pathways. What is most unusual about the reaction of **1** with thiiranes is the unprecedented production of trithiolanes and tetrathianes from thiiranes. In the tungsten complexes, the preferred products are cyclic oligomers of the thietanes in which S−S bonds do not exceed two sulfur atoms in length, whereas in this case S−S units extend to three or four sulfur atoms consecutively. A selectivity effect may be at work where ruthenium is able to activate attack at sulfur by free thiirane at steps downstream of dithietane formation over attack at carbon. These issues highlight the novelty of the observed chemistry reported here. The efficiencies and mild conditions of these reactions suggest synthetic accessibility to unusual trisulfide and tetrasulfide structures through application of this methodology.

Experimental Section

General Methods. All reagents used were obtained from available commercial sources and used without additional purification unless otherwise indicated. Deuterated solvents CD_2Cl_2, $CDCl_3$, acetone-d_6, DMSO-d_6, CD_3CN, and CD_3NO_2 were used as obtained from Aldrich Chemical or Cambridge Isotope Laboratories. ^{1}H and ^{13}C NMR spectra were obtained on 300 MHz GE and 270 MHz JEOL instruments. The ^{1}H NOESY spectrum of phenyltrithiolane was taken on a JEOL 500 MHz NMR instrument. MS of trithiolanes and tetrathianes was done at a temperature below 220 °C to avoid fragmentation and production of higher molecular weight polysulfides. Styrene sulfide[29] and *cis*- and *trans*-stilbene sulfides[30] were synthesized according to known procedures. For synthetic procedures, all solvents were freshly distilled and taken through three freeze−thaw cycles under vacuum to remove dissolved gases. Complex **1** was synthesized as reported.[9a]

Synthesis of Ru(L_1)(NO)(Cl) (L_1 = *R,R*-(−)-1,2-Cyclohexane-bis-(3,5-di-tertbutyl)salicylidene Aminate) (2b). Five hundred forty-six milligrams (1 mmol) of L_1 (Aldrich) in the protonated form and 50 mL of dry DMF were placed into a 125 mL round-bottom flask. Fifty milligrams (2 mmol) of NaH was added, and the mixture was stirred. After 1 h, 255 mg (1 mmol) of $Ru(Cl)_3(NO)(H_2O)$ in 20 mL of DMF was added, and the mixture was heated to 130 °C under an argon atmosphere overnight. The solvent was evaporated under high vacuum upon cooling, and the residual material was chromatographed on silica (CH_2Cl_2/heptane/EtOAc 4/8/1). The compound **2b** was isolated by recrystallization in CH_2Cl_2/heptane containing trace acetone. TLC: R_f = 0.5 in CH_2Cl_2/heptane 1:1. ^{1}H NMR ($CDCl_3$): δ 8.23 (s, 1H, C*H*═N), 8.15 (s, 1H, C*H*═N), 7.5 (s, 2H, *m-H*), 7.0 (s, 2H, *m-H*), 4.2 (m, 1H, CH−C*H*), 3.26 (m, 1H, C*H*−CH), 2.86 (m, 1H, C*H eq*), 2.82 (m, 1H, −C*H eq*), 2.05 (2m, 2H, C*H ax*), 1.55 (2s, 18H, $-C_4H_9$), 1.28 (2s, 18H, $-C_4H_9$). FAB-MS *m*/*z* (obsd rel intensity; calc rel intensity for $[Ru(L_1)(NO)(Cl)]^+$): 716 (12; 7), 715 (25; 17), 714 (39; 28), 713 (76; 75), 712 (48; 72), 711 (100; 100), 710 (78; 62), 709 (57; 41), 708 (47; 28), 707 (25; 10). Other major clusters centered at *m*/*z* = 681 ([Ru(L_1)(Cl)]+), 676 ([Ru(L_1)(NO)]+), and 646 ([Ru(L_1)]+). X-ray crystal structure: $[Ru(L_1)(NO)(Cl)]\cdot C_3H_6O$ (data not reported). IR (CH_2Cl_2): 1830 cm^{-1} (NO stretch). The compound obtained is identical to that reported by Leung et al. synthesized by a different method.[15]

Synthesis of [Ru(L_1)(NO)(H_2O)](SbF_6) (2). Fifty-two milligrams (0.073 mmol) of Ru(L_1)(NO)(Cl) **2b** was added to a 50 mL round-bottom flask and dissolved in 25 mL of CH_2Cl_2/acetone (90:10). Twenty-five milligrams (0.073 mmol) of $AgSbF_6$ was added to the flask in 5 mL of CH_2Cl_2/acetone. After refrigeration overnight, the solution was filtered to remove AgCl and rotoevaporated. Compound **2** was precipitated from acetone by H_2O addition and then recrystallized from EtOAc/heptane 1:5. TLC: R_f = 0.2, CH_2Cl_2/acetone 20/1. ^{1}H NMR ($CDCl_3$): δ 8.08 (s, 1H, C*H*═N), 7.91 (s, 1H, C*H*═N), 7.57 (s, 2H, *m*-H), 7.48 (s, 2H, *m*-H), 7.13 (s, 2H, *m*-H), 7.12 (s, 2H, *m*-H), 3.16 (m, 1H, C*H*−CH), 2.66 (m, 1H, CH−C*H*), 2.44 (m, 1H, C*H eq*), 2.44 (m, 1H, −C*H eq*), 2.0 (2m, 2H, C*H ax*), 1.372 (2s, 18H, $-C_4H_9$), 1.28 (2s, 18H, $-C_4H_9$). FAB-MS *m*/*z* (found rel intensity; calcd rel intensity for $[Ru(L_1)(NO)(H_2O)]^+$): 696 (23; 52), 695 (42; 35), 694 (65; 100), 693 (64; 58), 692 (100; 45), 691 (75; 31), 690 (71; 4). Other major clusters centered at *m*/*z* = 676 ([Ru(L_1)(NO)]+) and 646 ([Ru(L_1)]+). IR (CH_2Cl_2): 1858 cm^{-1} (NO stretch).

Synthesis of α-Deuterio-*cis*-stilbene Sulfide. α-Deuterio-*cis*-stilbene-oxide was synthesized according to the published procedure,[31] and ^{1}H NMR and GCMS verified 70% deuterium incorporation at one position. Three hundred seventy-five milligrams (1.90 mmol) of α-deuterium-*cis*-stilbene oxide in 5 mL of dioxane was treated with 1.90 mmol (1 equiv) of thiourea and 1.90 mmol (1 equiv) of H_2SO_4 premixed in 10 mL of H_2O. The reaction mixture was stirred at room temperature for 36 h, and the resulting white solid was washed with water and ether. The solid was then treated with a solution of 5%

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(29) Guss, C. O.; Chamberlain, D. L. *J. Am. Chem. Soc.* **1952**, *74*, 1342.
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(31) Collman, J. P.; Kodadek, T.; Brauman, J. I. *J. Am. Chem. Soc.* **1986**, *108*, 2588.

sodium carbonate. The suspension was stirred at room temperature for 2 h, and then the solid was filtered off. Filtration of the material through a silica plug using CH_2Cl_2 as an eluant gave a pure sample of α-deuterium-*cis*-stilbene sulfide (70% deuterium at one site). See Table 3 for GCMS data on this material.

Synthesis of *cis*-2-Deuterio-styrene Sulfide. Deuterium labeling of styrene in the cis-*β*-stereochemistry was effected by reduction of *β*-deuterio-phenylacetylene with a hindered borane and acetic acid workup.[31] Subsequent GCMS and ^{1}H NMR analysis of the isotopically substituted styrene showed 95% + deuterium incorporation in the Z-stereochemistry, as expected. Epoxidation of this styrene by MCPBA in CH_2Cl_2 formed the *cis*-*β*-deuterio-styrene oxide which was purified by silica gel chromatography. ^{1}H NMR of this material corresponded well to the reported spectrum for this compound.[31] Subsequent synthesis of styrene sulfide was performed as reported using potassium thiocyanate to generate *cis*-2-deuterio-styrene sulfide. ^{1}H NMR ($CDCl_3$): *δ* 7.18 (s, 5H, Ar−H), 3.81 (d, 1H, C*H*═CH2), 2.8 (d, 1H, *C*H−C*H* *trans*).

Reactions of Sulfides with Complexes. Typically, 100 *μ*mol of thiirane in 1 mL of CD_3NO_2 was added to a solution of 2−3 *μ*mol of **1** or **2** in 1 mL of CD_3NO_2 or CD_2CL_2, respectively, in a chilled NMR tube bathed in ice. The reaction mixture was monitored by ^{1}H NMR after the tube was tightly sealed and warmed to room temperature. The production of alkene and other products was monitored by ^{1}H NMR. Products were isolated by extraction into pentanes or by evaporation of solvent and trituration with pentane/CH_2Cl_2 (1:1). Components could be separated by silica gel chromatography using pentane followed by pentane/CH_2Cl_2 (1:1) elution. Comparison of products to authentic standards was used to identify products.

Synthesis of 5,6-Diphenyl-1,2,3,4-tetrathiane (5). Twenty milligrams (95 *μ*mol) of *cis*-stilbene sulfide was reacted with 2 mg (2.9 *μ*mol) of **1** in 1.5 mL of CD_3NO_2. The reaction was monitored by ^{1}H NMR until the disappearance of the starting thiirane was complete. The two products formed were *cis*-stilbene and **4** distinguished by singlets in the spectrum at *δ* 6.65 and 5.1. The products could be separated by evaporation of solvent, addition of 1 mL of CH_2Cl_2, followed by addition of pentane until the ruthenium complex precipitated. Filtration and concentration were followed by silica gel purification using cold pentane−CH_2Cl_2 (9:1, 73% yield). NMR and structural assignment are discussed in the text.

Synthesis of 4-Phenyltrithiolane (3). Two milligrams (2.9 *μ*mol) of **1** was reacted with 10 mg (74 *μ*mol) of styrene sulfide in 1.5 mL of CD_3NO_2. ^{1}H NMR spectrum taken at 2 h reaction time confirmed reaction completion based upon the disappearance of styrene sulfide resonances. Two products formed in the reaction could be identified by distinct midfield resonances (styrene *δ* 5.2, d and 5.7, d) and (**3**: *δ* 5.1, dd, 3.6, dd, and 3.9, dd). Styrene was isolated along with CD_3NO_2 by evaporation. The solid residue was redissolved in 1 mL of CH_2Cl_2, and the catalyst was precipitated by addition of pentane. The supernatant was evaporated to yield the mostly pure trithiolane. Silica gel chromatography using cold pentane/CH_2Cl_2 (8:2) gave pure trithiolane used to obtain analytical data (90% yield). ^{1}H NMR (CD_2Cl_2): *δ* 7.2−7.4 (m, 5H, C_6H_5), 4.9 (dd, α-*H* $^3J_{H-H}$ = 7.5 Hz, 5.5 Hz), 3.7 (dd, *trans*-*β*-*H* $^3J_{H-H}$ = 7.5, $^2J_{H-H}$ = 11.5 Hz), 3.5 (dd, *cis*-*β*-*H* $^3J_{H-H}$ = 5.5, $^2J_{H-H}$ = 11.5 Hz). ^{13}C NMR (CD_2Cl_2): ppm 130.0, 129.3, 129.0, 66.7, 52.9. NOESY NOE cross-peaks: *δ* 4.9, α-H to *δ* 3.7, *trans*-H; *δ* 4.9, α-H to *δ* 7.3, *ortho*-H; *δ* 3.5, *cis*-H to *δ* 7.3, *ortho*-H; *δ* 3.5, *cis*-H to *δ* 3.7, *trans*-H. MS (<220 °C): (M + 200, 51.1%), ([M − 2S − 1]+, 135, 93%), ([M − 3S]+, 104, 100%). Temperatures in excess of 220 °C resulted in the formation of the phenyl-tetrathiane (four-sulfur derivative), as determined by the MS spectrum obtained under these temperature conditions. A similar procedure to that used above was employed for the study of the reaction of *β*-*cis*-deuteriostyrene sulfide with **1** in CD_3NO_2.

Synthesis of 4-Methyl-trithiolane (4). Two milligrams (2.9 *μ*mol) of **1** was reacted with 7.5 mg (100 *μ*mol) of propylene sulfide (obtained from Aldrich) in 1.5 mL of CD_3NO_2. The reaction was allowed to react for 6 h at room temperature, and the reaction was determined to be complete by the full disappearance of resonances of propylene sulfide in ^{1}H NMR spectrum. Generated propylene was confirmed by the disappearance of resonances for propylene (*δ* 5.8, 5.05, 4.95, and 1.95) upon opening of the NMR tube to air. The 4-methyl-1,2,3-trithiolane was isolated by evaporation, CH_2Cl_2/pentane redissolution, and silica gel purification using cold pentane−CD_2Cl_2 (9:1). The compound was unstable to concentration; pentane could be removed by repetitive additions of neutral alumina-treated $CDCl_3$ followed by evaporation (91% yield). ^{1}H NMR (CD_2Cl_2): *δ* 4.25 (m, α-*H* $^3J_{H-H}$ = 6.96 Hz, 4.77 Hz), 3.57 (dd, *trans*-*β*-*H* $^3J_{H-H}$ = 6.96 Hz, $^2J_{H-H}$ = 11.16 Hz), 3.25 (dd, *cis*-*β*-*H* $^3J_{H-H}$ = 4.77 Hz, $^2J_{H-H}$ = 11.16 Hz), 1.6 (d, C*H*$_3$). ^{13}C NMR ($CDCl_3$): ppm 56.6, 52.6. 22.0. MS: (M + 138, 100%, 139, 5.8%, 140, 13.0%, 141, 0.754%, 142, 0.865%), ([M − S − 1]+, 105, 11.1%) ([M − 2S]+, 74, 35%).

Synthesis of *cis*-Stilbene Sulfide Salen Complex (6). [Ru(salen)-(NO)(*cis*-stilbene sulfide(S))](SbF_6) was prepared as follows: 4 mg (5.9 *μ*mol) of **1** was reacted with 10 mg (47 *μ*mol) of *cis*-stilbene sulfide (or α-deuterio-*cis*-stilbene sulfide) in an NMR tube containing 2 mL of CD_3NO_2. The reaction was prepared at 0 °C and monitored by ^{1}H NMR. The appearance of *cis*-stilbene and *trans*-diphenyltetrathiane was observed along with the formation of the desired compound identified by two imine singlets at *δ* 8.7 and 9.1 and by two doublets at *δ* 5.5 and 5.8. When these resonances were at their maximum, the solvent was cooled to 0 °C and removed in vacuo. The solid was redissolved in CH_2Cl_2, and pentane was added to precipitate the adduct. Evaporation removed residual solvent, and the complex was stable for hours at room temperature in CD_2Cl_2. ^{1}H NMR (CD_2Cl_2): *δ* 8.92 (s, 1H, C*H*═N), 8.45 (s, 1H, C*H*═N), 6.68−7.80 (m, 18H), 5.65 (d, α-*H* $^3J_{H-}$= 7.0 Hz), 5.4 (d, α-*H* $^3J_{H-H}$ = 7.0 Hz), 3.6−4.4 (m, 4H, CH_2−CH_2). For the α-deuterium-stilbene sulfide complex, all resonances were identical except for the peaks at *δ* 5.65 (s, α-H) and 5.4 (s, α-H).

Synthesis of [Ru(salen)(NO)(tetramethylethylenesulfide)](SbF_6) (7). Four milligrams (5.9 *μ*mol) of **1** was reacted with 10 mg (119 *μ*mol) of tetramethylethylene sulfide in an NMR tube containing 2 mL of CD_3NO_2. The reaction was prepared at 0 °C and monitored by ^{1}H NMR. The appearance of the desired compound was identified by two imine singlets at *δ* 8.7 and 9.1 and by additional singlets in the NMR spectrum at *δ* 2.0−1.0. When these resonances were at their maximum, the solvent was cooled to 0 °C and removed in vacuo. The solid was redissolved in CH_2Cl_2, and pentane was added to precipitate the adduct. The adduct was washed with additional pentane to remove excess ligand. Evaporation removed residual solvent, and the complex was stable for hours at room temperature in $CDCl_2$. ^{1}H NMR ($CDCl_3$): *δ* 8.82 (s, 1H, C*H*═N), 8.3 (s, 1H, C*H*═N), 6.8−7.80 (m, 8H), 3.6−4.7 (m, 4H, CH_2−CH_2), 2.2 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 1.7 (s, 3H, CH_3), 1.2 (s, 3H, CH_3).

Synthesis of [Ru(salen)(NO)(tetrahydrothiophene)](SbF_6) (8). Four milligrams (5.9 *μ*mol) of **1** was reacted with 20 mg (227*μ*mol) of tetrahydrothiophene in an NMR tube containing 2 mL of CD_3NO_2. The reaction was prepared at 0 °C and monitored by ^{1}H NMR. The appearance of the desired compound was identified by two imine singlets at *δ* 8.7 and 9.1 and by upfield signals at *δ* 2.5 and 1.5. When these resonances were at their maximum, the solvent was cooled to 0 °C and removed in vacuo. The solid was redissolved in CH_2Cl_2, and pentane was added to precipitate the adduct. The adduct was washed several times with pentane to remove excess ligand. Evaporation removed residual solvent, and the complex was stable for hours at room temperature in CD_2Cl_2. ^{1}H NMR (CD_2Cl_2): *δ* 8.85 (s, 1H, C*H*═N), 8.45 (s, 1H, C*H*═N), 6.8−7.7 (m, 8H), 3.6−4.4 (m, 4H, CH_2−CH_2), 2.8−3.0 (bm, 4H, SCH_2CH_2−), 2.0−2.1 (bm, 4H, SCH_2CH_2−).

Procedure for Study of Solvent Effects on Structure of Salen Complex. Three milligrams (5 *μ*mol) of **1** was placed in a NMR tube containing 1 mL of CD_3CN. The catalyst was monitored by ^{1}H NMR over a period of several hours during which the ^{1}H NMR spectrum

changed. The most pronounced change was in the form of a decline in the imine singlet resonance and the appearance of two new singlets on opposite sides of the original resonance of roughly equal intensity (δ 8.8 and 8.4). Changes resulting in greater complexity in the total spectrum evolved over time until the final spectrum indicated that the starting complex had largely vanished from solution leaving two new species, one major the other minor, as indicated by the NMR spectrum. The major product was assigned as *cis*-[Ru(salen)(NO)(CD_3CN)] (SbF_6) (**9**).

Procedure for Study of Reaction of *d*-6 and Unlabeled *cis*-Stilbene Sulfide and *h*-6 with Deuterium-Labeled *cis*-Stilbene Sulfide. Two micromoles of *d*-**6** was dissolved in 1.0 mL of CD_2Cl_2 in an NMR tube, and 6 μmol of *cis*-stilbene sulfide was added in 200 μL of CD_2Cl_2. The appearance of *cis*-stilbene and the disappearance of complex from solution were monitored over a 60 min period. The disappearance of complex was associated with the formation of precipitated **1** as the free complex is liberated into solution. The ratio of the stilbene peak at δ 6.6 and the peak of tetrahydrothiophene at δ 5.1 was used as a measure of deuterium enrichment in the cyclic product. The ratio was determined to be 4:1. The stilbene could be isolated by silica column chromatography using hexane as an eluant. GCMS analysis confirmed that the stilbene contains negligible deuterium label. The experimental above was performed where all-proteo **6** (*h*-**6**) and deuterium-labeled *cis*-stilbene sulfide was used as the sulfur donor. In this case, the ratio of peaks at 6.6 and 5.1 was found to be 2:1. In the GCMS analysis, the stilbene had a deuterium content (single position) of 70%. In a control experiment (*h*-**6** reacted with unlabeled *cis*-stilbene sulfide), the ratio of stilbene peak to tetrathiane peak by ^{1}H NMR was found to be 3:1. Table 3 contains GCMS data for stilbene controls and for reactions.

Kinetic Study of *cis*-Stilbene Sulfide Desulfurization Reaction. Compound **6** (2.9 μmoles) was dissolved in 3.0 mL of CD_2Cl_2, and the volume was equally divided into three separate NMR tubes. In separate experiments, 3 μmol, 6 μmol, and 12 μmol of *cis*-stilbene sulfide were added in 200 μL of CD_2Cl_2 to one of the three prepared NMR tubes. Each tube was monitored for appearance of *cis*-stilbene over a 60 min period with spectra obtained at 3−6 min intervals. The *cis*-stilbene formed was measured by integration of the vinyl resonance at δ 6.6. Plots of *cis*-stilbene produced versus time were used to determine the rate using the initial rate method. Separately, a second experiment was performed wherein 6 μmol of stilbene sulfide in 200 μL of CD_2Cl_2 was added to 0.6 μmol of the adduct in 1.0 mL of CD_2Cl_2. The rate of *cis*-stilbene production was measured with a method similar to that described above.

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