

Enantioselective syntheses of organosulfur compounds via [2,3] sigmatropic rearrangements of ylides derived from di(allyl), di(propargyl), and di(benzyl) sulfide complexes; control of carbon configuration by an easily resolved and recycled rhodium auxiliary

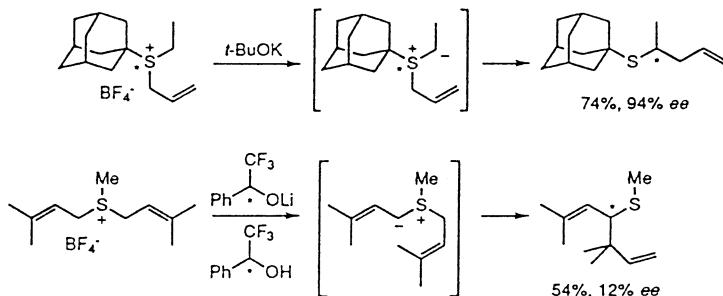
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Abstract: The [2,3] sigmatropic rearrangement of sulfur ylides with *S*-allyl or related substituents finds widespread use in organic synthesis, but enantioselective versions of this carbon–carbon bond forming reaction are relatively unexplored. We report that the chiral rhodium Lewis acid $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)]^+$ is a highly effective auxiliary for desymmetrizations of di(allyl), di(propargyl), and di(benzyl) sulfides. Additions of *t*-BuOK to the air-stable cationic sulfide adducts give neutral thiolate complexes of high diastereomeric purities. The thiolate ligands can be *S*-alkylated and detached as sulfides of high enantiomeric purities. The rhodium auxiliary is easily recovered and recycled without loss of configuration. Crystal structures establish product configurations, and mechanisms of diastereoselection are analyzed in detail.

Sulfur ylides that have allyl substituents undergo rapid [2,3] sigmatropic rearrangements to give sulfides or thioethers (1). This carbon–carbon bond forming reaction commonly generates a new carbon stereocenter, and sees extensive use in organic synthesis. The ylides are most often accessed by deprotonations of sulfonium salts. Surprisingly, there are only two cases in which sulfides have been generated in an enantioselective manner from sulfonium salts that lack resolved carbon stereocenters (2). These are depicted in Scheme 1. One involves an adamantyl sulfonium salt with a resolved sulfur stereocenter, and gives a sulfide of high enantiomeric purity. The other involves an achiral sulfonium salt and a chiral solvent and base, and gives a sulfide of low enantiomeric purity. Both were reported over twenty years ago by Trost.

Scheme 1. Enantioselective Syntheses of Sulfides via Deprotonation and Rearrangement of Allylic Sulfonium Salts that Lack Carbon Stereocenters



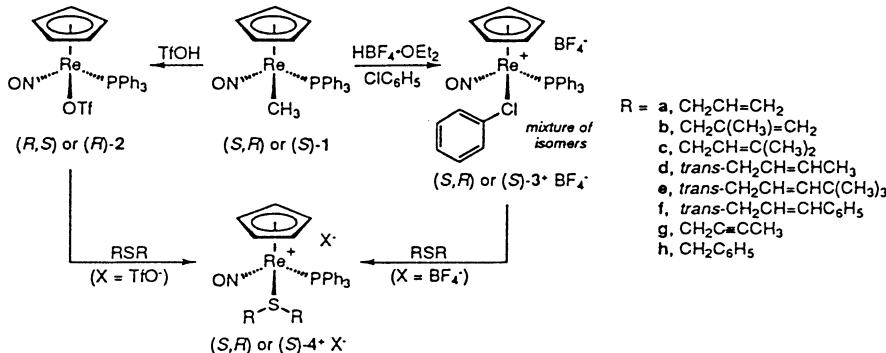
The protocols in Scheme 1 are obviously of limited generality or effectiveness. We thought that sulfur-bound chiral auxiliaries might be able to efficiently control the carbon configurations of the products. Surprisingly, such approaches have not been previously investigated. Since sulfides readily coordinate to transition metals, we viewed chiral metal fragments as particularly promising. Although numerous candidates exist, extensive studies from our laboratory have established that Lewis base adducts of the chiral rhodium Lewis acid $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)]^+$ (I) are easily prepared in enantiomerically pure form.

In this symposium account, we report that I serves as a readily recycled auxiliary for the conversion of achiral, symmetrical di(allyl), di(propargyl), and di(benzyl) sulfides to chiral, rearranged sulfides of high enantiomeric purities. In particular, alkoxide bases deprotonate the cationic adducts to sulfur ylides that undergo rapid [2,3] sigmatropic bond shifts at -80°C . To our knowledge, this constitutes the first time that such processes have been effected in a metal coordination sphere. Mechanistic and structural data that help rationalize the dominant carbon configurations are also described. Full experimental details are reported elsewhere (3).

Results

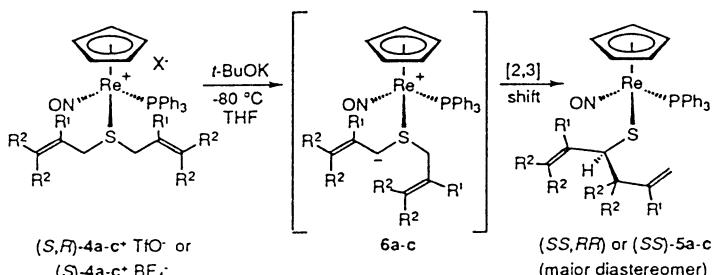
1. Syntheses of Sulfide Complexes. Racemic or enantiomerically pure di(allyl), di(propargyl), and di(benzyl) sulfide complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{SR}_2)]^+ \text{X}^-$ (4^+X^-) were prepared in 86-66% unoptimized yields as shown in Scheme 2. Configurations (retention) were assigned by analogy to other substitution reactions of 2 and 3^+BF_4^- (4,5), and were confirmed crystallographically below (6). The diastereotopic SR_2 groups gave only one set of NMR signals at room temperature. Low temperature NMR spectra of $4\text{b}^+ \text{TfO}^-$ established an inversion/rotation barrier of 9.4-9.5 kcal/mol. Hence, 4^+X^- have much lower sulfur inversion barriers than organic sulfonium salts (7,8).

Scheme 2. Syntheses of Di(allyl), Di(propargyl), and Di(Benzyl) Sulfide Complexes



2. [2,3] Sigmatropic Rearrangements. As shown in Scheme 3, reactions of the racemic di(allyl) sulfide complexes $4\text{a-c}^+ \text{TfO}^-$ and *t*-BuOK gave the air-stable thiolate complexes $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{SCHR}'\text{R}'')$ (5a-c) in 95-90% yields as 98:2 to 93:7 mixtures of Re,SC configurational diastereomers. Thus, chirality transfer to the new carbon stereocenters is strikingly efficient. Reactions were complete within one minute at -80°C , and were presumed to involve the ylides 6a-c and subsequent [2,3] sigma-tropic rearrangements. The non-racemic sulfide complexes $(S)\text{-4a-c}^+ \text{BF}_4^-$ gave similar or slightly better results. Product configurations were assigned from crystal structures (Fig. 2,3), and other data.

Scheme 3. Generation and Rearrangement of Rhenium-Substituted Sulfur Ylides

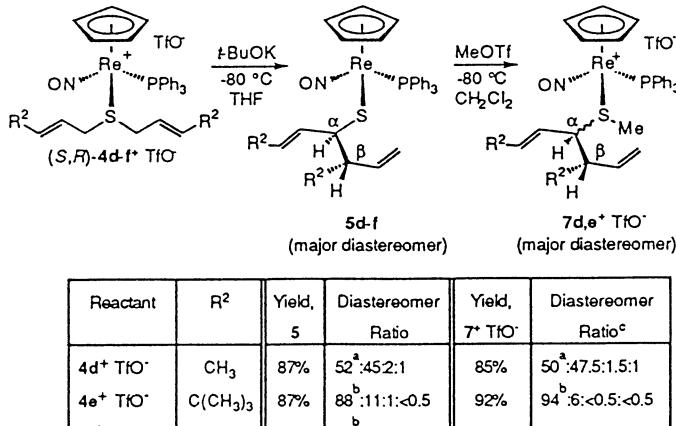


Reactant	R^1	R^2	Products	Ratio	Yield
$(S,R)\text{-4a}^+ \text{TfO}^-$	H	H	$(SS,RR)\text{-5a}/(SR,RS)\text{-5a}$	93:7	92%
$(S,R)\text{-4b}^+ \text{TfO}^-$	CH_3	H	$(SS,RR)\text{-5b}/(SR,RS)\text{-5b}$	98:2	95%
$(S,R)\text{-4c}^+ \text{TfO}^-$	H	CH_3	$(SS,RR)\text{-5c}/(SR,RS)\text{-5c}$	93:7	90%
$(S)\text{-4a}^+ \text{BF}_4^-$	H	H	$(SS)\text{-5a}/(SR)\text{-5a}$	93:7	79%
$(S)\text{-4b}^+ \text{BF}_4^-$	CH_3	H	$(SS)\text{-5b}/(SR)\text{-5b}$	>99.5:<0.5 ^a	79%
$(S)\text{-4c}^+ \text{BF}_4^-$	H	CH_3	$(SS)\text{-5c}/(SR)\text{-5c}$	97:3	85%

^a 99.3:0.7 before workup

Complexes $4\text{d-f}^+ \text{TfO}^-$ have unsymmetrically substituted allyl termini. As shown in Scheme 4, the resulting thiolates 5d-f therefore contain a *second* carbon stereocenter (SCC or C_β). Except for the *t*-butyl substituted sulfide $4\text{e}^+ \text{TfO}^-$, the SCC diastereoselectivities were much lower. However, the configuration of this stereocenter provides insight regarding the mechanism of chirality transfer (below).

Scheme 4. Reactions of Di(allyl) Sulfide Complexes that have Unsymmetrically Substituted Allyl Termini



^aSRS, RSR. ^bSRR, RSS. ^cdiastereomer ratios are slightly altered by workup.

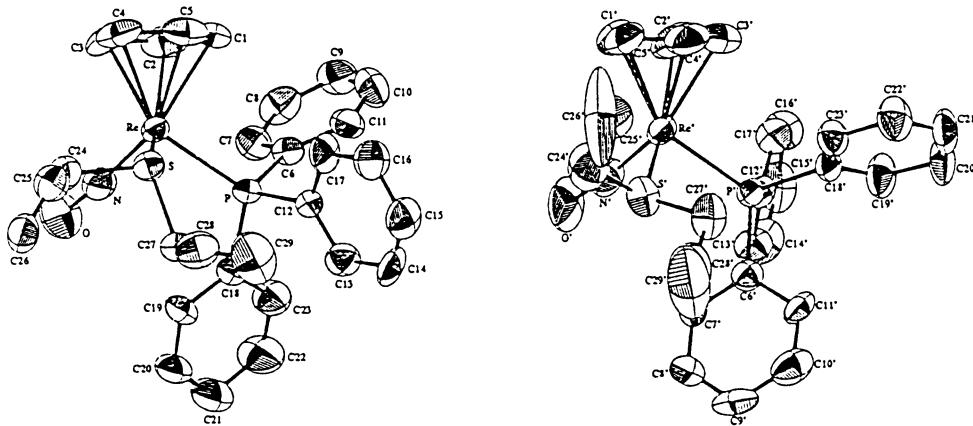
3. Reactant Conformations and Product Configurations. In order to help clarify the basis for the high diastereoselectivities in Scheme 3, we sought to probe the conformations of the sulfide ligands in $4^+ X^-$. However, the rapid exchange of SR_2 groups complicates NMR approaches. Thus, crystal structures were attempted. Suitable crystals of the non-racemic complex (S) -4a $^+$ BF_4^- could not be obtained. However, the corresponding hexafluoroantimonate salt (S) -4a $^+$ SbF_6^- , which was prepared by metathesis, readily crystallized. Two independent cations were present in the unit cell, as illustrated in Fig. 1. Key metrical parameters for all crystal structures are given in TABLE 1.

TABLE 1. Selected Bond Lengths (Å), Bond Angles (°), and Torsion Angles (°) of crystallographically characterized compounds

(S) -4a $^+$ SbF_6^-			(SRR, RSS) -5e			
Re-P	2.396(2)	Re'-P'	2.403(2)	Re-P	2.343(3)	
Re-S	2.372(2)	Re'-S'	2.404(3)	Re-S	2.392(2)	
Re-N	1.771(9)	Re'-N'	1.760(9)	P-Re-N	92.9(3)	
S-C24	1.81(1)	S'-C24'	1.78(1)	S-Re-P	87.53(9)	
S-C27	1.84(1)	S'-C27'	1.81(1)	P-Re-S-C24	-179.1(3)	
P-Re-N	94.4(3)	P'-Re'-N'	93.3(3)	N-Re-S-C24	-86.7(4)	
S-Re-P	98.00 (7)	S'-Re'-P'	92.67(9)	(SR, RS) -5a-Me ₅		
S-Re-N	98.4(3)	S'-Re'-N'	87.3(4)	Re-P	2.352(3)	
P-Re-S-LP	90.2(1)	P'-Re'-S'-LP'	-69.2(1)	Re-S	2.394(3)	
N-Re-S-C24	-46.8(4)	N'-Re'-S'-C24'	-97.5(6)	P-Re-N	94.6(5)	
N-Re-S-C27	67.0(4)	N'-Re'-S'-C27'	142.6(5)	S-Re-P	87.4(2)	
N-Re-S-LP	-174.1(3)	N'-Re'-S'-LP'	24.0(3)	P-Re-S-C24	-150.7(5)	
(SS) -5a			(SR, RS) -5h			
Re-P	2.384(1)	Re-N	1.741(5)	Re-P	2.354(2)	
Re-S	2.348(1)	S-C24	1.849(6)	Re-S	2.384(2)	
P-Re-N	93.2(2)	S-Re-N	100.7(2)	P-Re-N	91.8(2)	
S-Re-P	86.00(5)	Re-S-C24	109.5(2)	S-Re-P	89.31(5)	
P-Re-S-C24	-152.5(3)	N-Re-S-C24	-60.0(3)	P-Re-S-C24	-175.3(0.2)	

The structures in Fig. 1 verify the rhenium configuration (S), which corresponds to overall retention from methyl complex (S)-1 (Scheme 2). There is also good evidence that the intermediate chlorobenzene complex $3^+ BF_4^-$ is formed and reacts with retention (9). The fortuitous presence of two cations allows a better appreciation of the ensemble of ligand conformations that may be populated in solution. The cations differ primarily in the Re-S conformation, as reflected by the differences in P-Re-S-LP (lone pair) or N-Re-S-LP torsion angle (TABLE 1; Δ 160–150°).

Fig. 1. Structures of the two crystallographically independent cations of the di(allyl) sulfide complex (*S*)-4a⁺ SbF₆⁻. Ellipsoids are shown at the 50% probability level, except for C26' which is depicted at the 25% probability level.



The crystal structures of non-racemic thiolate (*SS*)-5a and racemic thiolate (*SRR,RSS*)-5e are depicted in Fig. 2. These represent the major diastereomers formed from (*S*)-4a⁺ BF₄⁻ and 4e⁺ TfO⁻, respectively. Analogous relative Re,SC configurations were assigned to the major diastereomers of the other thiolate complexes. The structure of (*SS*)-5a also establishes retention at rhenium for the deprotonation/re-arrangement sequence. The Re-S conformations of all crystallographically characterized compounds are compared in Fig. 3.

Fig. 2. Crystal Structures of Thiolate Complexes (*SS*)-5a (top, left), (*SRR,RSS*)-5e (top, right), (*SR,RS*)-5a-Me₅ (bottom, left), and (*SR,RS*)-5h (bottom, right).

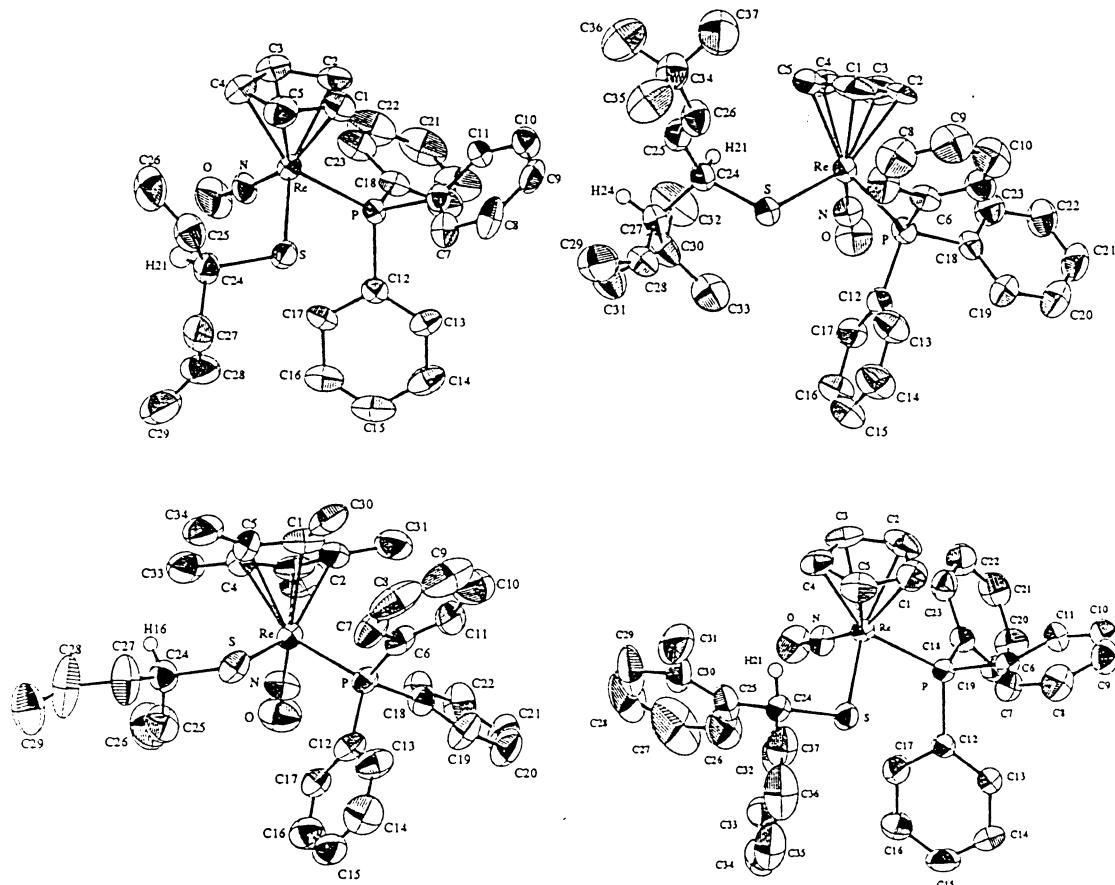
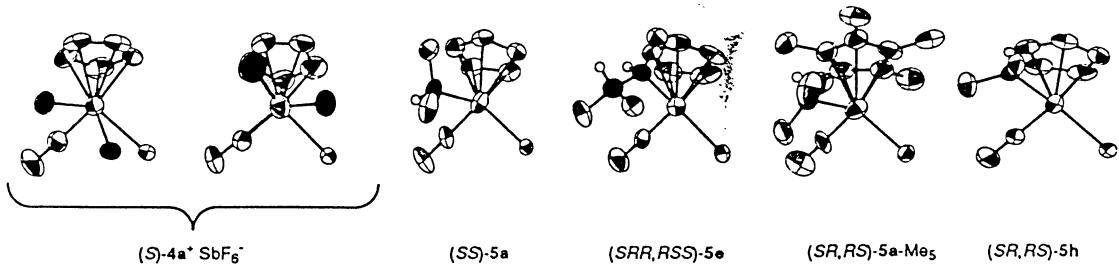
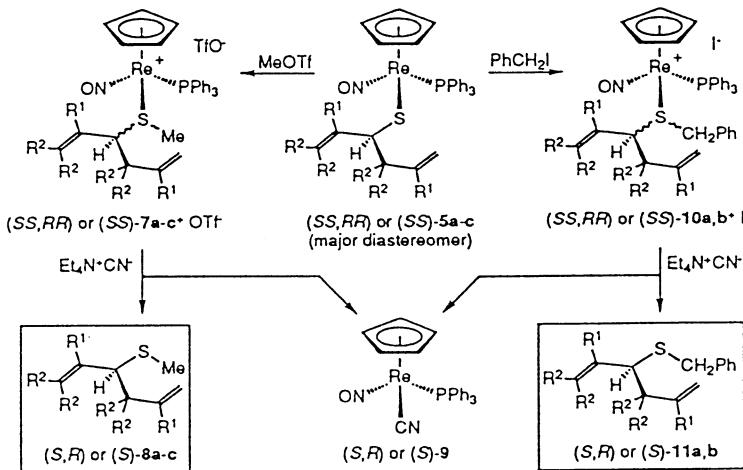


Fig. 3. Rhenium-Sulfur conformations in crystallographically characterized compounds: Newman projections down the S-Re bonds.



4. Chiral Organic Sulfides. We sought to detach the thiolate ligands from 5. The sulfur atoms of thiolate ligands are commonly more nucleophilic than those of organic sulfides (10). Thus, as shown in Scheme 5, 5a-c and MeOTf (1.0 equiv) were combined in CH_2Cl_2 at -80°C . The cationic methyl sulfide complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{S}(\text{Me})\text{CHR}'\text{R}'')]^+ \text{TfO}^-$ (7a-c+ TfO⁻) were isolated in 95-89% yields. These sulfur-based transformations were presumed to proceed with retention at rhenium.

Scheme 5. Conversion of Thiolate Complexes to Free Organic Sulfides



Reactant	R ¹	R ²	Diastereomer Ratio	Yield, Alkylation Product	Diastereomer Ratio	Yield, Sulfide	Enantiomer Ratio ^c	Yield, % ^d
5a	H	H	92:8 ^a	90%, 7a+ TfO^-	92:8 ^a	60%, 8a	..	87%
5b	CH ₃	H	98:2 ^a	89%, 7b+ TfO^-	98:2 ^a	65%, 8b	..	86%
5c	H	CH ₃	93:7 ^a	89%, 7c+ TfO^-	93:7 ^a	60%, 8c	..	89%
5a	H	H	92:8 ^b	89%, 7a+ TfO^-	92:8 ^b	67%, 8a	92:8	93%
5b	CH ₃	H	>99.5:<0.5 ^b	95%, 7b+ TfO^-	>99.5:<0.5 ^b	58%, 8b	>99:<1	92%
5c	H	CH ₃	97:3 ^b	93%, 7c+ TfO^-	97:3 ^b	65%, 8c	96:4	78%
5a	H	H	93:7 ^a	97%, 10a+ I ⁻	93:7 ^a	84%, 11a	..	84%
5b	CH ₃	H	98:2 ^a	84%, 10b+ I ⁻	98:2 ^a	85%, 11b	..	91%
5a	H	H	93:7 ^b	82%, 10a+ I ⁻	93:7 ^b	77%, 11a	93:7	93%
5b	CH ₃	H	>99.5:<0.5 ^b	79%, 10b+ I ⁻	>99.5:<0.5 ^b	82%, 11b	>99:<1	91%

^aSS,RR/SR,RS. ^bSS,SR. ^cS/R. ^dnon-racemic samples were >99:<1 S/R.

Subsequent reactions with $\text{Et}_4\text{N}^+ \text{CN}^-$ (1.5 equiv) gave the free methyl sulfides $\text{MeSCHR}'\text{R}''$ (8a-c) in 67-58% yields after distillation. The known cyanide complex $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{CN})$ (9) was obtained in 89-84% yields (11). This compound is easily recycled to the methyl complex 1 (12). Additional data are summarized in Scheme 5.

Separate NMR experiments showed the formation of 8 and 9 to be spectroscopically quantitative. Thus, the lower yields of the somewhat volatile methyl sulfides 8 were attributed to losses during solvent removal or distillation. In order to reduce this problem, 5a,b were treated with PhCH_2I , which transfers a

heavier alkyl group (Scheme 5). The benzyl sulfide complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{S}(\text{CH}_2\text{Ph})\text{-CHR}'\text{R}'')]^+\text{I}^-$ (10a,b⁺ I⁻) were isolated in 97-79% yields. Reactions with Et₄N⁺ CN⁻ and silica gel work-ups gave the free benzyl sulfides PhCH₂SCHR'R" (11a,b) in 85-84% yields.

Reactions were repeated with selected non-racemic thiolate complexes. As summarized in Scheme 5, (SS)-5a-c were alkylated to give (SS)-7a-c⁺ TfO⁻ and (SS)-10a,b⁺ I⁻ (95-79%). Reactions with Et₄N⁺ CN⁻ gave the free sulfides (S)-8a-c (67-58%) and (S)-11a,b (82-77%). Enantiomeric purities were assayed with chiral NMR shift reagents, and closely matched the diastereomeric purities of the precursors (S/R > 99:1 to 92:8; Scheme 5). The cyanide complex (S)-9 was recovered in 93-78% yields and >98% ee (11b,12). This shows that no racemization or epimerization of the rhenium occurs at any stage in Schemes 2-5. The configuration corresponds to retention from (SS)-7,10⁺ X⁻, as established for closely related cyanide ion substitutions (12).

5. Optimization and Mechanistic Experiments. We explored various possibilities for increasing the ratio of diastereomers of 5a obtained in Scheme 3 (93:7). The diastereomer ratio was unaffected when the concentration of 4a⁺ TfO⁻ was varied fifty-fold or reactions were conducted at -105 °C. The ratio decreased when reactions were run at higher temperatures. As summarized in TABLE 2, solvent significantly influenced diastereomer ratios. However, only diglyme gave improved results (95.5:4.5). A variety of other bases could also be employed. Stronger R₂N⁺ or R⁻ bases gave much lower diastereomer ratios, sometimes with reversed selectivities.

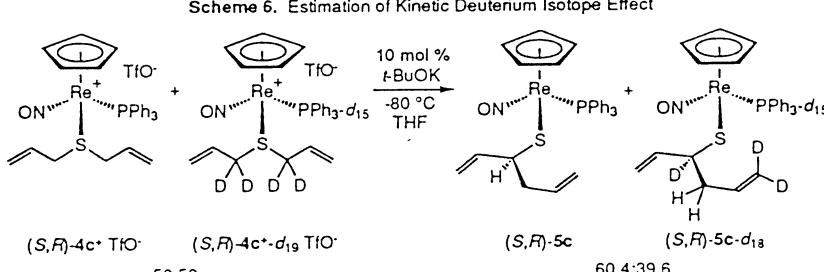
TABLE 2. Effects of Solvent and Base on the Conversion of 4a⁺ TfO⁻ to 5a

Solvent ^a	Base/Solvent	SS,RR/SS,RS
THF	t-BuOK/THF	93.07
acetone	t-BuOK/THF	91.09
CH ₂ Cl ₂	t-BuOK/THF	71.29
EtOAc ^b	t-BuOK/THF	93.07
toluene ^c	t-BuOK/THF	78.22
diglyme ^d	t-BuOK/THF	95.5:4.5
THF	MeONa/MeOH	92.08
THF	t-BuOLi/THF	87:13
THF	(Me ₃ Si) ₂ NLi/THF	40.60
THF	(Me ₃ Si) ₂ NK/THF	66.34
THF	(Me ₃ Si) ₂ NK/toluene	43.57
THF	(i-Pr) ₂ NLi·THF/cyclohexane	47.53
THF	n-BuLi/hexane	51:49

^aca. 0.001 M, -80 °C. ^b4a⁺ TfO⁻ is slightly soluble in EtOAc. ^c4a⁺ TfO⁻ is insoluble in toluene and some byproducts form (ca. 6%). ^d conducted at -66 °C.

In theory, either the first or second step in Scheme 3 might be rate determining. We sought to assay the reversibility of the deprotonation of 4⁺ X⁻ to ylide 6. Thus, 4a,c⁺ TfO⁻ were dissolved in THF containing the *deuterated* alcohol t-BuOD (16 equiv), and a deficiency of t-BuOK (0.5 equiv) was added. Any return of 6a,c to 4a,c⁺ TfO⁻ would then be accompanied by deuterium incorporation. The products 5a,c and unreacted 4a,c⁺ TfO⁻ were isolated, and mass spectrometry showed very low levels of deuteration (1-7%). Hence, the deprotonation of 4⁺ X⁻ to 6 cannot be a reversible, pre-equilibrium step.

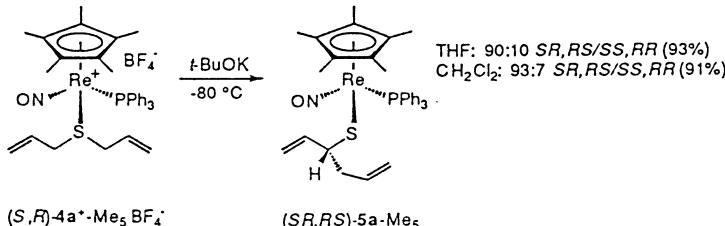
Scheme 6. Estimation of Kinetic Deuterium Isotope Effect



As shown in Scheme 6, a mixture of $4c^+ \text{TfO}^-$ and the deuterated sulfide complex $4c^+ \text{-} d_{19} \text{TfO}^-$ was reacted with a deficiency of *t*-BuOK (mol ratio 50:50:10). A mass spectrum of the resulting thiolate **5c** showed a 60.4:39.6 d_{18}/d_0 mixture, implying a k_H/k_D of 1.53. This establishes, together with the previous experiment, that the deprotonation of 4^+X^- to **6** is rate determining. The low value is presumably due to a bent or unsymmetrical transition state.

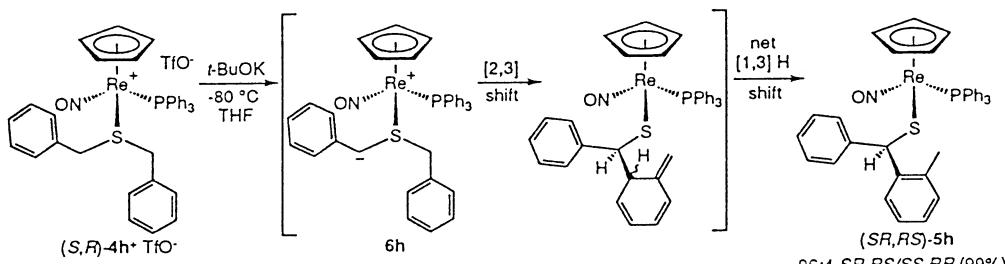
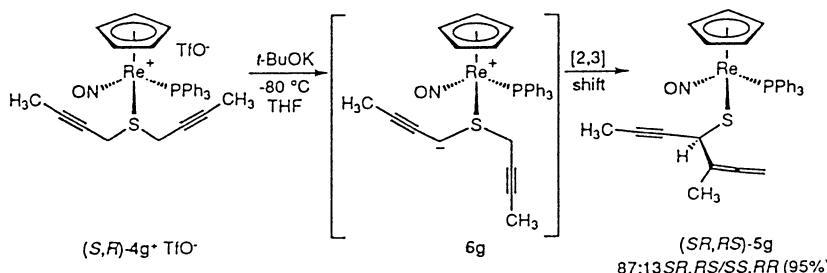
6. Pentamethylcyclopentadienyl Complexes. We thought that diastereoselectivities might increase with bulkier, pentamethylcyclopentadienyl analogs of 4^+X^- . As shown in Scheme 7, reactions of the parent di(allyl) sulfide complex $4a^+ \text{-Me}_5 \text{BF}_4^-$ and *t*-BuOK gave the thiolate **5a**-Me₅ as 93:7 to 90:10 mixtures of diastereomers — comparable to the result with $4a^+ \text{BF}_4^-$ and **5a**. However, a crystal structure of the major diastereomer (Fig. 2,3) showed that the *opposite* (*SR,RS*) diastereomer preferentially forms. The implications of this surprising result are analyzed below.

Scheme 7. Reaction of Pentamethylcyclopentadienyl Di(allyl) Sulfide Complex $4a^+ \text{-Me}_5 \text{BF}_4^-$



7. Di(propargyl) and Di(benzyl) Sulfide Complexes. We wondered if other types of unsaturated sulfide ligands would give similar chemistry. As depicted in Scheme 8 (top), reaction of the di(propargyl) sulfide complex $4g^+ \text{TfO}^-$ and *t*-BuOK gave the thiolate **5g** as a 87:13 mixture of diastereomers. Thus, an analogous rearrangement occurs with a diastereoselectivity only slightly lower than those of the di(allyl) sulfide complexes. The relative Re,SC configuration of the major diastereomer was presumed to be identical with that of **5a**.

Scheme 8. Reactions of Di(propargyl) and Di(benzyl) Sulfide Complexes $4g,h^+ \text{TfO}^-$

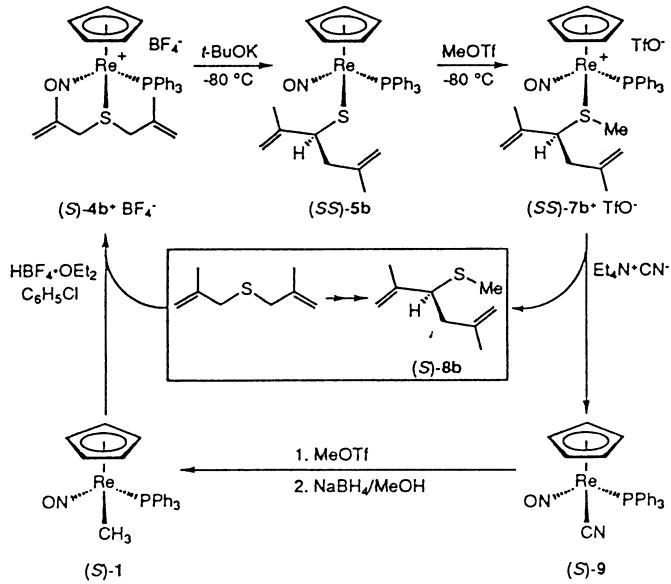


As shown in Scheme 8 (bottom), reaction of the parent di(benzyl) sulfide complex $4h^+ \text{TfO}^-$ and *t*-BuOK gave the thiolate **5h** as a 96:4 mixture of diastereomers. Thus, a similar rearrangement occurs with a diastereoselectivity comparable to those of the di(allyl) sulfide complexes. However, the intermediate ylide **6h** (Scheme 8) initially yields a thiolate complex with a dearomatized ring, which isomerizes to **5h** in a subsequent step. A crystal structure of the major diastereomer (Fig. 2,3) showed that the relative Re,SC configuration was identical with that of **5a**.

Discussion

1. Scope and Merits of Methodology. Schemes 3-8 establish the following new or previously unexploited chemical phenomena: (a) sulfur ylides can be generated from cationic transition metal complexes of di(allyl), di(propargyl), and di(benzyl) sulfides and bases; (b) these undergo rapid [2,3] sigmatropic rearrangements to give neutral thiolate complexes; (c) with chiral metal fragments, the configurations of the resulting *SC* carbon stereocenters can be efficiently controlled; (d) non-racemic chiral metal fragments can be used to prepare chiral organosulfur compounds of high enantiomeric purities. The net organic transformation accomplished is highlighted in the middle of Scheme 9, using di(2-methylallyl) sulfide for illustration.

Scheme 9. Summary: Enantioselective Conversion of Achiral Di(allyl) Sulfides to Rearranged Chiral Sulfides Mediated by the Recyclable Chiral Rhodium Auxiliary I



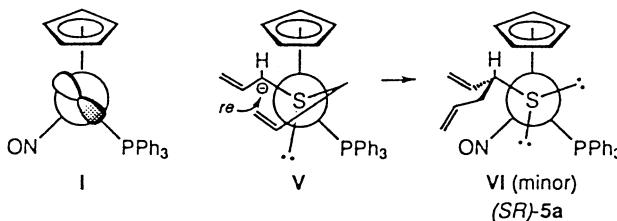
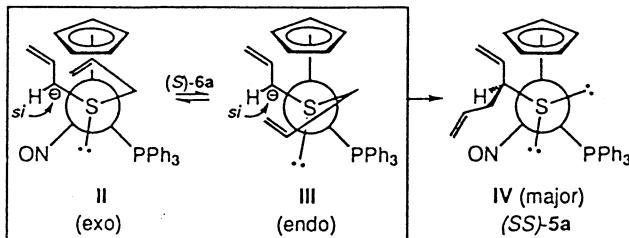
The starting material for this desymmetrization process, methyl complex **1**, can be prepared from commercially available $\text{Re}_2(\text{CO})_{10}$ in three steps and 57% overall yield (4). The enantiomers are easily resolved *en route* in two steps and 76% yield. All of the compounds in Scheme 9, and precursors thereof, are air-stable and amenable to multigram scale preparations. Each of the individual steps in Schemes 2-8 is spectroscopically quantitative, and isolated yields have not been optimized. At present, (S,R) -**4b**⁺ TfO^- and (S) -**4b**⁺ BF_4^- can be converted to the free methyl sulfides (S,R) - and (S) -**8b** in 55-44% overall yields, and the cyanide complexes (S,R) - and (S) -**9** in 73-69% overall yields. With the benzyl sulfides (S,R) - and (S) -**11b**, yields increase to 68-51%. The cyanide complexes can be recycled to the methyl complexes (S,R) - and (S) -**1** (>99.9% ee) in 88-53% yields in two steps as shown in Scheme 9 (12). Studies in progress show that it is possible to combine consecutive steps with improved overall yields. Also, it should be possible to use electrophiles other than alkylating agents to derivatize thiolates **5**.

2. Mechanism of Diastereoselection. As diagrammed in Scheme 10, the dominant *SC* configurations of thiolates **5** (Schemes 3,4,8) require that when the rhodium configuration is *S*, the allyl moiety in ylide **6** preferentially migrates to the *si* face of the carbanion. However, other key transition state variables remain undefined, such as (a) the rhodium-sulfur conformation, (b) the configuration of the sulfur stereocenter, and (c) the conformation of the migrating allyl group. To help frame these possibilities, the transition states II and III (Scheme 10) are analyzed first. Both lead to the major thiolate diastereomer IV.

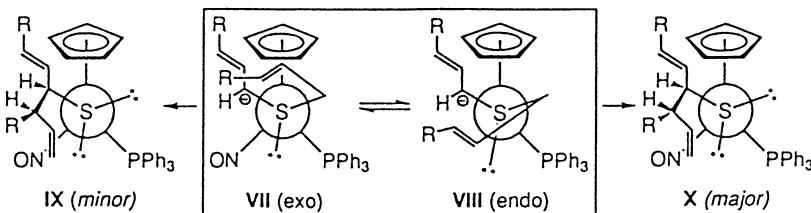
The rhodium-sulfur conformations in II and III correspond to those that would be the most stable in sulfide complexes **4**⁺ X^- (7). Adducts of the rhodium fragment I are formally octahedral, and numerous studies have established that the interstice between the large PPh_3 and small nitrosyl ligands is the most congested (7,11b,13). Note that the idealized $\text{P}-\text{Re}-\text{N}$ bond angle (90°) is smaller than those involving the cyclopentadienyl centroid (125°). Thus, ligands preferentially adopt conformations that direct their least bulky groups into this region (14).

Similarly, the interstice between the small nitrosyl and medium cyclopentadienyl ligands is the least congested (7,13). Thus, ligands preferentially adopt conformations that direct their largest groups into this

Scheme 10. Some Transition State Models for [2,3] Sigmatropic Rearrangements



-rhenium-sulfur rotamers of II, III, or V give rhenium-sulfur rotamers of IV or VI
 -second series of transition states possible that are epimeric at sulfur



region. The rhenium-sulfur conformation depicted in thiolate IV should therefore be the most stable. As supporting evidence, the four thiolate complexes in Fig. 2-3 crystallize accordingly, with N-Re-S-C torsion angles between $-56.7(6)^\circ$ and $-86.7(4)^\circ$. Hence, II and III directly give thiolate complexes in the lowest energy rhenium-sulfur conformation.

Additional families of transition states can be generated from II or III by (a) rotating ca. 120° about the rhenium-sulfur bond, or (b) inversion at sulfur. However, all of these will involve a less stable rhenium-sulfur conformation of the ylide and/or thiolate product. Although these possibilities cannot at present be rigorously excluded, there is a good probability that their energies will be higher.

In view of the low sulfur inversion/rotation barriers in $4^+ X^-$, we suspect that the ylide 6 undergoes rapid sulfur inversion/rotation on the time scale of rearrangement. Conformational processes involving the SC substituents are also likely rapid. In this familiar Curtin-Hammett limit (15), diastereomer ratios reflect the absolute energies of the competing transition states. In the opposite limit, kinetic selectivities become important. For example, the sulfur configuration is initially determined by which of the two diastereotopic allyl groups of $4^+ X^-$ is deprotonated. Regardless of the limit that applies, we propose that base preferentially attacks the allyl group in the least hindered interstice between the nitrosyl and cyclopentadienyl ligands. Further, in the more stable of the rhenium-sulfur conformers in crystalline $(S)-4a^+ SbF_6^-$ (Fig. 1, right), one $SC\text{H}_2$ proton is sterically more accessible. Abstraction would give III directly (16).

The question remains as to what is disfavored about analogs of II or III that involve the *re* face of the ylide carbanion, such as V. We initially thought that III would be less stable than V due to steric interactions of the vinyl carbanion substituent and the cyclopentadienyl ligand. However, there is also precedent for attractive edge/face interactions involving cyclopentadienyl ligands and aryl or other unsaturated moieties (17). This would account for the highly diastereoselective reaction of di(benzyl) sulfide complex $4h^+ \text{ TfO}^-$, which would involve an ylide in which a bulkier phenyl substituent is proximal to the cyclopentadienyl ligand. The pentamethylcyclopentadienyl complex $4a^+ - \text{Me}_5 \text{BF}_4^-$ provides another probe of this model. In the corresponding transition state III-Me₅, the vinyl group should experience much greater steric repulsion, and attractive edge/face interactions would no longer be possible. Accordingly, the diastereomer of thiolate

5a-Me₅ that would be derived from V-Me₅ is formed preferentially.

Finally, transition states II and III differ in the conformations of the migrating allyl group. These can be viewed as *exo* and *endo*, respectively, with respect to the sulfur lone pair. As detailed in a theoretical study, the former is generally favored with organic sulfur ylides (18). Importantly, 4d-f⁺ TfO⁻, which have unsymmetrically substituted allyl termini, give different SCC diastereomers depending upon the *exo/endo* sense of the transition state. This is illustrated with VII and VIII in Scheme 10. The crystal structure of (SRR,SRS)-5f establishes that the latter is greatly favored with the *t*-butyl substituted complex 4e⁺ TfO⁻. However, the methyl substituted complex 4e⁺ TfO⁻ shows little selectivity. Hence, we presume that II and III are usually close in energy.

3. Summary. The preceding chemistry raises many attractive possibilities for new research directions. Extensions involving unsymmetrical sulfide complexes (19), and chiral iron and ruthenium Lewis acids (20), are currently under investigation. We predict that other types of heteroatom donor ligands will give similar chemistry, and that variants that are catalytic in metal can be developed. Progress towards these objectives will be reported in due course.

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