Enantioselective Syntheses of Organosulfur Compounds via [2,3] Rearrangements of Ylides Derived from Di(allyl) and Di(propargyl) Sulfide Complexes. Control of Carbon Configuration by an Easily Resolved and Recycled Chiral Transition Metal Auxiliary

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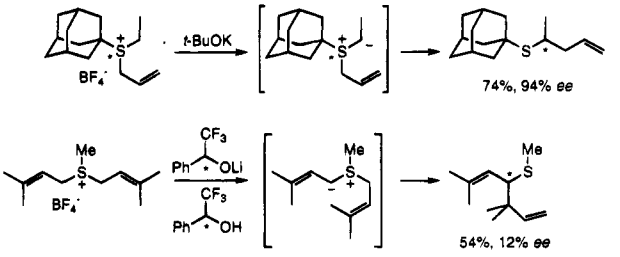
Abstract: The di(allyl) sulfide complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(S(CH_2CR{=}CR'_2)_2)]^+TfO^-$ (**4**$^+$TfO$^-$; R/R′ = **a**, H/H; **b**, CH_3/H; **c**, H/CH_3) and *t*-BuOK (THF, −80 °C) give thiolates $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(SCH(CR'_2CR{=}CH_2)CR{=}CR'_2)$ (**5a**−**c**, 95−90%) as 93:7, 98:2, and 93:7 mixtures of *SS,RR/SR,RS* Re,S*C* diastereomers. Pure enantiomers (*S*)-**4a**−**c**$^+BF_4^-$ give **5a**−**c** as 93:7, ≥99.3:0.7, and 97:3 *SS/SR* mixtures (85−79%). Reactions with MeOTf yield $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(S(Me)CH(CR'_2CR{=}CH_2)CR{=}CR'_2)]^+TfO^-$ (95−89%), which are treated with $Et_4N^+CN^-$ to give $MeSCH(CR'_2CR{=}CH_2)CR{=}CR'_2$ (**8a**−**c**, 67−58%; 92:8, >99:<1, 96:4 *S/R* from (*S*)-**4a**−**c**$^+BF_4^-$) and $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CN)$ (**9**, 93−78%; >98% ee). Complex (*S*)-**9** can be recycled to (*S*)-**4a**−**c**$^+BF_4^-$ in 2−3 steps. Analogous sequences with **5a,b** and $PhCH_2I$ give $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(S(CH_2Ph)CH(CR'_2CR{=}CH_2)CR{=}CR'_2)]^+I^-$ (97−79%) and $PhCH_2SCH(CR'_2CR{=}CH_2)CR{=}CR'_2$ (**11a,b**, 82−77%; 93:7, >99:<1 *S/R* from (*S*)-**4a,b**$^+BF_4^-$). Similar $S(CH_2C{\equiv}CCH_3)_2$ (**d**) and $S(CH_2CH{=}CHR)_2$ (*E*; R = **e**, CH_3; **f**, $C(CH_3)_3$; **g**, C_6H_5) complexes give thiolates **5d**−**g** as comparable Re,S*C* diastereomer mixtures. However, **5e**−**g** contain new SC*C* stereocenters, and only **5f** gives high selectivity (89:11). The *pentamethyl*cyclopentadienyl complex **4a**-$Me_5^+TfO^-$ yields **5a**-Me_5 of *opposite* stereochemistry (7:93 *SS,RR/SR,RS*). Crystal structures of (*S*)-**4a**$^+SbF_6^-$ (triclinic, *a* 9.800(2), *b* 10.516(2), *c* 16.152(3), α 93.20(2), β 107.16(2), γ 81.57(2), (*SS*)-**5a** (monoclinic, *a* 9.881(2), *b* 12.483(3), *c* 10.877(2), β 100.23(2)), (*SRR,RSS*)-**5f** (triclinic, *a* 9.578(3), *b* 14.019(5), *c* 15.999(4), α 93.22(3), β 97.83(3), γ 107.63(3)), and (*SR,RS*)-**5a**-Me_5 (monoclinic, *a* 8.780(2), *b* 17.379(4), *c* 20.801(3), β 92.49(2)) establish the configurations given above. The mechanism of diastereoselection is analyzed in detail.

Sulfur ylides with allyl or related substituents undergo rapid [2,3] sigmatropic rearrangements to give sulfides or thioethers.[1] This carbon−carbon bond forming reaction usually generates a new carbon stereocenter and is extensively utilized in organic synthesis. The ylides are most commonly 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] Both are illustrated in Scheme 1 and were reported over 20 years ago by Trost. One involves a 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.

The methodology in Scheme 1 is obviously of limited generality or effectiveness. We though that sulfur-bound chiral auxiliaries might be able to efficiently control the carbon configurations of the products. Curiously, such approaches have not been previously investigated.[3] 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

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



adducts of Lewis bases and the chiral rhenium Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (**I**) are easily prepared in enantiomerically pure form.

In this paper, we report that **I** serves as a readily recycled auxiliary for the conversion of achiral, symmetrical di(allyl) and di(propargyl) 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

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(1) (a) Markó, I. E. In *Comprehensive Organic Synthesis*; Trost, B. M., Editor-in-Chief, Fleming, I., Deputy Editor-in-Chief, Pattenden, G., Volume Editor, Pergamon: New York, 1991; Vol 3, Chapter 3.10. (b) Vedejs, E. *Acc. Chem. Res.* **1984**, *17*, 358.

(2) (a) Trost, B. M.; Hammen, R. F. *J. Am. Chem. Soc.* **1973**, *95*, 962. (b) Trost, B. M.; Biddlecom, W. G. *J. Org. Chem.* **1973**, *38*, 3438.

(3) For special classes of ylides in which (a) an S*C* substituent can serve as a recyclable chiral auxiliary, see: Kurth, M. J.; Tahir, S. H.; Olmstead, M. M. *J. Org. Chem.* **1990**, *55*, 2286. (b) An amine C=C substituent can serve as a recyclable chiral auxiliary, see: Hiroi, K.; Sato, S. *Chem. Pharm. Bull.* **1985**, *33*, 2331, 4691.

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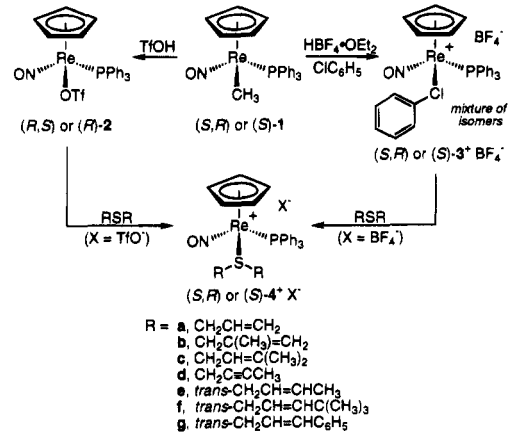
Scheme 2. Syntheses of Di(allyl) and Di(propargyl) Sulfide Complexes[9]



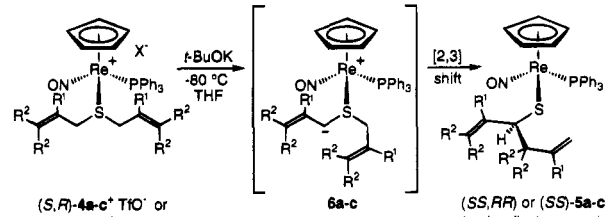
that help rationalize the dominant carbon configurations are also described. A small portion of this work has been communicated.[4]

Results

1. Syntheses of Sulfide Complexes. Functional equivalents of the chiral Lewis acid **I** were prepared as summarized in Scheme 2. First, the readily available, air-stable racemic methyl complex (η^5-C_5H_5)Re(NO)(PPh_3)(CH_3) (**1**)[5] and triflic acid (TfOH) were reacted to give the triflate complex (η^5-C_5H_5)Re(NO)(PPh_3)(OTf) (**2**).[6] Alternatively, **1** and HBF_4•OEt_2 were combined in chlorobenzene (−45 °C) to generate the chlorobenzene complex [(η^5-C_5H_5)Re(NO)(PPh_3)(ClC_6H_5)]$^+BF_4^-$ (**3**$^+BF_4^-$).[7] Subsequent additions of the di(allyl) or di(propargyl) sulfides listed in Scheme 2 (ca. 1.5 equiv) gave the air stable sulfide complexes [(η^5-C_5H_5)Re(NO)(PPh_3)(SR_2)]$^+X^-$(**4**$^+X^-$) in 86−66% yields. These, and other new compounds below, were characterized by IR, NMR (^{1}H, ^{13}C, ^{31}P), and microanalysis, unless noted. Data are summarized in the Experimental Section. Most properties were similar to those of *dialkyl* sulfide complexes of **I**, which were analogously prepared earlier.[8]

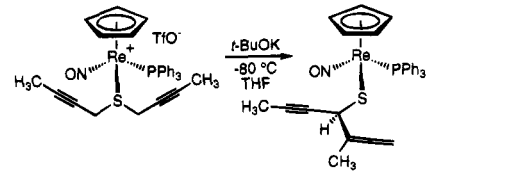
Nonracemic complexes were sought for enantioselective syntheses detailed below. Accordingly, the methyl complex (*S*)-**1** (>99% *ee*)[5] was similarly converted to the triflate complex (*R*)-**1** and the di(allyl) and di(methallyl) sulfide complexes (*S*)-**4a,b**$^+$TfO$^-$.[9] However, these were less crystalline than the racemates and more difficult to purify. Thus, (*S*)-**1** was converted to the chlorobenzene complex[7] (*S*)-**3**$^+BF_4^-$ and then (*S*)-**4a**−**c**$^+BF_4^-$. These tetrafluoroborate salts could be isolated as analytically pure powders in 80−70% yields. Configurations (retention) were assigned by analogy to other substitution reactions of **2** and **3**$^+BF_4^-$ [6,7] and were confirmed crystallographically below.

Scheme 3. Generation and Rearrangement of Rhenium-Substituted Sulfur Ylides[9]



Reactant	R^1	R^2	Products	Ratio	Yield
(*S,R*)-**4a**$^+$ TfO$^-$	H	H	(*SS,RR*)-**5a**/(*SR,RS*)-**5a**	93:7	92%
(*S,R*)-**4b**$^+$ TfO$^-$	CH_3	H	(*SS,RR*)-**5b**/(*SR,RS*)-**5b**	98:2	95%
(*S,R*)-**4c**$^+$ TfO$^-$	H	CH_3	(*SS,RR*)-**5c**/(*SR,RS*)-**5c**	93:7	90%
(*S*)-**4a**$^+$ BF_4^-	H	H	(*SS*)-**5a**/(*SR*)-**5a**	93:7	79%
(*S*)-**4b**$^+$ BF_4^-	CH_3	H	(*SS*)-**5b**/(*SR*)-**5b**	>99.5:<0.5[a]	79%
(*S*)-**4c**$^+$ BF_4^-	H	CH_3	(*SS*)-**5c**/(*SR*)-**5c**	97:3	85%

[a] 99.3:0.7 before workup



The diastereotopic SR_2 groups in **4**$^+X^-$ gave only one set of NMR signals at ambient temperature. Data with deuterated complexes (below) excluded rapid ligand dissociation. As analyzed earlier,[8] such SR_2 group exchange requires both sulfur inversion and rhenium−sulfur bond rotation. Low temperature NMR spectra of **4b**$^+$TfO$^-$ established an inversion/rotation barrier of 9.4−9.5 kcal/mol ($\Delta G^{\ddagger}$, 199−202 K).[10] The dimethyl sulfide complex of **I** gives a similar value.[8] Thus, sulfide complexes **4**$^+X^-$ have *much lower sulfur inversion barriers* than organic sulfonium salts.[11]

2. [2,3] Sigmatropic Rearrangements. As summarized in Scheme 3, THF solutions of the racemic sulfide complexes **4a**−**d**$^+$TfO$^-$ and *t*-BuOK (1.0 equiv) were combined at −80 °C. Reactions were complete in less than 1 min, as assayed in separate NMR experiments. No intermediates were detected. Workups gave the air-stable thiolate complexes (η^5-C_5H_5)Re(NO)(PPh_3)(SCHR′R″) (**5a**−**d**) in 95−90% yields as 93:7, 98:2, 93:7, and 87:13 mixtures of Re,C configurational diastereomers.[12] These transformations were presumed to involve the intermediate ylides **6** (Scheme 3), which have sulfur stereocenters, and subsequent [2,3] sigmatropic rearrangements. The transfer of chirality to the new carbon stereocenters is strikingly efficient and analyzed further below. Identical diastereomer ratios were obtained from crude samples and *in situ* analyses of NMR tube reactions.

Analogous reactions of the nonracemic sulfide complexes (*S*)-**4a**−**c**$^+BF_4^-$ and *t*-BuOK gave the thiolates **5a**−**c** in 85−79%

(4) Cagle, P. C.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1994**, *116*, 3655.

(5) (a) Agbossou, F.; O'Connor, E. J.; Garner, C. M.; Quirós Méndez, N.; Fernández, J. M.; Patton, A. T.; Ramsden, J. A.; Gladysz, J. A. *Inorg. Synth.* **1992**, *29*, 211. (b) Improved PPh_3 substitution step: Zhou, Y.; Dewey, M. A.; Gladysz, J. A. *Organometallics* **1993**, *12*, 3918.

(6) Merrifield, J. H.; Fernández, J. M.; Buhro, W. E.; Gladysz, J. A. *Inorg. Chem.* **1984**, *23*, 4022.

(7) Kowalczyk, J. J.; Agbossou, S. K.; Gladysz, J. A. *J. Organomet. Chem.* **1990**, *397*, 333.

(8) Quirós Méndez, N.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1991**, *10*, 2199.

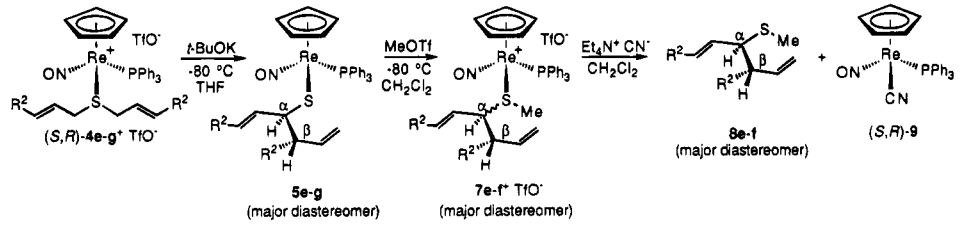
(9) The configuration at rhenium is specified first (and according to conventions described previously),[7] followed by those of any *SCC* (C_α) and *SCC* (C_β) stereocenters. In some schemes, racemates are depicted with specific configurations. These always correspond to the first enantiomer in the compound caption (e.g., *SR* enantiomer for *SR,RS* complex).

(10) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982; Chapters 6 and 7. The calculation utilized eq 7.4b, a T_C of 199−202 K, and a $\delta\nu$ of 103.8 Hz (CD_2Cl_2, −95 °C, CH_3 ^{13}C resonances).

(11) Anderson, K. K. In *The Chemistry of the Sulphonium Group*; Stirling, C. J. M., Patai, S., Eds.; Wiley: New York, 1981; Chapter 10.

(12) Diastereomer ratios were determined by integration of the following NMR signals: **5a**−**f**, **7a,b,e,f**$^+$TfO$^-$, and **10a,b**$^+$I$^-$, ^{31}P; **5g**, =CH_2 and *CH*Ph ^{13}C; **5a**-Me_5, average of five ^{13}C resonances; **7c**$^+$TfO$^-$, η^5-C_5H_5 ^{13}C; **8e**, SCH_3 ^{1}H; **8f**, average of SCH and CHCC*H*$_3$ ^{1}H and SCH, four =C, and two C(*C*H_3)$_3$ ^{13}C. Except for **5a**-Me_5, **5e**, **7e**$^+$TfO$^-$, **8e** and (*SS*)-**10a,b**$^+$I$^-$, all ratios were obtained from at least two independently prepared samples. With **5g**, ^{31}P and ^{1}H NMR suggested slightly different ratios than ^{13}C NMR (69:14:11:6 vs 77:13:10 or 72:15:14).

Scheme 4. Reaction Sequences Starting with Di(allyl) Sulfide Complexes That Have Unsymmetrically Substituted Allyl Termini[9]



Reactant	R^2	Yield, 5	Diastereomer Ratio	Yield, 7+ TfO⁻	Diastereomer Ratio[c]	Yield, 8	Diastereomer Ratio	Yield, 9
4e+ TfO⁻	CH_3	87%	52[a]:45:2:1	85%	50[a]:47.5:1.5:1	79%	52[d]:48	89%
4f+ TfO⁻	$C(CH_3)_3$	87%	88[b]:11:1:<0.5	92%	94[b]:6:<0.5:<0.5	54%	94[e]:6	84%
4g+ TfO⁻	Ph	89%	69[b]:14:11:6	--	--	--	--	--

[a] *SRS,RSR.* [b] *SRR,RSS.* [c] diastereomer ratios are slightly altered by workup. [d] *RS,SR* [e] *RR,SS.*

Table 1. Summary of Crystallographic Data[a]

complex	(*S*)-**4a**$^+SbF_6^-$	(*SS*)-**5a**	(*SRR,RSS*)-**5f**	(*SR,RS*)-**5a**-Me_5
molecular formula	$C_{29}H_{30}F_6NOPReSSb$	$C_{29}H_{29}NOPReS$	$C_{37}H_{45}NOPReS\cdot CDCl_3$	$C_{34}H_{39}NOPReS$
molecular weight	893.547	656.799	889.401	726.934
crystal system	triclinic	monoclinic	triclinic	monoclinic
space group	*P1* (no. 1)	$P2_1$ (no. 4)	$P\bar{1}$ (no. 2)	C_C (no. 9)
a, Å	9.800(2)	9.881(2)	9.578(3)	8.780(2)
b, Å	10.517(2)	12.483(3)	14.019(5)	17.379(4)
c, Å	16.152(3)	10.877(2)	15.999(4)	20.801(3)
α, deg	93.20(2)		93.22(3)	
β, deg	107.16(2)	100.23(2)	97.83(3)	92.49(2)
γ, deg	81.57(2)		107.63(3)	
V, Å^3	1573.31	1320.33	2017.50	2472.60
Z	2	2	2	4
d_{calc}, g/cm^3	1.886	1.652	1.464	1.523
d_{obs}, g/cm^3	1.86 ($CHCl_3/CH_2I_2$)	1.65 ($CHCl_3/CH_2I_2$)	1.47 (Et_2O/CH_2I_2)	1.53 (Et_2O/CH_2I_2)
crystal dimensions, mm	0.35 × 0.30 × 0.12	0.43 × 0.41 × 0.34	0.32 × 0.28 × 0.13	0.40 × 0.30 × 0.25
reflcns measd	5909	4214	6711	3106
range/indices (*h,k,l*)	0 to 11, −11 to 12, −19 to 18	0 to 13, 0 to 17, −15 to +15	0 to 10, −15 to 14, −17 to 15	0 to 10, 0 to 20, −24 to 24
scan width, deg			0.80 + 0.34 tanθ	0.80 + 0.34 tanθ
2θ limit, deg	4.0−50.0	4.0−60.0	4.0−48.0	4.0−50.0
total unique data	5530	4009	6282	2799
obsd data, $I > 3\sigma(I)$	5295	3607	5233	2565
abs coeff, cm^{-1}	49.32	48.21	33.69	40.22
min transmission, %	69.04	77.25	69.11	85.81
max transmission, %	99.81	99.99	99.96	99.90
no. of variables	736	304	419	350
goodness of fit	1.31	1.70	2.21	1.70
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.027	0.030	0.055	0.036
$R_w = \sum\|\|F_o\| - \|F_c\|\|w^{1/2}/\sum\|F_o\|w^{1/2}$.	0.037	0.037	0.075	0.050
Δ/σ (max)	0.012	0.001	0.016	0.007
$\Delta\rho$ (max), e/Å^3	0.939	1.125[b]	1.687[c]	0.704

[a] Common to all structures: diffractometer, CAD-4; radiation, λ(Mo Kα) 0.71073 Å; data collection method, θ−2θ; scan speed (deg/min), variable; standard reflections check, 1 X-ray hour. [b] Ca. 1.043 Å from Re. [c] Ca. 1.033 Å from Re.

yields as 93:7, >99.5:<0.5, and 97:3 mixtures of diastereomers. Before workup, **5b** was a 99.3:0.7 mixture. Thus, (*S*)-**4b,c**$^+$-BF_4^- give slightly higher diastereoselectivities than the corresponding racemic triflate salts. Product configurations in Scheme 3 were assigned from a crystal structure and other data below.

Complexes **4a**−**c**$^+X^-$ have symmetrically substituted allyl termini. In contrast, **4e**−**g**$^+$TfO$^-$ have unsymmetrically substituted termini (hydrogen vs methyl, *tert*-butyl, or phenyl). As shown in Scheme 4, the resulting thiolates **5e**−**g** will therefore contain a *second* carbon stereocenter (SC*C* or C_β).[13] Regardless of diastereoselectivity, the configuration of this stereocenter provides insight regarding the mechanism of chirality transfer, as elaborated in the discussion section.

Accordingly, **4e**−**g**$^+$TfO$^-$ and *t*-BuOK gave the thiolates **5e**−**g** in 89−87% yields. The *tert*-butyl substituted thiolate **5f** was a 88:11:1[14]:<0.5 mixture of Re,C,C diastereomers. The configuration of the major isomer (*SRR,RSS*)[9] was established crystallographically as described below. The next most abundant isomer was presumed to be epimeric at the SC*C* stereocenter (*SRS,RSR*). The phenyl substituted thiolate **5g** was 69:14:11:6 mixture of diastereomers.[12] The configuration of the major isomer was assumed to be analogous to that of **5f** (*SRR,RSS*), but those of the other isomers could not be assigned from the available data. The methyl substituted thiolate **5e** was a 52:45:2:1[14] mixture of diastereomers. The configurations of the two major isomers were presumed to be analogous to those of **5f** (*SRS,RSR* and *SRR,RSS*). This gives a Re,S*C* diastereomer ratio (97:3) similar to those in Scheme 3, as would be intuitively expected.

3. Reactant Conformations and Product Configurations. In order to help clarify the basis for the high diastereoselec-

(13) Any *cis* C=C or [1,3] allyl shift isomers of **4e**−**g**$^+$TfO$^-$ could compromise product analysis. Within NMR detection limits, samples were isomerically pure.

(14) With species formed in ≤2% yields, only partial sets of NMR resonances could be assigned. Therefore, it is possible that these represent constitutional isomers, or other byproducts, as opposed to diastereomers.

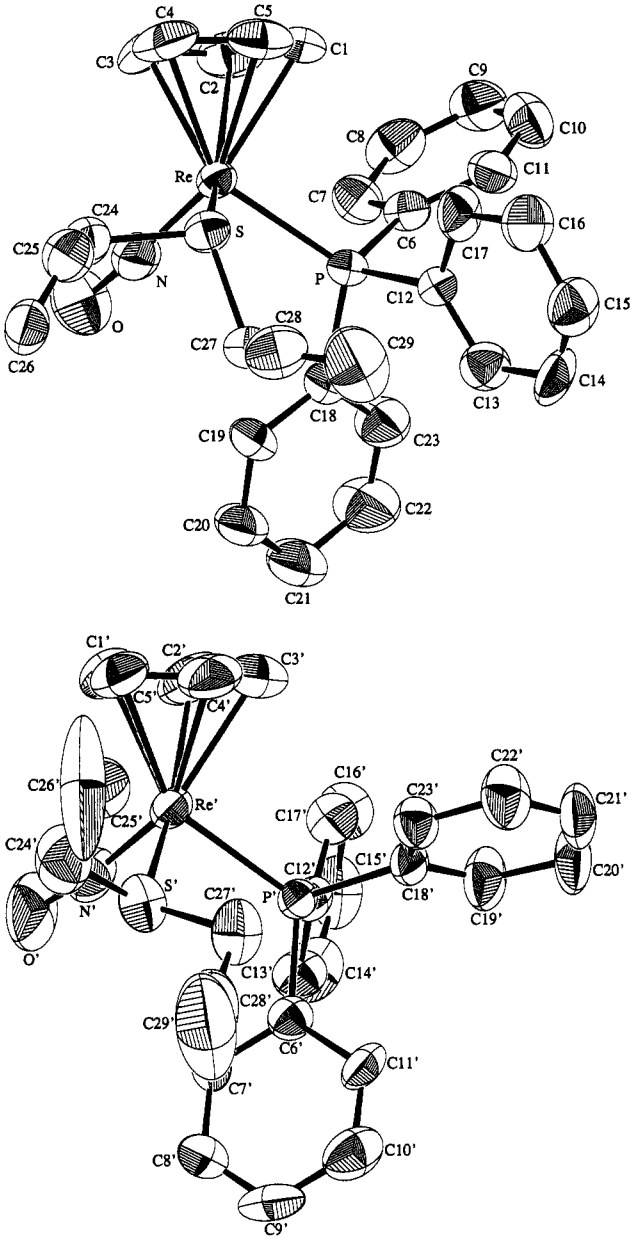


Figure 1. Structures of the two crystallographically independent cations of the di(allyl) sulfide complex (*S*)-**4a**$^+$$SbF_6^-$. Ellipsoids are shown at the 50% probability level, except for C26′ which is depicted at the 25% probability level.

tivities in Scheme 3, we sought to probe the conformations of the sulfide ligands in **4**$^+$$X^-$. However, the rapid exchange of SR_2 groups complicates NMR approaches. Thus, crystal structures were attempted. Suitable crystals of the nonracemic complex (*S*)-**4a**$^+$$BF_4^-$ could not be obtained. However, the corresponding hexafluoroantimonate salt (*S*)-**4a**$^+$$SbF_6^-$, which was prepared by metathesis, readily crystallized. The structure was determined as outlined in Table 1. Refinement, described in the Experimental Section, revealed two independent cations in the unit cell, as shown in Figure 1. Key bond lengths, bond angles, and torsion angles for all crystal structures are given in Table 2.

The structures in Figure 1 verify the rhenium configuration (*S*), which corresponds to overall retention from methyl complex (*S*)-**1** (Scheme 2). Although the configuration of the intermediate chlorobenzene complex **3**$^+$ BF_4^- has not been rigorously proven, (*S*)-**1** is converted to a related dichloromethane complex and then other Lewis base adducts with retention at each step.[15] The two cations in Figure 1 differ primarily in the Re−S conformation, as illustrated in Figure 2 and quantified by the differences in P−Re−S−LP (lone pair) or N−Re−S−LP torsion angles (Table 2; 160−150°). The fortuitous presence of both cations allows a better appreciation of the ensemble of ligand conformations that may be populated in solution.

The nonracemic thiolate complex obtained from (*S*)-**4a**$^+$$BF_4^-$, **5a**, was crystallized. NMR spectra of the macroscopic sample showed that only the major diastereomer was present. The structure was similarly determined, and is depicted in Figures 2 and 3 (top). This verifies the relative and absolute Re,C configurations given above (*SS*) and establishes retention at rhenium from (*S*)-**4a**$^+$$BF_4^-$. Analogous configurations were assigned to the major diastereomers of **5b,c** (*SS,RR* or *SS*) and **5d** (*SR,RS*). Also, the cyclopentadienyl ^{1}H NMR signals of the major diastereomers were always upfield from those of the minor diastereomers. However, other NMR signals did not correlate with configuration.

Finally, the crystal structure of the major diastereomer of the racemic, *tert*-butyl substituted thiolate **5f** was determined. Views are given in Figures 2 and 3 (bottom). This verifies the relative Re,C,C configurations given above (*SRR,RSS*). Furthermore, the S*C* configuration matches those assigned in Scheme 3.

4. Chiral Organic Sulfides. Attention was turned to detaching the thiolate ligands from **5**. The sulfur atoms of thiolate ligands are commonly more nucleophilic than those of organic sulfides and are readily attacked by electrophiles.[16] Thus, as shown in Schemes 4 and 5, **5a−c,e,f** and MeOTf (1.0 equiv) were combined in CH_2Cl_2 at −80 °C. The cationic methyl sulfide complexes [(η^5-C_5H_5)Re(NO)(PPh_3)(S(Me)CHR′R″)]$^+$ TfO^- (**7a−c,e,f**$^+$$TfO^-$) were isolated in 92−85% yields and characterized by NMR. These sulfur-based transformations were presumed to proceed with retention at rhenium. Subsequent reactions with $Et_4N^+CN^-$ (1.5 equiv) gave the free methyl sulfides MeSCHR′R″ (**8a−c,e,f**) in 79−54% yields after distillation. The known cyanide complex (η^5-C_5H_5)Re(NO)(PPh_3)(CN) (**9**)[17] was obtained in 89−84% yields. As detailed earlier, **9** and (*S*)-**9** are easily recycled to the methyl complexes **1** and (*S*)-**1**.[18] Additional data are summarized in Schemes 4 and 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 handling losses during solvent removal or distillation. In an attempt to reduce this problem, **5a,b** were treated with $PhCH_2I$, which transfers a heavier alkyl group (Scheme 5). The benzyl sulfide complexes [(η^5-C_5H_5)Re(NO)(PPh_3)(S(CH_2Ph)CHR′R″)]$^+$$I^-$ (**10a,b**$^+$$I^-$) were isolated in 97−79% yields. Reactions with $Et_4N^+CN^-$ and silica gel workups gave the free benzyl sulfides $PhCH_2$SCHR′R″ (**11a,b**) in 85−84% yields. The sulfides **8a,c** have been reported previously.[2b,19,20] The others are new compounds and were characterized by NMR and microanalysis or high resolution mass spectrometry.

Reactions were repeated with representative nonracemic thiolate complexes. As summarized in Scheme 5, (*SS*)-**5a−c** were alkylated to give (*SS*)-**7a−c**$^+$$TfO^-$ and (*SS*)-**10a,b**$^+$$I^-$ (95−

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(18) Richter-Addo, G. B.; Knight, D. A.; Dewey, M. A.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 11863.

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(20) Ducep, J. B. Fr. Patent 2 098 601, 1972.

Table 2. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) in (*S*)-**4a**$^+$$SbF_6^-$, (*SS*)-**5a**, (*SRR,RSS*)-**5f**, and (*SR,RS*)-**5a**-Me_5

		Complex (*S*)-**4a**$^+$$SbF_6^-$	
Re–P	2.396(2)	Re′–P′	2.403(2)
Re–S	2.372(2)	Re′–S′	2.404(3)
Re–N	1.771(9)	Re′–N′	1.760(9)
N–O	1.15(1)	N′–O′	1.17(1)
Re–C1	2.338(8)	Re′–C1′	2.25(1)
Re–C2	2.26(1)	Re′–C2′	2.26(1)
Re–C3	2.245(9)	Re′–C3′	2.32(1)
Re–C4	2.255(9)	Re′–C4′	2.31(1)
Re–C5	2.28(1)	Re′–C5′	2.29(1)
S–C24	1.81(1)	S′–C24′	1.78(1)
C24–C25	1.45(2)	C24′–C25′	1.48(2)
C25–C26	1.30(2)	C25′–C26′	1.35(4)
S–C27	1.84(1)	S′–C27′	1.81(1)
C27–C28	1.48(1)	C27′–C28′	1.46(2)
C28–C29	1.26(2)	C28′–C29′	1.08(3)[a]
P–Re–N	94.4(3)	P′–Re′–N′	93.3(3)
S–Re–P	98.00(7)	S′–Re′–P′	92.67(9)
S–Re–N	98.4(3)	S′–Re′–N′	87.3(4)
Re–N–O	176.0(8)	Re′–N′–O′	172.2(9)
C1–C2–C3	108(1)	C1′–C2′–C3′	107(1)
C3–C4–C5	107(1)	C3′–C4′–C5′	108(1)
C2–C1–C5	106(1)	C2′–C1′–C5′	110(1)
C2–C3–C4	106(1)	C2′–C3′–C4′	108(1)
C4–C5–C1	113(1)	C4′–C5′–C1′	107(1)
Re–S–C24	106.6(3)	Re′–S′–C24′	115.6(5)
Re–S–C27	119.5(3)	Re′–S′–C27′	118.9(4)
C24–S–C27	101.3(4)	C24′–S′–C27′	100.7(7)
S–C24–C25	113.3(8)	S′–C24′–C25′	115(1)
S–C27–C28	110.7(8)	S′–C27′–C28′	108(1)
C24–C25–C26	125(1)	C24′–C25′–C26′	122(3)
C27–C28–C29	126(1)	C27′–C28′–C29′	135(3)
P–Re–S–C24	−142.5(4)	P′–Re′–S′–C24′	169.3(6)
P–Re–S–C27	−28.7(4)	P′–Re′–S′–C27′	49.4(5)
P–Re–S–LP	90.2(1)	P′–Re′–S′–LP′	−69.2(1)
N–Re–S–C24	−46.8(4)	N′–Re′–S′–C24′	−97.5(6)
N–Re–S–C27	67.0(4)	N′–Re′–S′–C27′	142.6(5)
N–Re–S–LP	−174.1(3)	N′–Re′–S′–LP′	24.0(3)
Re–S–C24–C25	−168.5(7)	Re′–S′–C24′–C25′	−78(1)
Re–S–C27–C28	154.0(6)	Re′–S′–C27′–C28′	−162.0(8)
S–C24–C25–C26	−119(1)	S′–C24′–C25′–C26′	−136(2)
S–C27–C28–C29	−113(1)	S′–C27′–C28′–C29′	126(2)
C24–S–C27–C28	−89.4(8)	C24′–S′–C27′–C28′	71(1)
C27–S–C24–C25	65.8(8)	C27′–S′–C24′–C25′	52(1)
		Complex (*SS*)-**5a**	
Re–P	2.384(1)	Re–C5	2.335(6)
Re–S	2.348(1)	S–C24	1.849(6)
Re–N	1.741(5)	C24–C25	1.48(1)
N–O	1.209(6)	C24–C27	1.517(9)
Re–C1	2.294(6)	C25–C26	1.33(1)
Re–C2	2.247(5)	C27–C28	1.46(1)
Re–C3	2.274(6)	C28–C29	1.29(1)
Re–C4	2.337(6)		
P–Re–N	93.2(2)	S–Re–N	100.7(2)
S–Re–P	86.00(5)	Re–S–C24	109.5(2)
C1–C2–C3	104.8(7)	C2–C3–C4	111.1(7)
C3–C4–C5	106.5(6)	C4–C5–C1	110.5(6)
C2–C1–C5	107.0(6)	C24–C25–C26	125.9(8)
S–C24–C25	111.3(5)	C24–C27–C28	115.2(6)
S–C24–C27	108.3(4)	C27–C28–C29	127.3(8)
Re–N–O	174.3(5)		
P–Re–S–C24	−152.5(3)	Re–S–C24–C25	−82.8(6)
N–Re–S–C24	−60.0(3)	Re–S–C24–C27	152.8(5)
		Complex (*SRR,RSS*)-**5f**	
Re–P	2.343(3)	Re–C5	2.31(1)
Re–S	2.392(2)	S–C24	1.85(1)
Re–N	1.748(8)	C24–C25	1.48(2)
N–O	1.21(1)	C24–C27	1.57(1)
Re–C1	2.32(1)	C25–C26	1.27(2)
Re–C2	2.27(1)	C27–C28	1.50(2)
Re–C3	2.27(1)	C28–C29	1.28(2)
Re–C4	2.31(1)		

Table 2 (Continued)

P–Re–N	92.9(3)	S–Re–N	102.5(3)
S–Re–P	87.53(9)	Re–S–C24	106.9(3)
C1–C2–C3	106(1)	C2–C3–C4	109(1)
C2–C3–C4	109(1)	C3–C4–C5	109(1)
C2–C1–C5	105(1)	C24–C25–C26	130(1)
S–C24–C25	114.0(8)	C24–C27–C28	110(1)
S–C24–C27	114.4(7)	C27–C28–C29	125(1)
Re–N–O	173.5(8)		
P–Re–S–C24	−179.1(3)	Re–S–C24–C25	−105.1(7)
N–Re–S–C24	−86.7(4)	Re–S–C24–C27	−128.1(6)
	Complex (*SR,RS*)-**5a**-Me_5		
Re–P	2.352(3)	Re–C5	2.50(2)
Re–S	2.394(3)	S–C24	1.83(2)
Re–N	1.68(1)	C24–C25	1.47(2)
N–O	1.18(2)	C24–C27	1.52(2)
Re–C1	2.44(2)	C25–C26	1.23(4)
Re–C2	2.34(1)	C27–C28	1.48(3)
Re–C3	2.29(1)	C28–C29	1.17(3)[a]
Re–C4	2.38(1)		
P–Re–N	94.6(5)	S–Re–N	104.8(4)
S–Re–P	87.4(2)	Re–S–C24	108.5(6)
C1–C2–C3	105(1)	C2–C3–C4	108(1)
C3–C4–C5	110(1)	C3–C4–C5	110(1)
C2–C1–C5	111(2)	C24–C25–C26	129(2)
S–C24–C25	109(1)	C24–C27–C28	115(2)
S–C24–C27	109(1)	C27–C28–C29	135(2)
Re–N–O	170(1)		
P–Re–S–C24	−150.7(5)	Re–S–C24–C25	69.5(1.1)
N–Re–S–C24	−56.7(6)	Re–S–C24–C27	−165.0(1.0)

[a] These shortened values likely reflect some disorder.

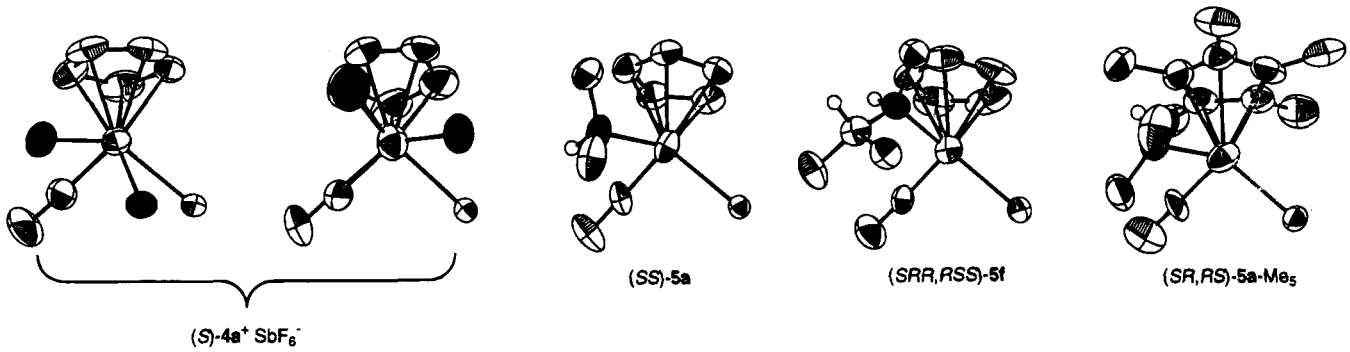


Figure 2. Rhenium–sulfur ligand conformations in crystallographically characterized compounds: Newman projections down the S–Re bonds.

79%). Reactions with $Et_4N^+CN^-$ gave the free sulfides (*S*)-**8a–c** (67–58%) and (*S*)-**11a,b** (82–77%). Enantiomeric purities were assayed with the chiral NMR shift reagent combination Ag(fod)/Eu(hfc)$_3$ (1:1:1)[21] 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 (Eu(hfc)$_3$ analysis).[17b,18] 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.[18]

5. Mechanistic and Optimization Experiments. In principle, either of the two steps in Scheme 3 can be rate determining. We sought to assay the reversibility of the deprotonation of **4**$^+X^-$ to ylide **6**. Thus, **4a**$^+$TfO$^-$ was dissolved in THF containing the *deuterated* alcohol *t*-BuOD (16 equiv) and treated with a *deficiency* of *t*-BuOK (0.5 equiv). Any return of **6a** to **4a**$^+$TfO$^-$ would then be accompanied by deuterium incorporation. The product **5a** and unreacted **4a**$^+$ TfO$^-$ were isolated and analyzed by mass spectrometry, together with natural abundance deuterium samples. A computer fit of the data showed **5a** and **4a**$^+$TfO$^-$ to be ca. 2% and 1% deuterated, respectively, above natural abundance levels. An analogous experiment with **4c**$^+$TfO$^-$ gave **5c** and **4c**$^+$TfO$^-$ that were ca. 1% and 7% deuterated. From these low label levels, the deprotonation of **4**$^+X^-$ to **6** cannot be a reversible, pre-equilibrium step.

Next, the doubly labeled sulfide complex [(η^5-C_5H_5)Re(NO)(PPh$_3$-d_{15})(S(CD_2CH=$C(CH_3)_2$)$_2$)]$^+$TfO$^-$ (**4c**$^+$-d_{19}TfO$^-$) was prepared. As shown in Scheme 6, a mixture of **4c**$^+$TfO$^-$ and **4c**$^+$-d_{19}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 value 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. Surprisingly, isotope effects for deprotonations of allyl sulfonium salts do not appear to have been reported earlier. The mass spectrum also showed the absence of crossover products such as **5c**-d_{15}. Hence, the PPh$_3$ and sulfur donor ligands do not dissociate at any stage of the reaction coordinate.

Enantioselectivities and diastereoselectivities are often sensi-

(21) Offermann, W.; Mannschreck, A. *Tetrahedron Lett.* **1981**, *22*, 3227. In all cases, the $=CH_2$ ^{13}C NMR signals were integrated.

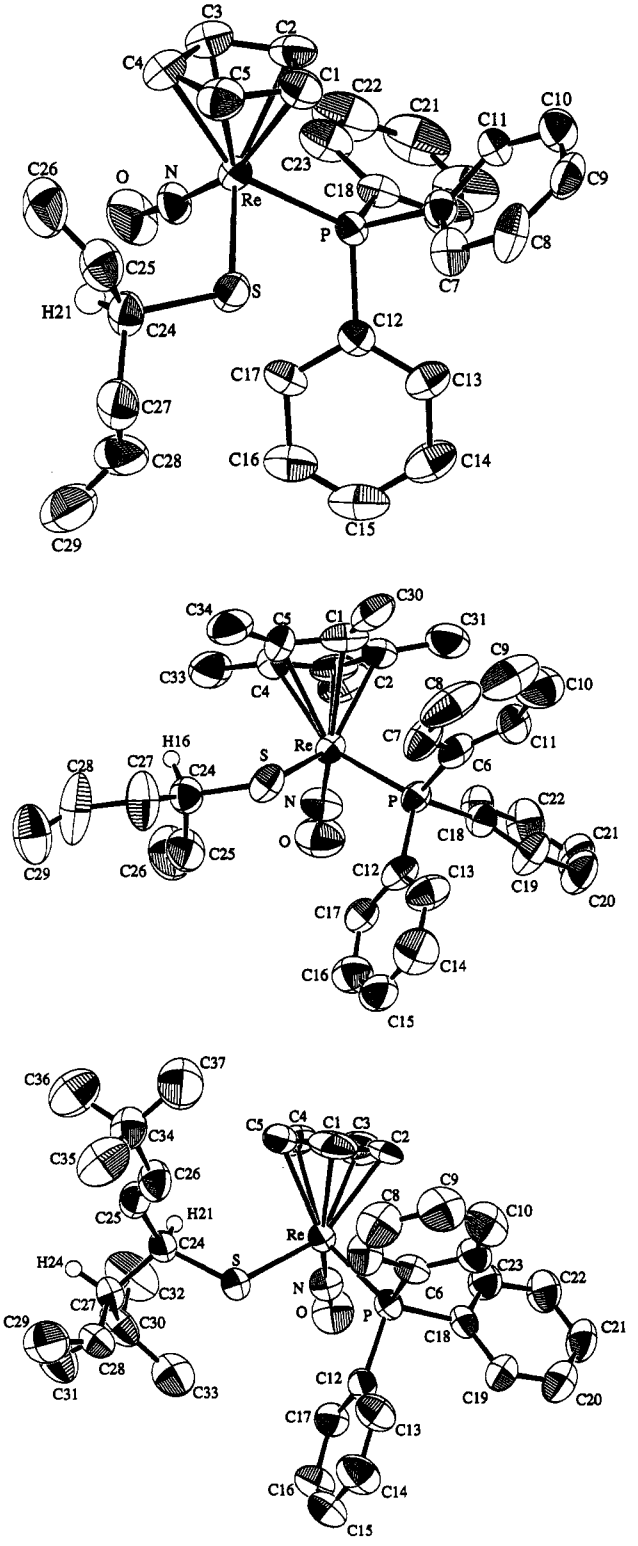


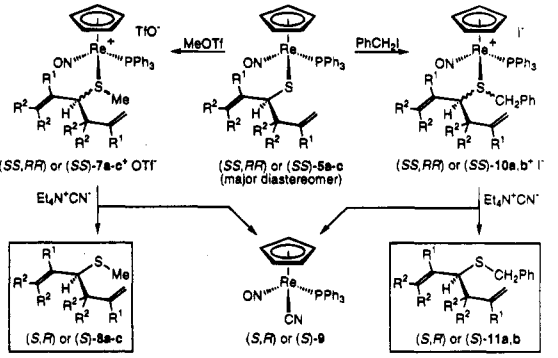
Figure 3. Crystal structures of thiolate complexes (*SS*)-**5a** (top), (*SR,RS*)-**5a**-Me_5 (middle), and (*SRR,RSS*)-**5f** (bottom).

tive functions of reaction conditions.[22] Thus, we attempted to maximize the **5a** diastereomer ratio by varying the conditions in Scheme 3 (0.001 M **4a**$^+$$TfO^-$ in THF, 1.0 M *t*-BuOK in THF, −80 °C). First, the diastereomer ratio (93:7) was unaffected when the concentration of **4a**$^+$$TfO^-$ was increased 50-fold or reactions were conducted at −105 °C. However, the ratio decreased when reactions were run at −40 °C (80:20) or room temperature (74:26).

As summarized in Table 3, solvent significantly influenced diastereomer ratios. Except in the case of toluene, conversions

(22) Keck, G. E.; Krishnamurthy, D. *J. Am. Chem. Soc.* **1995**, *117*, 2363.

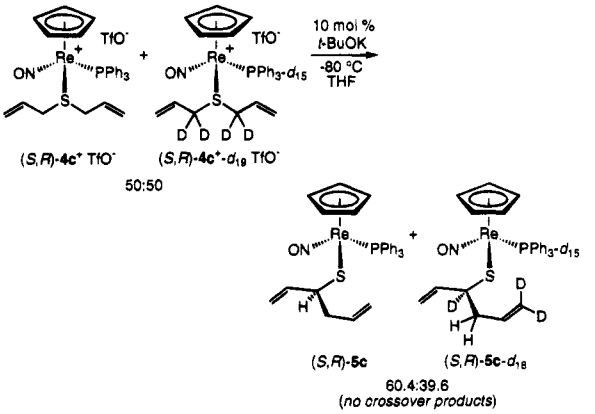
Scheme 5. Conversion of Thiolate Complexes to Free Organic Sulfides[9]



Reactant	R^1	R^2	Diastereomer Ratio[a]	Yield, Alkylation Product	Diastereomer Ratio[a]	Yield, Sulfide	Enantiomer Ratio[b]	Yield, 9[c]
5a	H	H	92:8	90%, **7a**$^+$ TfO^-	92:8	60%, **8a**	--	87%
5b	CH_3	H	98:2	89%, **7b**$^+$ TfO^-	98:2	65%, **8b**	--	86%
5c	H	CH_3	93:7	89%, **7c**$^+$ TfO^-	93:7	60%, **8c**	--	89%
5a	H	H	92:8	89%, **7a**$^+$ TfO^-	92:8	67%, **8a**	92:8	93%
5b	CH_3	H	>99.5:<0.5	95%, **7b**$^+$ TfO^-	>99.5:<0.5	58%, **8b**	>99:<1	92%
5c	H	CH_3	97:3	93%, **7c**$^+$ TfO^-	97:3	65%, **8c**	96:4	78%
5a	H	H	93:7	97%, **10a**$^+$ I^-	93:7	84%, **11a**	--	84%
5b	CH_3	H	98:2	84%, **10b**$^+$ I^-	98:2	85%, **11b**	--	91%
5a	H	H	93:7	82%, **10a**$^+$ I^-	93:7	77%, **11a**	93:7	93%
5b	CH_3	H	>99.5:<0.5	79%, **10b**$^+$ I^-	>99.5:<0.5	82%, **11b**	>99:<1	91%

[a] *SS,RR/SR,RS* or *SS/SR*. [b] *S/R*. [c] non-racemic samples were >99:<1 *S/R*.

Scheme 6. Estimation of Kinetic Deuterium Isotope Effect[9]



to **5a** were quantitative by NMR. However, only diglyme gave an increased diastereomer ratio (95.5:4.5). This reaction was conducted at a slightly higher temperature due to the solvent freezing point. Conversely, CH_2Cl_2 gave the lowest diastereomer ratio (71:29). A variety of other bases could also be employed (Table 3). Alkoxides gave the best results (93:7 to 87:13). Stronger R_2N^- or R^- bases gave much lower diastereomer ratios, sometimes with reversed selectivities (66:34 to 40:60).

6. Pentamethylcyclopentadienyl Complexes. We thought that diastereoselectivities might increase with bulkier, pentamethylcyclopentadienyl analogs of **4**$^+$$X^-$. Accordingly, the parent di(allyl) sulfide complex [(η^5-C_5Me_5)Re(NO)(PPh_3)(S(CH_2-CH=CH_2)$_2$)]$^+$$BF_4^-$ (**4a**-$Me_5^+BF_4^-$) was prepared from the corresponding racemic chlorobenzene complex (**3**$^+$-$Me_5^+BF_4^-$; see Scheme 2).[23] As shown in Scheme 7, reactions with *t*-BuOK gave the thiolate (η^5-C_5Me_5)Re(NO)(PPh_3)(SCH(CH=CH_2)CH_2-CH=CH_2) (**5a**-Me_5) as 93:7 (CH_2Cl_2, 93%) or 90:10 (THF, 91%) mixtures of diastereomers.

Thus, the pentamethylcyclopentadienyl and cyclopentadienyl analogs **4a**-$Me_5^+BF_4^-$ and **4a**$^+$$BF_4^-$ gave similar diastereose-

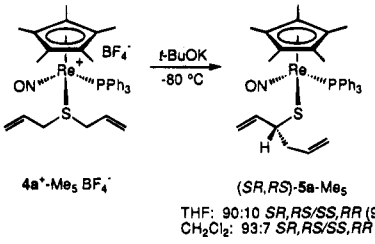
(23) Peng, T.-S.; Winter, C. H.; Gladysz, J. A. *Inorg. Chem.* **1994**, *33*, 2534.

Table 3. Effects of Solvent and Base on the Conversion of **4a**$^+$TfO$^-$ to **5a**[a]

solvent[b]	base/solvent	*SS,RR/SR,RS*
THF	*t*-BuOK/THF	93:07
acetone	*t*-BuOK/THF	91:09
CH_2Cl_2	*t*-BuOK/THF	71:29
EtOAc[c]	*t*-BuOK/THF	93:07
toluene[d]	*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	$(Me_3Si)_2$NLi/THF	40:60
THF	$(Me_3Si)_2$NK/THF	66:34
THF	$(Me_3Si)_2$NK/toluene	43:57
THF	$(i\text{-}Pr)_2$NLi·THF/cyclohexane	47:53
THF	*n*-BuLi/hexane	51:49

[a] Reactions were conducted in NMR tubes and *SS,RR/SR,RS* ratios were assayed by ^{31}P NMR. [b] Ca. 0.001 M, −80 °C. [c] **4a**$^+$TfO$^-$ is slightly soluble in EtOAc. [d] **4a**$^+$TfO$^-$ is insoluble in toluene and some byproducts form (ca. 6%). [e] Conducted at −66 °C.

Scheme 7. Reaction of Pentamethylcyclopentadienyl Di(allyl) Sulfide Complex[9]



lectivities. However, we gradually became skeptical that the configurations of the major diastereomers were identical. Accordingly, **5a**-Me_5 was crystallized to diastereomeric purity. X-ray data were collected, and a ^{31}P NMR spectrum of the crystal employed verified that it was the major diastereomer. Views of the crystal structure are given in Figures 2 (right) and 3 (middle). These show that the *opposite* (*SR,RS*) diastereomer preferentially forms. The implications of this surprising result are discussed below.

Discussion

1. Scope and Merits of Methodology. Schemes 3−7 establish the following new or previously unexploited chemical phenomena: (1) sulfur ylides can be generated from cationic transition metal complexes of di(allyl) or di(propargyl) sulfides and bases; (2) these undergo rapid [2,3] sigmatropic rearrangements to give neutral thiolate complexes; (3) with chiral metal fragments, the configurations of the resulting S*C* carbon stereocenters can be efficiently controlled; and (4) nonracemic chiral metal fragments can be used to prepare chiral organosulfur compounds of high enantiomeric purities.

As precedent for (1), sulfur donor ligands have been previously found to undergo a variety of types of deprotonation reactions.[24−29] Some of the more relevant are summarized in

(24) Review: Linford, L.; Raubenheimer, H. G. *Adv. Organomet. Chem.* **1991**, *32*, 1.

(25) Bennett, M. A.; Goh, L. Y.; Willis, A. C. *J. Chem. Soc., Chem. Commun.* **1992**, 1180, and references therein.

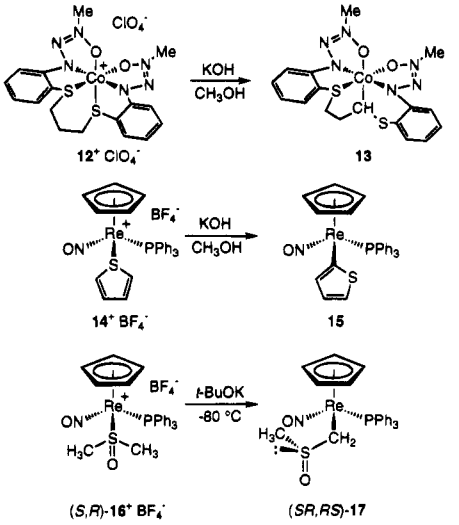
(26) Chakraborty, P.; Chandra, S. K.; Chakravorty, A. *Organometallics* **1993**, *12*, 4726, and references therein.

(27) Devery, M. P.; Dickson, R. S. *J. Chem. Soc., Chem. Commun.* **1994**, 1721.

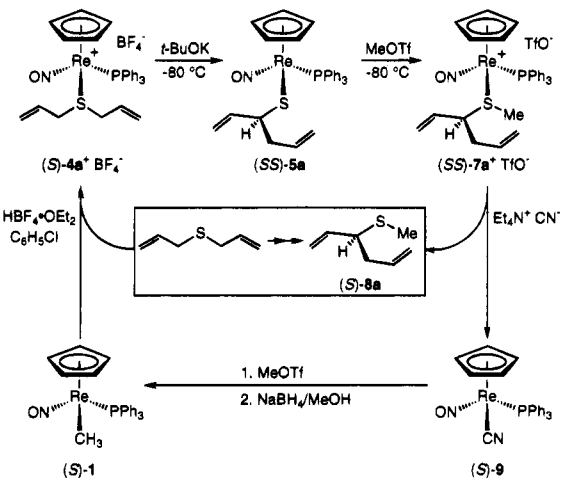
(28) (a) Robertson, M. J.; White, C. J.; Angelici, R. J. *J. Am. Chem. Soc.* **1994**, *116*, 5190. (b) White, C. J.; Angelici, R. J. *Organometallics* **1994**, *13*, 5132.

(29) Meyer, O.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1995**, *14*, 1844.

Scheme 8. Other Reactions of Sulfur Donor Ligands and Bases that Likely Involve Intermediate Ylides[9]



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



Scheme 8. As exemplified with **12**$^+$$ClO_4^-$ (top), cationic complexes of chelating sulfides can react with bases to give neutral metal−carbon bonded products.[26] Angelici has reported a conceptually similar reaction of a thiophene adduct of the rhenium Lewis acid **I**, **14**$^+$$BF_4^-$ (middle).[28] We have discovered a related process with the DMSO complex **16**$^+$$BF_4^-$ (bottom).[29] All of these transformations likely entail the initial formation of an ylide, followed by a [1,2] shift of the metal to the carbanionic center.[30]

The net organic transformation accomplished by the preceding chemistry is highlighted in the middle of Scheme 9, using di(allyl) sulfide for illustration. The starting material for this desymmetrization process, methyl complex **1**, can be prepared from commercially available $Re_2(CO)_{10}$ in four steps and 57% overall yield.[5] The enantiomers are easily resolved *in transitu* 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.

Importantly, each of the individual steps in Schemes 2−7 is spectroscopically quantitative and isolated yields have not been optimized. At present, (*S,R*)-**4a**$^+$$TfO^-$ and (*S*)-**4a**$^+$$BF_4^-$ can

(30) The ylide **6** (Scheme 3) could also potentially undergo a [1,2] shift of rhenium, but no evidence for the formation of alkyl complexes has been observed. Apparently, the migratory aptitude of the allyl group is much greater.

be converted to the free methyl sulfides (*S,R*)- and (*S*)-**8a** in 50−47% overall yields and the cyanide complexes (*S,R*)- and (*S*)-**9** in 72−65% overall yields. With the benzyl sulfides (*S,R*)- and (*S*)-**11a**, yields increase to 67−44%. 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.[18]

Preliminary studies show that it is possible to combine consecutive steps in Scheme 9, with improved overall yields. Also, it should be possible to use electrophiles other than alkylating agents to derivatize thiolates **5**. In this context, *S*-benzyl groups such as in **11a,b** are frequently used to protect thiols and can be easily removed.[31] Furthermore, complexes in which one or both of the allyl moieties in $\mathbf{4}^{+}X^{-}$ are replaced by benzyl groups give similar reactions.[32a] Importantly, analogous transformations can be effected with less expensive metals, such as iron and ruthenium.[32b] These data will be reported in the near future.

2. Mechanism of Diastereoselection. As diagrammed in Scheme 10, the dominant S***C*** configurations of thiolates **5** (Schemes 3 and 4) require that when the rhenium 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 (1) the rhenium−sulfur conformation, (2) the configuration of the sulfur stereocenter, and (3) 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**.

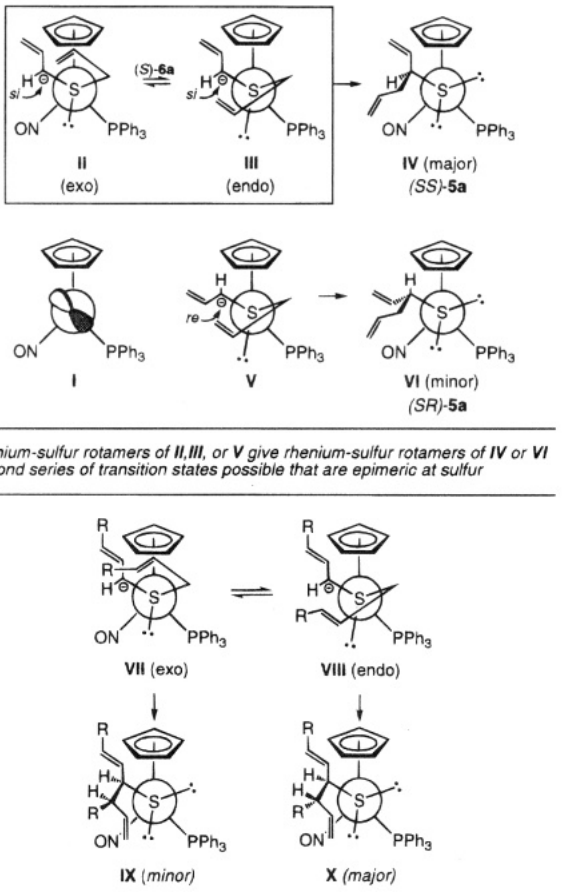
The rhenium−sulfur conformations in **II** and **III** correspond to those that would be the most stable in sulfide complexes $\mathbf{4}^{+}X^{-}$.[8] Adducts of the rhenium fragment **I** are formally octahedral, and numerous studies have established that the interstice between the large PPh_3 and small nitrosyl ligands is the most congested.[8,17b,33] Note that the idealized P−Re−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.[34]

Similarly, the interstice between the small nitrosyl and medium cyclopentadienyl ligands is the least congested.[8,33] Thus, ligands preferentially adopt conformations that direct their largest groups into this region. The rhenium−sulfur conformation depicted in thiolate **IV** should therefore be the most stable. As supporting evidence, the three thiolate complexes in Figures 2−3 crystallize accordingly, with N-Re-S-C torsion angles between −56.7(6)° and −86.7(4)°. 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 (1) rotating ca. 120° about the rhenium−sulfur bond or (2) inverting the 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 $\mathbf{4}^{+}X^{-}$, we suspect that the ylide **6** undergoes rapid sulfur inversion/

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



rotation on the time scale of rearrangement. Conformational processes involving the S***C*** substituents are also likely rapid. In this familiar Curtin−Hammett limit,[36] 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 $\mathbf{4}^{+}X^{-}$ is deprotonated. Also, the stereochemistry of the ylide carbanion (*si*/*re*) may at first be a function of which diastereotopic SCH_2 proton is abstracted. As shown in transition state **V** (Scheme 10), migration of an allyl group to the *re* face gives the minor thiolate diastereomer **VI**.

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. As analyzed elsewhere, the highly diastereoselective conversion of DMSO complex $\mathbf{16}^{+}BF_4^{-}$ (Scheme 8, bottom) to (*SR,RS*)-**17** suggests an analogous deprotonation stereochemistry.[29] Further, in the more stable of the rhenium−sulfur conformers in crystalline (*S*)-$\mathbf{4a}^{+}SbF_6^{-}$ (Figure 1, bottom), one SCH_2 proton is sterically more accessible. Abstraction would give **III** directly.[37]

The question remains as to what is *dis*favored about analogs of **II** or **III** that involve the *re* face of the ylide carbanion, such as **V**. Initially, we thought that **III** would be less stable than **V**

(31) Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 2nd ed.; Wiley: New York, 1991; pp 279−285.

(32) (a) Cagle, P. C.; Meyer, O.; Vichard, D.; Weickhardt, K.; Arif, A. M.; Gladysz, J. A. *Organometallics*, in press. (b) Bell, P. T.; Cagle, P. C.; Gladysz, J. A. Manuscript in preparation.

(33) (a) Crocco, G. L.; Lee, K. E.; Gladysz, J. A. *Organometallics* **1990**, *9*, 2819. (b) Davies, S. G.; Dordor-Hedgecock, I. M.; Sutton, K. H.; Whittaker, M. *J. Am. Chem. Soc.* **1987**, *109*, 5711. (c) Mackie, S. C.; Baird, M. C. *Organometallics* **1992**, *11*, 3712.

(34) Interestingly, half of the cations in crystalline (*S*)-$\mathbf{4a}^{+}SbF_6^{-}$ have an allyl group in this region (Figure 1, top; Figure 2, left). This constitutes the first time (out of numerous opportunities) that an adduct of **I** and a Lewis base with a hydrogen or lone pair on the ligating atom has crystallized *without* the hydrogen or lone pair in this position.[8,17b,33a,35]

(35) Zwick, B. D.; Dewey, M. A.; Knight, D. A.; Buhro, W. E.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1992**, *11*, 2673.

(36) Seeman, J. I. *Chem. Rev.* **1983**, *83*, 83.

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.[38,39] Regardless, the pentamethylcyclopentadienyl complex **4a**$^+$-$Me_5$$^+BF_4^-$ provides a probe of this model. In the corresponding transition state **III**-Me_5, the vinyl group should experience much greater steric repulsion, and attractive edge/face interactions are no longer possible. Accordingly, the diastereomer of thiolate **5a**-Me_5 that would be derived from **V**-Me_5 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.[40] Importantly, **4e**$^+$**−g**$^+$$TfO^-$, which have unsymmetrically substituted allyl termini, give different SC*C* diastereomers depending upon the *exo*/*endo* sense of the transition state. This is illustrated with **VII** and **VIII** in Scheme 10. The crystal structure of (*SRR*,*RSS*)-**5f** establishes that the latter is greatly favored with the *tert*-butyl substituted complex **4f**$^+$$TfO^-$. However, the methyl substituted complex **4e**$^+$$TfO^-$ shows little selectivity. Hence, we presume that **II** and **III** are usually close in energy.

3. Prospective. The preceding chemistry raises many attractive possibilities for new research directions. For example, oxygen and nitrogen ylides undergo similar [2,3] rearrangements.[1a] Thus, there would seem to be excellent prospects for effecting and analogous reactions with ether and amine ligands. Also, ylides can be generated by routes that do not involve base—such as carbene transfers from diazo compounds to sulfides, ethers, or amines in the presence of metal catalysts.[1a] These themes, and extensions to other metals and sulfide ligands as noted above,[32] will be the subject of future reports from this laboratory.

Experimental Section[41,42]

[(η^5-C_5H_5)Re(NO)(PPh_3)(S($CH_2CH{=}CH_2$)$_2$)]$^+X^-$ (4a$^+X^-$). A. A Schlenk flask was charged with (η^5-C_5H_5)Re(NO)(PPh_3)(OTf) (**2**;[6] 0.390 g, 0.563 mmol) and C_6H_5Cl (10 mL). Then S($CH_2CH{=}CH_2$)$_2$ (109 μL, 0.845 mmol) was added with stirring. After 48 h, volatiles were removed under oil pump vacuum. The residue was dissolved in acetone (5 mL). The solution was added dropwise to rapidly stirred ether (110 mL). The yellow-brown powder was collected by filtration and washed with ether (10 mL) and pentane (50 mL). After 15 min, a powder formed in the filtrate, which was collected and washed with pentane (20 mL). The combined crops were dried under oil pump vacuum to give **4a**$^+$$TfO^-$ (0.405 g, 0.485 mmol, 86%): mp 158 °C dec; IR 1702.[42] Calcd for $C_{30}H_{30}F_3NO_4PReS_2$: C, 44.66; H, 3.75. Found: C, 44.59; H, 3.70. **B.** A Schlenk flask was charged with (*S*)-(η^5-C_5H_5)Re(NO)(PPh_3)(CH_3) ((*S*)-**1**;[5] 0.627 g, 1.12 mmol, >99% *ee*) and C_6H_5Cl (20 mL) and cooled to −45 °C (CH_3CN/CO_2). Then HBF_4·OEt_2 (4.5 M in ether; 250 μL, 1.12 mmol) was added with stirring.[7] After 5 min, S($CH_2CH{=}CH_2$)$_2$ (210 μL, 1.68 mmol) was added. The cold bath was allowed to warm to room temperature. After 16 h, volatiles were removed under oil pump vacuum. The residue was dissolved in acetone (5 mL). The solution was added dropwise to rapidly stirred ether (110 mL). The yellow powder was collected by filtration, washed with ether (10 mL), and dried under oil pump vacuum to give (*S*)-**4a**$^+BF_4^-$ (0.668 g, 0.896 mmol, 80%): mp 157 °C dec (slight darkening, 85 °C): $[\alpha]_{589}^{29}$ 124° ± 3° (*c* 0.742 mg/mL, $CHCl_3$);[43,44a] IR 1711.[42] Calcd for $C_{29}H_{30}BF_4NOPReS$: C, 46.78; H, 4.06. Found: C, 46.61; H, 4.02. **C.** Acetone (50 mL), (*S*)-**4a**$^+BF_4^-$ (0.424 g, 0.569 mmol), and $NaSbF_6$ (1.47 g, 5.69 mmol) were combined with stirring. After 15 min, solvent was removed by rotary evaporation. The residue was extracted with CH_2Cl_2 (50 mL). The extract was filtered through a fine frit, and solvent was removed by rotary evaporation. The yellow-brown oil was dissolved in acetone (2 mL) and layered with ether (10 mL). After 3 days, yellow-brown plates were collected by filtration, washed with ether (10 mL) and pentane (10 mL), and dried under oil pump vacuum to give (*S*)-**4a**$^+SbF_6^-$: mp 135−136 °C; IR 1706.[42] Calcd for $C_{29}H_{30}F_6NOPReSSb$: C, 38.98; H, 3.38. Found: C, 38.88; H, 3.36.[44b]

NMR, 4a$^+$TfO$^-$ ($CDCl_3$/THF-d_8):[42] ^{1}H 7.54−7.22/7.56−7.31 (m, 3 Ph), 5.69/5.59 (s, C_5H_5), 5.54−5.41/5.56−5.48 (m, 2 CH=), 5.35−5.29/5.39−5.24 (m, 2 $=CH_2$), 3.50/3.67 (m, 2 SC*H*H′), 3.36/3.40 (m, 2 SCH*H*′); ^{13}C{^{1}H} 133.2/134.5 (d, J_{CP} = 11, *o*-Ph), 132.3/133.8 (d, J_{CP} = 56, *i*-Ph), 131.7/132.3 (d/s, J_{CP} = 2, *p*-Ph), 129.6/130.1 (d, J_{CP} = 11, *m*-Ph), 130.3/132.3 (s, CH=), 122.9/122.6 (s, $=CH_2$), 92.8/94.3 (s, C_5H_5), 46.6/47.8 (s, SCH_2); ^{31}P{^{1}H} 12.2/12.8 (s).

[(η^5-C_5H_5)Re(NO)(PPh_3)(S($CH_2C(CH_3){=}CH_2$)$_2$)]$^+X^-$ (4b$^+X^-$). A. Complex **2** (0.381 g, 0.550 mmol), C_6H_5Cl (10 mL), and S($CH_2C(CH_3){=}CH_2$)$_2$ (130 μL, 0.825 mmol) were combined in a procedure analogous to that for **4a**$^+$$TfO^-$. The residue was dissolved in acetone (5 mL). The solution was added dropwise to rapidly stirred ether (110 mL). Pentane (50 mL) was added, and the yellow-brown powder was collected by filtration, washed with ether (20 mL) and pentane (20 mL), and dried under oil pump vacuum to give **4b**$^+$$TfO^-$ (0.390 g, 0.468 mmol, 85%): mp 190−191 °C dec; IR 1704.[42] Calcd for $C_{32}H_{34}F_3NO_4PReS_2$: 46.03; H, 4.10. Found: C, 45.78; H, 4.07. **B.** Complex (*S*)-**1** (0.876 g, 1.27 mmol), C_6H_5Cl (20 mL), HBF_4·OEt_2 (8.0 M in ether; 158 μL, 1.27 mmol), and S($CH_2C(CH_3){=}CH_2$)$_2$ (300 μL, 1.90 mmol) were combined in a procedure analogous to that for (*S*)-**4a**$^+$$BF_4^-$. Volatiles were removed under oil pump vacuum (4 h). The residue was dissolved in acetone (5 mL). The solution was quickly added dropwise to rapidly stirred ether (110 mL). The yellow powder was collected by filtration and washed with pentane (10 mL). Solvent was removed from the filtrate by rotary evaporation. The residue was dissolved in acetone (5 mL). The solution was quickly added to rapidly stirred ether (75 mL). The powder was collected and washed with pentane (10 mL). The crops were combined and dried under oil pump vacuum to give (*S*)-**4b**$^+BF_4^-$ (0.739 g, 0.889 mmol, 70%): mp 113 °C dec (slight darkening, 97 °C); IR 1702;[42] $[\alpha]_{589}^{29}$ 154° ± 13° (*c* 0.872 mg/mL, $CHCl_3$).[43,44a] Calcd for $C_{31}H_{34}BF_4NOPReS$: C, 48.19; H, 4.44. Found: C, 48.18; H, 4.42.

NMR, 4b$^+$TfO$^-$ ($CDCl_3$):[42] ^{1}H 7.52−7.18 (m, 3 Ph), 5.67 (s, C_5H_5), 5.17 (s, 2 = C*H*H′), 5.07 (s, 2 $=$CH*H*′), 3.58 (d, J_{HH} = 13, 2 SC*H*H′), 3.31 (d, J_{HH} = 13, 2 SCH*H*′), 1.47 (s, 2 CH_3); ^{13}C{^{1}H} 133.2 (d, J_{CP} = 11, *o*-Ph), 132.3 (d, J_{CP} = 56, *i*-Ph), 131.7 (d, J_{CP} = 2, *p*-Ph), 129.3 (d, J_{CP} = 11, *m*-Ph), 137.3 (s, *C*(CH_3)=), 119.5 (s, $=CH_2$), 94.3 (s, C_5H_5), 52.6 (s, SCH_2), 20.4 (s, CH_3); ^{31}P{^{1}H} 12.3 (s).

[(η^5-C_5H_5)Re(NO)(PPh_3)(S($CH_2CH{=}C(CH_3)_2$)$_2$)]$^+X^-$ (4c$^+X^-$). A. Complex **2** (0.866 g, 1.25 mmol), C_6H_5Cl (20 mL), and S($CH_2CH{=}C(CH_3)_2$)$_2$ (0.358 g, 2.10 mmol) were combined in a procedure analogous to that for **4a**$^+$$TfO^-$. Volatiles were removed under oil pump vacuum (12 h). The residue was dissolved in acetone (5 mL) and filtered through a 4 cm silica gel plus on a frit, which was rinsed with 1:1 acetone/CH_2Cl_2 (v/v, 100 mL). Solvent was removed from the filtrate by rotary evaporation. The residue was dissolved in acetone (5 mL).

(37) One rationale for the lower diastereoselectivities with the stronger bases in Table 3 would be lower deprotonation selectivities. However, if as we propose the Curtin−Hammett limit applies, interactions between **6** and the various conjugate acids may be invoked. An obvious possibility would be hydrogen bonding, which has been observed with amine[17b] and phosphine[35] adducts of **I**.

(38) (a) Brunner, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 897; see sections 6−8. (b) Hunter, R.; Haueisen, R. H.; Irving, A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 566, and references therein. (c) Dance, I.; Scudder, M. *J. Chem. Soc., Chem. Commun.* **1995**, 1039.

(39) We have also considered the possibility that the rhenium−sulfur conformational minima are rotated slightly counterclockwise from those in **III** and **V**. For example, there is the potential for a repulsive interaction between the ylide carbanion and the d orbital HOMO of the rhenium fragment (see **I**, Scheme 10). However, extended Hückel calculations on model compounds give minima identical with those of the corresponding sulfides.

(40) Wu, Y. D.; Houk, K. N. *J. Org. Chem.* **1991**, *56*, 5657, and references therein.

(41) Most instrumental procedures, reagent purifications, and reactant syntheses are routine. Details are given in the supporting information.

(42) All ^{1}H, ^{13}C, and ^{31}P NMR data are in δ, ppm, and ppm, respectively. All *J* values are in Hz. All IR data are in cm^{-1} (KBr, ν_{NO}, vs).

(43) Dewey, M. A.; Gladysz, J. A. *Organometallics* **1993**, *12*, 2390.

(44) NMR spectra were identical with those of the racemic or nonracemic analog: (a) ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H}; (b) ^{1}H and ^{31}P{^{1}H}; (c) ^{1}H and ^{13}C{^{1}H}; and (d) ^{13}C{^{1}H} and ^{31}P{^{1}H}.

The solution was added dropwise to rapidly stirred ether (250 mL). The yellow powder was collected by filtration, washed with ether (10 mL) and pentane (50 mL), and dried under oil pump vacuum to give **4c**$^+$TfO$^-$ (0.891 g, 1.03 mmol, 83%): mp 143 °C dec; IR 1709.[42] Calcd for $C_{34}H_{38}F_3NO_4PReS_2$: C, 47.32; H, 4.44. Found: C, 47.39; H, 4.47. **B.** Complex (*S*)-**1** (2.55 g, 4.57 mmol), C_6H_5Cl (35 mL), and S(CH_2-CH=$C(CH_3)_2$)$_2$ (2.34 g, 13.7 mmol) were combined in a procedure analogous to that for (*S*)-**4a**$^+BF_4^-$. The solution was slowly warmed to room temperature over 48 h and filtered through a 3 cm silica gel plug on a frit. The plug was rinsed with CH_2Cl_2 (10 mL), ether (40 mL), and THF (200 mL). Solvent was removed from the THF rinse by rotary evaporation. The residue was dissolved in CH_2Cl_2 (30 mL). Solvent was removed under oil pump vacuum (24 h) to give (*S*)-**4c**$^+BF_4^-$ as a yellow powder (2.86 g, 3.57 mmol, 78%): mp 72−74 °C; IR 1702;[42] $[\alpha]_{589}^{25}$ 126° ± 1° (*c* 1.274 mg/mL, $CHCl_3$).[43,44a] Calcd for $C_{33}H_{38}BF_4NOPReS$: C, 49.50; H, 4.78. Found: C, 49.57; H, 4.83.

NMR, 4c$^+$**TfO**$^-$ ($CDCl_3$):[42] ^{1}H 7.53−7.22 (m, 3 Ph), 5.64 (s, C_5H_5), 4.98−4.97 (m, 2 CH=), 3.40−3.30 (m, 2 SCH_2), 1.70, 1.55 (2 s, 4 CH_3); ^{13}C{^{1}H} 133.3 (d, J_{CP} = 11, *o*-Ph), 132.7 (d, J_{CP} = 56, *i*-Ph), 131.6 (d, J_{CP} = 2, *p*-Ph), 129.3 (d, J_{CP} = 11, *m*-Ph), 141.0 (s, ***C***$(CH_3)_2$), 116.9 (s, CH=), 92.6 (s, C_5H_5), 42.5 (s, SCH_2), 25.9, 18.3 (2 s, 2 CH_3); ^{31}P{^{1}H} 12.1 (s).

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(S(CH_2C≡CCH_3)$_2$)]$^+$TfO$^-$ (4d$^+$TfO$^-$). Complex **2** (0.356 g, 0.515 mmol), C_6H_5Cl (25 mL), and S(CH_2C≡CH_3)$_2$ (110 μL, 0.721 mmol) were combined in a procedure analogous to that for **4a**$^+$TfO$^-$. The yellow powder was collected by filtration, washed with ether (150 mL), H_2O (30 mL), and ether (50 mL), dried under oil pump vacuum, and dissolved in CH_2Cl_2 (5 mL). The solution was layered with ether (50 mL) and kept in a freezer. After 4 days, yellow-brown needles were collected by filtration, washed with ether (50 mL) and pentane (10 mL), and dried under oil pump vacuum to give **4d**$^+$TfO$^-$ (0.338 g, 0.407 mmol, 79%): mp 169 °C dec; IR 1711.[42] Calcd for $C_{32}H_{30}F_3NO_4PReS_2$: C, 46.26; H, 3.64. Found: C, 46.17; H, 3.64.

NMR ($CDCl_3$):[42] ^{1}H 7.55−7.27 (m, 3 Ph), 5.64 (s, C_5H_5), 3.73 (dq, J_{HH} = 16, 2, 2 SC***H***H′), 3.28 (dq, J_{HH} = 16, 2, 2 SCH***H***′), 1.82 (t, J_{HH} = 3, 2 CH_3); ^{13}C{^{1}H} 133.2 (d, J_{CP} = 11, *o*-Ph), 132.6 (d, J_{CP} = 56, *i*-Ph), 131.8 (d, J_{CP} = 2, *p*-Ph), 129.5 (d, J_{CP} = 11, *m*-Ph), 92.7 (s, C_5H_5), 84.7 (s, ≡***C***CH_3), 71.3 (s, CH_2***C***≡), 34.2 (s, SCH_2), 3.8 (s, CH_3); ^{31}P{^{1}H} 12.0 (s).

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(S(CH_2CH=$CHCH_3$)$_2$)]$^+$TfO$^-$ (4e$^+$TfO$^-$). Complex **2** (0.618 g, 0.893 mmol), C_6H_5Cl (30 mL), and S(CH_2-CH=$CHCH_3$)$_2$ (0.508 g, ca. 2.93 mmol, ca. 18 wt% in heptane; >97% *E*[13]) were combined in a procedure analogous to that for **4a**$^+$TfO$^-$. After 15 h, the solution was filtered through a 3 cm silica gel plug on a frit, which was rinsed with ether (30 mL) and THF (100 mL). Solvent was removed from the THF rinse by rotary evaporation. The residue was dissolved in dimethoxyethane (5 mL). The solution was layered with 1:1 ether/cyclohexane (v/v, 25 mL). After 24 h, yellow needles were collected by filtration, washed with ether (30 mL), and dried under oil pump vacuum to give **4e**$^+$TfO$^-$ (0.997 g, 1.29 mmol, 86%; >98% *E*): mp 149 °C dec; IR 1708.[42] Calcd for $C_{32}H_{34}F_3NO_4PReS_2$: C, 46.03; H, 4.10. Found: C, 46.27; H, 4.09.

NMR ($CDCl_3$):[42] ^{1}H 7.52−7.20 (m, 3 Ph), 5.69 (dq, J_{HH} = 15, 7, 2 =C***H***CH_3), 5.59 (s, C_5H_5), 5.10 (dtq, J_{HH} = 15, 7, 2, 2 CH=), 3.27 (m, 2 SCH_2), 1.65 (dd, J_{HH} = 6, 2, 2 CH_3); ^{13}C{^{1}H} 133.2 (d, J_{CP} = 10, *o*-Ph), 132.4 (d, J_{CP} = 56, *i*-Ph), 131.6 (d, J_{CP} = 2, *p*-Ph), 129.2 (d, J_{CP} = 11, *m*-Ph), 134.4 (s, =***C***HCH_3), 123.0 (s, CH=), 92.6 (s, C_5H_5), 46.0 (s, SCH_2), 18.0 (s, CH_3); ^{31}P{^{1}H} 12.5 (s).

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(S(CH_2CH=CHC(CH_3)$_3$)$_2$)]$^+$TfO$^-$ (4f$^+$TfO$^-$). Complex **2** (1.385 g, 2.000 mmol), C_6H_5Cl (30 mL) and S(CH_2CH=CHC(CH_3)$_3$)$_2$ (0.670 g, 2.96 mmol; >97% *E*[13]) were combined in a procedure analogous to that for **4a**$^+$TfO$^-$. After 21 days, volatiles were removed under oil pump vacuum (12 h). The residue was dissolved in acetone (5 mL). The solution was filtered through a 2 cm silica gel plus on a frit, which was rinsed with 1:1 acetone/CH_2-Cl_2 (v/v, 3 × 50 mL). Volatiles were removed from the rinses by rotary evaporation. The residue was chromatographed on silica gel (20 × 2 cm column packed in ether) with 1:1 CH_2Cl_2/acetone (v/v). Solvent was removed from a yellow fraction. The residue was dissolved in acetone (5 mL). The solution was added dropwise to rapidly stirred ether (250 mL). The yellow powder was collected by filtration, washed with ether (10 mL) and pentane (50 mL), and dried under oil pump vacuum to give **4f**$^+$TfO$^-$ (1.203 g, 1.310 mmol, 66%; >98% *E*): mp 180 °C dec; IR 1691.[42] Calcd for $C_{38}H_{46}F_3NO_4PReS_2$: C, 49.66; H, 5.04. Found: C, 49.38; H, 4.99.

NMR ($CDCl_3$):[42] ^{1}H 7.55−7.23 (m, 3 Ph), 5.67 (d, J_{HH} = 15, 2 =C***H***C$(CH_3)_3$), 5.64 (s, C_5H_5), 5.00 (dt, J_{HH} = 15, 7, 2 SCH_2C***H***=), 3.33 (m, 2 SCH_2), 1.00 (s, 6 CH_3); ^{13}C{^{1}H} 133.5 (d, J_{CP} = 11, *o*-Ph), 132.7 (d, J_{CP} = 56, *i*-Ph), 131.9 (d, J_{CP} = 2, *p*-Ph), 129.5 (d, J_{CP} = 11, *m*-Ph), 150.3 (s, =***C***HC$(CH_3)_3$), 117.3 (s, SCH_2***C***H=), 93.0 (s, C_5H_5), 46.3 (s, SCH_2), 33.8 (s, ***C***$(CH_3)_3$), 29.4 (s, CH_3); ^{31}P{^{1}H} 12.6 (s).

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(S(CH_2CH=CHC_6H_5)$_2$)]$^+$TfO$^-$ (4g$^+$TfO$^-$). A Schlenk flask was charged with **2** (0.329 g, 0.475 mmol), toluene (10 mL), and S(CH_2CH=CHC_6H_5)$_2$ (0.189 g, 0.713 mmol; 90% *E*[13]) and fitted with a condenser. The mixture was refluxed (2 h), cooled, and filtered through a 5 cm silica gel plug on a frit. The plug was rinsed with toluene (150 mL), CH_2Cl_2 (50 mL), and THF (200 mL). Solvent was removed from the THF rinse by rotary evaporation. The residue was dissolved in acetone (10 mL). The solution was added dropwise to rapidly stirred ether (500 mL). The yellow powder was collected by filtration, washed with ether (100 mL) and pentane (250 mL), and dried under oil pump vacuum to give **4g**$^+$TfO$^-$ (0.354 g, 0.369 mmol, 78%; >98% *E*): mp 173 °C dec; IR 1704.[42] Calcd for $C_{42}H_{38}F_3NO_4PReS_2$: C, 52.60; H, 3.99. Found: C, 52.78; H, 4.13.

NMR ($CDCl_3$):[42] ^{1}H 7.55−7.24 (m, 5 Ph), 6.62 (d, J_{HH} = 16, 2 =CHPh), 5.85 (ddd, J_{HH} = 15, 8, 7, 2 CH=), 5.68 (s, C_5H_5), 3.79 (dd, J_{HH} = 13, 8, 2 SC***H***H′), 3.57 (dd, J_{HH} = 13, 7, 2 SCH***H***′); ^{13}C{^{1}H} 133.5 (d, J_{CP} = 11, *o*-PPh), 132.7 (d, J_{CP} = 56, *i*-PPh), 132.0 (d, J_{CP} = 2, *p*-PPh), 129.6 (d, J_{CP} = 11, *m*-PPh), 137.6 (s, =***C***HPh), 136.0 (s, *i*-CPh), 128.9 (s, *m*-CPh), 128.6 (s, *p*-CPh), 126.9 (s, *o*-CPh), 121.8 (s, CH=), 93.2 (s, C_5H_5), 47.6 (s, SCH_2); ^{31}P{^{1}H} 12.5 (s).

[(η^5-C_5Me_5)Re(NO)(PPh$_3$)(S(CH_2CH=CH_2)$_2$)]$^+BF_4^-$ (4a-Me$_5^+$ BF$_4^-$). A Schlenk flask was charged with **1**-Me_5 (1.025 g, 1.630 mmol)[45] and C_6H_5Cl (20 mL) and cooled to −45 °C. Then HBF_4·OEt_2 (5.5 M in ether; 296 μL, 1.63 mmol) was added with stirring.[23] After 10 min, S(CH_2CH=CH_2)$_2$ (314.5 μL, 2.445 mmol) was added with stirring. After 2 h, the cold bath was removed. After 14 h, volatiles were removed under oil pump vacuum. The dark brown residue was dissolved in acetone (20 mL). The solution was filtered through a 1 cm Celite plug, which was rinsed with acetone (100 mL). The filtrate was concentrated to 20 mL by rotary evaporation and added dropwise to rapidly stirred ether (300 mL). The dark yellow powder was collected by filtration. The filtrate was concentrated and the precipitation repeated twice. The combined crops were dried under oil pump vacuum to give **4a**-$Me_5^+BF_4^-$ (1.234 g, 1.515 mmol, 93%): mp 183 °C dec; IR 1671.[42] (darkening, 165 °C). Calcd for $C_{34}H_{40}$-$BF_4NOPReS$: C, 50.12; H, 4.95. Found: C, 49.98; H, 5.03.

NMR:[42] ^{1}H ($CDCl_3$) 7.40−7.20 (m, 3 Ph), 5.80 (m, 2 CH=), 5.40 (br d, J_{HH} = 10, 2 =CH***H***′), 5.12 (br d, J_{HH} = 17, 2 =C***H***H′), 3.35 (dd, J_{HH} = 10, 13, 2 SC***H***H′), 2.89 (dd, J_{HH} = 13, 5, SCH***H***′), 1.73 (s, 5 CH_3); ^{13}C{^{1}H} ($CDCl_3$) 133.4 (d, J_{CP} = 11, *o*-Ph), 131.7 (d, J_{CP} = 2, *p*-Ph), 129.3 (d, J_{CP} = 11, *m*-Ph), 130.3 (s, CH=), 122.9 (s, =CH_2), 103.2 (d, J_{CP} = 1, ***C***CH_3), 45.1 (s, SCH_2), 9.7 (s, CH_3), *i*-Ph not observed; ^{31}P{^{1}H} ($CDCl_3$/CD_2Cl_2) 19.7/17.7 (s).

(η^5-C_5H_5)Re(NO)(PPh$_3$)(SCH(CH=CH_2)CH_2CH=CH_2) (5a). A. An oven-dried Schlenk flask was charged with **4a**$^+$TfO$^-$ (1.167 g, 1.446 mmol) and THF (30 mL) and cooled to −80 °C. Then *t*-BuOK (1.0 M in THF; 1.446 mL, 1.446 mmol) was added with stirring. After 5 min, the cold bath was removed. After 30 min, volatiles were removed under oil pump vacuum. The residue was extracted with benzene (50 mL). The extract was filtered through a 3 cm silica gel plug on a frit, which was rinsed with benzene (100 mL). Solvent was removed from the filtrate by rotary evaporation. The residue was dissolved in CH_2-Cl_2 (15 mL) and heptane (35 mL) was slowly added. The bright orange powder was collected by filtration, washed with pentane (10 mL), and dried under oil pump vacuum to give **5a** (0.873 g, 1.37 mmol, 92%; 93:7 *SS,RR/SR,RS*):[12,46] IR 1629.[42] Calcd for $C_{29}H_{29}NOPReS$: C, 53.03; H, 4.45. Found: C, 52.76; H, 4.38. **B.** Complex (*S*)-**4a**$^+BF_4^-$ (0.563 g, 0.756 mmol), THF (30 mL), and *t*-BuOK (1.0 M in THF; 756 μL, 0.756 mmol) were combined in a procedure analogous to **A**. The residue was extracted with benzene (30 mL). The extract was filtered through a 3 cm silica gel plug on a frit, which was rinsed with benzene (150 mL). Solvent was removed from the filtrate by rotary evaporation.

The residue was dissolved in benzene (10 mL). The solution was added dropwise to rapidly stirred pentane (50 mL). After 15 min crystallization had begun, and the sample was moved to a freezer. After 3 h, the orange microcrystalline powder was collected by filtration, washed with pentane (10 mL), and dried under oil pump vacuum to give **5a** (0.392 g, 0.597 mmol, 79%; 93:7 *SS/SR*): $[\alpha]_{589}^{29}$ 156° ± 11° (*c* 0.500 mg/mL, $CHCl_3$).[43] A benzene solution of this sample was layered with hexanes. Red prisms of diastereomerically pure (*SS*)-**5a** formed (^1H NMR assay) and were simularly collected: mp 141 °C dec; IR 1642.[42] Anal. Found: C, 52.96; H, 4.39.

NMR, (*SS,RR*)-5a/(*SS*)-5a:[42] ^1H (CD_2Cl_2/C_6D_6) 7.57−7.41/7.66−6.97 (m, 3 Ph), 5.95/6.22 (ddt, J_{HH} = 17, 10, 7, CH_2CH=), 5.84/6.03 (ddd, J_{HH} = 17, 10, 9, CHCH=), 5.30/4.91 (s, C_5H_5), 5.09/5.18, 5.50/5.01 (2 m, 2 =CH_2), 3.13/3.32 (m, SCH), 2.67/2.94 (m, SCHCHH′), 2.40/2.70 (m, SCHCHH′); $^{13}C\{^1H\}$ ($CDCl_3/C_6D_6$) 134.7/135.7 (d, J_{CP} = 54, *i*-Ph), 133.4/134.3 (d, J_{CP} = 11, *o*-Ph), 130.5/130.3 (d, J_{CP} = 2, *p*-Ph), 128.2/128.3 (d, J_{CP} = 11, *m*-Ph), 144.2/145.1, 138.1/138.3 (2 s, 2 CH=), 115.1/115.4, 111.9/111.7 (2 s, 2 =CH_2), 92.7/90.9 (s/d, J_{CP} = 1, C_5H_5), 59.0/59.5 (d, J_{CP} = 7/8, SCH), 43.6/44.6 (s, SCHCH_2); $^{31}P\{^1H\}$ (CD_2Cl_2/C_6D_6) 19.3/20.4 (s); (*SR,RS*)-**5a**/(*SR*)-**5a** (partial): ^1H 5.26/4.86 (s, C_5H_5); $^{13}C\{^1H\}$ 92.7/91.4 (s/d, J_{CP} = 1, C_5H_5); $^{31}P\{^1H\}$ 19.7/20.9 (s).

(η^5-C_5H_5)Re(NO)(PPh_3)(SCH(C(CH_3)=CH_2)CH_2C(CH_3)=CH_2) (5b). A. Complex **4b**$^+$$TfO^-$ (1.39 g, 1.67 mmol), THF (30 mL), and *t*-BuOK (1.0 M in THF; 1.666 mL, 1.666 mmol) were combined in a procedure analogous to that for **5a**. The residue ($^{31}P\{^1H\}$ NMR, C_6D_6: 20.5 and 20.3 ppm; 98:2 *SS,RR/SR,RS*) was dissolved in CH_2Cl_2 (25 mL). The solution was layered with pentane (50 mL). Bright orange crystals began to form within 15 min. After 1 h, the flask was shaken and moved to a freezer. Crops were collected after 3 and 12 h, combined, and dried under oil pump vacuum to give **5b** (1.11 g, 1.58 mmol, 95%; 98:2 *SS,RR/SR,RS*).[46] IR 1631.[42] Calcd for $C_{31}H_{33}$NOPReS: C, 54.37; H, 4.86. Found: C, 54.20; H, 4.83. **B.** Complex (*S*)-**4b**$^+$$BF_4^-$ (0.420 g, 0.543 mmol), THF (50 mL), and *t*-BuOK (1.0 M in THF; 543 μL, 0.543 mmol) were combined in a procedure analogous to that for (*SS*)-**5a**. The residue after silica gel filtration ($^{31}P\{^1H\}$ NMR, C_6D_6: 20.5 and 20.3 ppm; 99.3:0.7 *SS/SR*) was dissolved in benzene (10 mL), and hexanes (50 mL) were added. The sample was kept in a freezer. After 5 days, orange crystals were collected by filtration and washed with pentane. Heptane (20 mL) was added to the filtrate, which was concentrated by rotary evaporation to 20 mL. An orange powder was similarly collected. The combined crops were dried under oil pump vacuum to give (*SS*)-**5b** (0.290 g, 0.423 mmol, 79%; >99.5:<0.5 *SS/SR*): IR 1633;[42] $[\alpha]_{589}^{29}$ −156° ± 9° (*c* 0.532 mg/mL, $CHCl_3$).[43] Anal. Found: C, 54.34; H, 4.85.

NMR, (*SS,RR*)-5b/(*SS*)-5b (CD_2Cl_2/C_6D_6):[42] ^1H 7.52−7.34/7.67−6.93 (m, 3 Ph), 5.27/4.97 (s, C_5H_5), 4.79+4.69/5.00−4.80 (2m/m, 2 =CH_2), 3.37/3.67 (dd, J_{HH} = 11, 5, SCH), 2.65/3.04 (br apparent dd, J_{HH} = 14, 5, SCHCHH′), 2.32/2.68 (apparent ddd, J_{HH} = 14, 11, 1, SCHCHH′), 1.78/1.98+1.89 (m/2m, 2 CH_3); $^{13}C\{^1H\}$ 135.2/134.3 (d, J_{CP} = 11, *o*-Ph), 134.3/135.7 (d, J_{CP} = 54, *i*-Ph), 130.7/130.3 (d, J_{CP} = 2, *p*-Ph), 128.5/128.3 (d, J_{CP} = 11/10, *m*-Ph), 150.3/150.4, 145.5/145.0 (2 s, 2 C(CH_3)=), 111.2/111.7, 109.9/110.0 (2 s, 2 =CH_2), 91.6/90.9 (d, J_{CP} = 1, C_5H_5), 61.4/62.1 (d, J_{CP} = 7, SCH), 47.1/47.4 (s, SCHCH_2), 22.2/22.5, 18.2/18.3 (2 s, 2 CH_3); $^{31}P\{^1H\}$ 19.7/20.3 (s). (*SR,RS*)-**5b** (CD_2Cl_2, partial): ^1H 5.23 (s, C_5H_5); $^{13}C\{^1H\}$ 134.2 (d, J_{CP} = 11, *o*-Ph), 129.0 (d, J_{CP} = 10, *m*-Ph), 91.8 (d, J_{CP} = 1, C_5H_5); $^{31}P\{^1H\}$ 20.7 (s).

(η^5-C_5H_5)Re(NO)(PPh_3)(SCH(C(CH_3)$_2$CH=CH_2)CH=C(CH_3)$_2$) (5c). A. Complex **4c**$^+$$TfO^-$ (0.863 g, 1.00 mmol), THF (30 mL), and *t*-BuOK (1.0 M in THF; 1.00 mL, 1.00 mmol) were combined in a procedure analogous to that for **5a**. The benzene silica gel filtrate was concentrated to ca. 50 mL, and heptane (50 mL) was added. The mixture was concentrated to ca. 20 mL. The bright orange powder was collected by filtration, washed with pentane (30 mL), and dried under oil pump vacuum to give **5c** (0.640 g, 0.900 mmol, 90%; 93:7 *SS,RR/SR,RS*):[46] IR 1637.[42,44a] Calcd for $C_{33}H_{37}$NOPReS: C, 55.60; H, 5.23. Found: C, 55.64; H, 5.21. **B.** Complex (*S*)-**4c**$^+$$BF_4^-$ (1.20 g, 1.50 mmol), THF (35 mL), and *t*-BuOK (1.0 M in THF; 1.50 mL, 1.50 mmol) were combined in a procedure analogous to that for (*SS*)-**5a**. The silica gel plug was rinsed with ether (100 mL). Solvents were removed from the filtrate by rotary evaporation. The residue ($^{31}P\{^1H\}$ NMR, $CDCl_3$: 20.9 and 20.4 ppm; 97:3 *SS/SR*) was chromatographed on silica gel (25 × 2.5 cm column) with 1:1 (v/v) ether/hexane. Solvent was removed from an orange fraction by rotary evaporation. The foam was dried under diffusion pump vacuum (48 h) to give **5c** as an orange powder (0.911 g, 1.28 mmol, 85%; 97:3 *SS/SR*):[46] IR 1642;[42] $[\alpha]_{589}^{25}$ −320° ± 2° (*c* 0.736 mg/mL, $CHCl_3$).[43,44a] Anal. Found: C, 55.50; H, 5.28.

NMR, (*SS,RR*)-5c ($CDCl_3$):[42] ^1H 7.56−7.35 (m, 3 Ph), 6.06 (dd, J_{HH} = 18, 11, CH=CH_2), 5.14 (s, C_5H_5), 4.92−4.82 (m, =CH_2), 3.25 (d, J_{HH} = 11, SCH), 1.73, 1.66 (2 d, J_{HH} = 1, 2 =CCH_3), 1.06, 1.04 (2 s, 2 SCHCCH_3), SCHCH= obscured by C_5H_5 resonance; $^{13}C\{^1H\}$ 135.8 (d, J_{CP} = 54, *i*-Ph), 134.3 (d, J_{CP} = 11, *o*-Ph), 130.2 (d, J_{CP} = 2, *p*-Ph), 128.3 (d, J_{CP} = 11, *m*-Ph), 148.4, 130.9 (2 s, 2 CH=), 128.2 (s, =$C(CH_3)_2$), 110.3 (s, =CH_2), 91.0 (s, C_5H_5), 67.4 (d, J_{CP} = 7, SCH), 43.3 (s, $C(CH_3)_2$), 26.2, 26.0, 25.0, 18.8 (4 s, 4 CH_3); $^{31}P\{^1H\}$ 20.9 (s), (*SR,RS*)-**5c** (partial): ^1H 4.93 (s, C_5H_5); $^{31}P\{^1H\}$ 20.0 (s).

(η^5-C_5H_5)Re(NO)(PPh_3)(SCH(C≡CCH_3)C(CH_3)=C=CH_2) (5d). Complex **4d**$^+$$TfO^-$ (0.127 g, 0.152 mmol), THF (10 mL), and *t*-BuOK (1.0 M in THF; 152 μL, 0.152 mmol) were combined in a procedure analogous to that for **5a**. The residue was extracted with benzene (3 × 10 mL). The extract was filtered through a 2 cm silica gel plug in a pipet. Volatiles were removed under oil pump vacuum (3 h) to give **5d** as an orange foam (0.0984 g, 0.144 mmol, 95%; 87:13 *SR,RS/SS,RR*):[46] IR 1654.[42] Calcd for $C_{31}H_{29}$NOPReS: C, 54.69; H, 4.29. Found: C, 54.48; H, 4.33.

NMR, (*SR,RS*)-5d:[42] ^1H (C_6D_6) 7.67−7.57, 6.94−7.05 (m, 3 Ph), 5.07 (s, C_5H_5), 4.76 (m, =CH_2), 4.42 (m, SCH), 2.19 (t, J_{HH} = 3, =CCH_3), 1.73 (d, J_{HH} = 3, ≡CCH_3); $^{13}C\{^1H\}$ (C_6D_6) 135.7 (d, J_{CP} = 54, *i*-Ph), 134.5 (d, J_{CP} = 11, *o*-Ph), 130.3 (d, J_{CP} = 2, *p*-Ph), 128.3 (d, J_{CP} = 10, *m*-Ph), 207.3 (s, =C=), 103.5 (s, $C(CH_3)$=), 91.2 (s, C_5H_5), 83.2 (s, CHC≡), 79.0 (s, ≡$C$$CH_3$), 74.9 (s, =$CH_2$), 46.7 (d, J_{CP} = 9, SCH), 16.4 (s, =CCH_3), 4.2 (s, ≡CCH_3); $^{31}P\{^1H\}$ (CD_2Cl_2) 20.9 (s). (*SS,RR*)-**5d** (partial): ^1H 4.92 (s, C_5H_5), 4.27 (m, SCH), 2.36 (d, J_{HH} = 3, ≡CCH_3), 1.55 (t, J_{HH} = 3, =CCH_3); $^{13}C\{^1H\}$ 134.2 (d, J_{CP} = 11, *o*-Ph), 102.7 (s, $C(CH_3)$=), 91.4 (s, C_5H_5), 82.5 (s, CHC≡), 79.4 (s, ≡$C$$CH_3$), 74.2 (s, =$CH_2$), 49.6 (d, J_{CP} = 9, SCH), 15.1 (s, =CCH_3), 3.8 (s, ≡CCH_3); $^{31}P\{^1H\}$ 21.7 (s).

(η^5-C_5H_5)Re(NO)(PPh_3)(SCH(CH(CH_3)CH=CH_2)-CH=CHCH_3) (5e). Complex **4e**$^+$$TfO^-$ (0.457 g, 0.547 mmol; >98% *E*[13]), THF (25 mL), and *t*-BuOK (1.0 M in THF, 547 μL, 0.547 mmol) were combined in a procedure analogous to that for **5a**. The silica gel plug was rinsed with ether (30 mL) and benzene (20 mL). Solvent was removed from the filtrate by rotary evaporation. The residue was dissolved in CH_2Cl_2 (15 mL), and cyclohexane (30 mL) was added. The mixture was concentrated to ca. 10 mL. The orange powder was collected by filtration, washed with pentane (10 mL), and dried under oil pump vacuum to give **5e** (0.325 g, 0.474 mmol, 87%; 52:45:2:1[14] *SRS,RSR/SRR,RSS/SSS,RRR* or *SSR,RRS*; see text): IR 1654.[42] Calcd for $C_{31}H_{34}$NOPReS: C, 54.37, H, 4.86. Found: C, 54.29, H, 4.89.

NMR, (*SRS,RSR*)- and (*SRR,RSS*)-5e ($CDCl_3$):[42] ^1H 7.54−7.37 (m, 6 Ph), 6.11−5.85 (m, 2 CH=CH_2), 5.48−5.29 (m, 2 CHCH=, 2 =CHCH_3), 5.226, 5.225 (2 s, 2 C_5H_5), 5.05−4.94 (m, 2 =CH_2), 3.07−2.95 (m, 2 CHCH=CH_2), 2.62 (m, 2 SCH), 1.69, 1.67 (2 s, 2 =CHCH_3), 1.10, 1.09 (2 d, J_{HH} = 7, 2 C(CH$_3$)CH=); $^{13}C\{^1H\}$ 134.9, 134.9 (2 d, J_{CP} = 55, 2 *i*-Ph), 133.8 (d, J_{CP} = 11, 2 *o*-Ph), 130.1 (d, J_{CP} = 3, 2 *p*-Ph), 124.1 (J_{CP} = 11, 2 *m*-Ph), 144.6, 142.4, 134.8, 134.1, 123.6, 123.4 (6 s, 6 CH=), 113.1, 112.3 (2 s, 2 =CH_2), 91.0, 90.9 (2 d, J_{CP} = 1, 2 C_5H_5), 64.9, 63.9 (2 d, J_{CP} = 6, 2 SCH), 45.1, 44.1 (2 s, 2 CHCH=CH_2), 18.4, 18.0, 18.0, 15.4 (4 s, 4 CH_3); $^{31}P\{^1H\}$ 19.9, 19.8 (2 s). (*SSS,RRR*)- and (*SSR,RRS*)-**5e** (partial): ^1H 5.17, 5.16 (2 s, 2 C_5H_5), 1.75, 1.74 (2 s, 2 CH_3); $^{13}C\{^1H\}$ 91.5, 91.4 (2 d, J_{CP} = 1, 2 C_5H_5); $^{31}P\{^1H\}$ 20.5, 20.2 (2 s).

(η^5-C_5H_5)Re(NO)(PPh_3)(SCH(CH(C(CH_3)$_3$)CH=CH_2)-CH=CHC(CH_3)$_3$) (5f). Complex **4f**$^+$$TfO^-$ (0.224 g, 0.244 mmol; >98% *E*[13]), THF (10 mL) and *t*-BuOK (1.0 M in THF; 244 μL, 0.244 mmol) were combined in a procedure analogous to that for **5a**. The residue was extracted with toluene (30 mL). The extract was filtered through a 2 cm Celite plug on a frit, which was rinsed with toluene (100 mL). Solvent was removed from the filtrate by rotary evaporation. The foam was stirred with pentane (1 h), and the orange powder was

(45) Patton, A. T.; Strouse, C. E.; Knobler, C. B.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5804.

(46) Melting points are not reported for mixtures of diastereomers.

collected by filtration and dried under oil pump vacuum to give **5f** (0.162 g, 0.211 mmol, 87%; 88:11:1[14]:<0.5 *SRR,RSS/SRS,RSR*/other; see text). IR 1637.[42] Calcd for $C_{37}H_{45}NOPReS$: C, 57.79; H, 5.90. Found: C, 57.83; H, 5.96. A $CDCl_3$ solution of this sample was layered with heptane. Orange prisms of diastereomerically pure (*SRR,RSS*)-**5f** (^{31}P NMR assay) formed over 2 days and were similarly collected.

NMR, (*SRR,RSS*)-5f ($CDCl_3$):[42] ^1H 7.49−7.10 (m, 3 Ph), 6.04 (dt, J_{HH} = 17, 10, C*H*=CH_2), 5.45 (dd, J_{HH} = 16, 9, CHC*H*=*CH*), 5.35 (d, J_{HH} = 16, CHCH=C*H*), 5.20 (s, C_5H_5), 5.00 (dd, J_{HH} = 10, 3, =C*H*H′), 4.80 (dd, J_{HH} = 17, 3, =CH*H*′), 3.64 (dd, J_{HH} = 9, 3, SCH), 1.75 (dd, J_{HH} = 10, 3, *CH*CH=CH_2), 1.03, 0.99 (2 s, 6 CH_3); $^{13}C\{^1H\}$ 135.3 (d, J_{CP} = 54, *i*-Ph), 134.1 (d, J_{CP} = 11, *o*-Ph), 130.2 (d, J_{CP} = 2, *p*-Ph), 128.3 (d, J_{CP} = 11, *m*-Ph), 138.6 (s, *C*H=CH_2), 136.0 (s, =*C*HC$(CH_3)_3$), 134.4 (s, CH*C*H=CH), 115.9 (s, =CH_2), 90.6 (d, J_{CP} = 1, C_5H_5), 64.7 (s, *C*HCH=CH_2), 62.5 (d, J_{CP} = 7, SCH), 33.8, 32.9 (2 s, 2 *C*$(CH_3)_3$), 29.8, 29.3 (2 s, 2 CH_3); $^{31}P\{^1H\}$ 19.6 (s). (*SRS,RSR*)-**5f** (partial): ^1H 1.02, 0.95 (2 s, 6 CH_3); $^{13}C\{^1H\}$ 91.1 (d, J_{CP} = 1, C_5H_5), 33.1, 34.4 (2 s, 2 *C*$(CH_3)_3$), 29.7, 28.9 (2 s, 6 CH_3); $^{31}P\{^1H\}$ 19.2 (s). Other diastereomer (partial): $^{31}P\{^1H\}$ 19.9 (s).

(η^5-C_5H_5)Re(NO)(PPh_3)(SCH(CH(C_6H_5)CH=CH_2)CH=CHC_6H_5) (5g). Complex **4g**$^+$TfO$^-$ (0.281 g, 0.293 mmol; >98% *E*[13]), THF (10 mL), and *t*-BuOK (1.0 M in THF, 293 μL, 0.293 mmol) were combined in a procedure analogous to that for **5f**. An identical workup gave **5g** as an orange powder (0.212 g, 0.301 mmol, 89%; 69:14:11:6 *SRR,RSS*/other/other/other; see text): IR 1631.[42] Calcd for $C_{41}H_{37}NOPReS$: C, 60.87; H, 4.61. Found: C, 60.92; H, 4.68.

NMR, (*SRR,RSS*)-5g ($CDCl_3$):[42] ^1H 7.50−7.05 (m, 5 Ph), 6.40 (m, C*H*=CH_2), 6.17 (d, J_{HH} = 16, =CHPh), 5.98 (dd, J_{HH} = 16, 10, CHC*H*=CH), 5.16 (s, C_5H_5), 5.11 (br dd, J_{HH} = 10, 1, =C*H*H′), 5.06 (dt, J_{HH} = 16, 1, =CH*H*′), 3.68 (apparent t, J_{HH} = 7, C*H*CH=CH_2), 3.59 (dd, J_{HH} = 10, 7, SCH); $^{13}C\{^1H\}$ 134.9 (d, J_{CP} = 54, *i*-PPh), 133.9 (d, J_{CP} = 11, *o*-PPh), 130.2 (d, J_{CP} = 2, *p*-PPh), 128.2 (d, J_{CP} = 11, *m*-PPh), 142.6, 141.9, 138.1, 135.3, 129.1, 128.4, 127.8, 127.3, 126.4, 126.0, 125.8 (11 s, 2 *CPh*, 3 CH=), 114.9 (s, =CH_2), 91.0 (d, J_{CP} = 1, C_5H_5), 65.2 (d, J_{CP} = 7, SCH), 57.8 (s, *C*HCH=CH_2); $^{31}P\{^1H\}$ 19.7 (s). Other diastereomers (partial): $^{13}C\{^1H\}$ 116.0, 115.6, 115.4 (3 s, =CH_2), 91.6, 91.5, (2 s, C_5H_5), 64.8, 63.5 (2 d, J_{CP} = 1, SCH), 58.8, 58.3, 57.3 (s, *C*HCH=CH_2); $^{31}P\{^1H\}$ 20.10, 20.08 (2 s).

(η^5-C_5Me_5)Re(NO)(PPh_3)(SCH(CH=CH_2)CH_2CH=CH_2) (5a-Me_5). A. Complex **4a**-$Me_5^+BF_4^-$ (0.115 g, 0.141 mmol), CH_2Cl_2 (10 mL), and *t*-BuOK (141 μL, 0.134 mmol) were combined in a procedure analogous to that for **5a**. The residue was extracted with toluene (30 mL) and filtered through a 1 cm Celite plug on a frit. The plug was rinsed with toluene until the filtrate was colorless. Solvent was removed from the filtrate by rotary evaporation to give **5a**-Me_5 as an orange-red foam (0.093 g, 0.128 mmol, 91%; 93:7 *SR,RS/SS,RR*). The foam was dissolved in CH_2Cl_2, and a layer of heptane was added (open tube). After 3 days, orange microcrystals of **5a**-Me_5 were collected by filtration, washed with pentane (10 mL), and dried under oil pump vacuum: mp 157 °C; IR 1632.[42] Calcd for $C_{34}H_{39}NOPReS$: C, 56.18; H, 5.41. Found: C, 56.06; H, 5.50. A sample was dissolved in CH_2Cl_2 and layered with heptane. Orange prisms of diastereomerically pure (*SR,RS*)-**5a**-Me_5 (^{31}P NMR assay) were similarly collected. $^{31}P\{^1H\}$ NMR (ppm, C_6D_6, crystal used for X-ray structure below) 19.1 ppm (*SR,RS/SS,RR* mixture, 19.1/18.9 ppm). **B.** Complex **4a**-$Me_5^+BF_4^-$ (0.481 g, 0.591 mmol), THF (10 mL), and *t*-BuOK (591.0 μL, 0.591 mmol) were combined in a procedure analogous to **A**. An identical workup gave **5a**-Me_5 as an orange powder (0.400 g, 0.550 mmol, 93%; 90:10 *SR,RS/SS,RR*).

NMR, (*SR,RS*)-5a-Me_5 (CD_2Cl_2):[42] ^1H 7.55−7.40 (m, 3 Ph), 5.89 (ddt, J_{HH} = 17, 10, 7, CH_2C*H*=), 5.66 (ddd, J_{HH} = 17, 11, 9, CHC*H*=), 5.02−4.87 (m, 2 =CH_2), 2.95 (dt, J_{HH} = 5, 9, SCH), 2.51 (m, SCHC*H*H′), 2.30 (m, SCHCH*H*′), 1.69 (s, 5 CH_3); $^{13}C\{^1H\}$ 134.5 (d, J_{CP} = 11, *o*-Ph), 130.1 (d, J_{CP} = 2, *p*-Ph), 128.2 (d, J_{CP} = 10, *m*-Ph), 145.2, 138.6 (2 s, 2 CH=), 114.6, 111.5 (2 s, 2 =CH_2), 100.8 (d, J_{CP} = 2, *C*CH_3), 56.7 (d, J_{CP} = 8, SCH), 45.1 (s, SCH*C*H_2), 10.1 (s, CH_3), *i*-Ph not observed; $^{31}P\{^1H\}$ 19.0 (s). (*SS,RR*)-**5a**-Me_5 (partial): $^{13}C\{^1H\}$ 144.9, 138.5 (2 s, 2 CH=), 114.8, 111.2 (2 s, 2 =CH_2), 101.2 (d, J_{CP} = 2, *C*CH_3), 56.5 (d, J_{CP} = 8, SCH), 43.4 (s, SCH*C*H_2), 10.2 (s, CH_3).

[(η^5-C_5H_5)Re(NO)(PPh_3)(S(Me)CH(CH=CH_2)CH_2CH=CH_2)]$^+$ TfO$^-$ (7a$^+$TfO$^-$). A. A Schlenk flask was charged with **5a** (1.264 g, 1.924 mmol; 92:8 *SS,RR/SR,RS*) and CH_2Cl_2 (25 mL) and cooled to −80 °C. Then MeOTf (218 μL, 1.92 mmol) was added dropwise with stirring. After 5 min, the cold bath was removed. After 30 min, volatiles were removed under oil pump vacuum. The oily residue was dissolved in CH_2Cl_2 (5 mL). The solution was added dropwise to rapidly stirred pentane (75 mL). An orange powder was collected by filtration, washed with pentane (20 mL), and dried under oil pump vacuum to give **7a**$^+$TfO$^-$ (1.421 g, 1.731 mmol, 90%; 92:8 *SS,RR/SR,RS*).[44a] **B.** Complex **5a** (0.556 g, 0.846 mmol; 92:8 *SS/SR*), CH_2Cl_2 (20 mL), and MeOTf (96 μL, 0.85 mmol) were combined in a procedure analogous to **A**. An identical workup gave **7a**$^+$TfO$^-$ (0.630 g, 0.753 mmol, 89%; 92:8 *SS/SR*).

NMR, (*SS*)-7a$^+$TfO$^-$ (C_6D_6):[42] ^1H 7.44−7.14 (m, 3 Ph), 5.69−5.58, 5.38−5.30 (2 m, 2 CH=), 5.58 (s, C_5H_5), 5.50−5.43, 5.11−5.05 (2 m, 2 =CH_2), 3.38 (m, SCH), 2.48, 2.26 (2 m, SCHC*H*H′, SCHCH*H*′), 2.05 (s, SCH_3); $^{13}C\{^1H\}$ 133.2 (d, J_{CP} = 11, *o*-Ph), 132.2 (d, J_{CP} = 57, *i*-Ph), 131.7 (s, *p*-Ph), 129.3 (d, J_{CP} = 11, *m*-Ph), 133.2 (s, CH=; other CH= obscured), 123.7, 118.9 (2 s, 2 =CH_2), 93.0 (s, C_5H_5), 61.9 (d, J_{CP} = 3, SCH), 37.6 (s, SCH*C*H_2), 25.0 (s, SCH_3); $^{31}P\{^1H\}$ 10.8 (s). (*SR*)-7a$^+$TfO$^-$: ^1H 2.06 (s, SCH_3); $^{31}P\{^1H\}$ 11.4 (s).

[(η^5-C_5H_5)Re(NO)(PPh_3)(S(Me)CH(C(CH_3)=CH_2)CH_2-C(CH_3)=CH_2)]$^+$TfO$^-$ (7b$^+$TfO$^-$). A. Complex **5b** (0.862 g, 1.26 mmol; 98:2 *SS,RR/SR,RS*), CH_2Cl_2 (30 mL), and MeOTf (142 μL, 1.26 mmol) were combined in a procedure analogous to that for **7a**$^+$TfO$^-$. An identical workup gave **7b**$^+$TfO$^-$ as an orange powder (0.955 g, 1.12 mmol, 89%; 98:2 *SS,RR/SR,RS*).[44d] **B.** Complex (*SS*)-**5b** (1.26 g, 1.84 mmol; >99.5:<0.5 *SS/SR*), CH_2Cl_2 (25 mL), and MeOTf (208 μL, 1.84 mmol) were combined in a procedure analogous to **A**. An identical workup gave (*SS*)-**7b**$^+$TfO$^-$ (1.49 g, 1.74 mmol, 95%; >99.5:<0.5 *SS,SR*).

NMR, (*SS*)-7b$^+$TfO$^-$ (C_6D_6):[42] ^1H 7.53−7.21 (m, 3 Ph), 5.72 (s, C_5H_5), 5.30, 5.12, 4.86, 4.76 (4 s, 2 =C*H*H′, 2 =CH*H*′), 3.70 (apparent dd, *J* = 13, 4, SCH), 2.53−2.48, 2.26−2.21 (2 m, SCHC*H*H′, SCHCH*H*′), 2.17 (s, SCH_3), 1.78, 1.63 (2 s, 2 CH_3); $^{13}C\{^1H\}$ 133.2 (d, J_{CP} = 11, *o*-Ph), 131.9 (d, J_{CP} = 56, *i*-Ph), 131.7 (d, J_{CP} = 2, *p*-Ph), 129.3 (d, J_{CP} = 11, *m*-Ph), 140.6, 137.9 (2 s, 2 *C*(CH_3)=), 121.4, 114.2 (2 s, 2 =CH_2), 92.9 (s, C_5H_5), 64.5 (d, J_{CP} = 3, SCH), 39.9 (s, SCH*C*H_2), 25.5, 16.5 (2 s, 2 CH_3), 21.8 (s, SCH_3); $^{31}P\{^1H\}$ 10.7 (s). (*SR,RS*)-7b$^+$TfO$^-$: $^{31}P\{^1H\}$ 11.2 (s).

[(η^5-C_5H_5)Re(NO)(PPh_3)(S(Me)CH(C$(CH_3)_2$CH=CH_2)-CH=C$(CH_3)_2$)]$^+$TfO$^-$ (7c$^+$TfO$^-$). A. Complex **5c** (0.570 g, 0.813 mmol; 93:7 *SS,RR/SR,RS*), CH_2Cl_2 (30 mL), and MeOTf (88 μL, 0.80 mmol) were combined in a procedure analogous to that for **7a**$^+$TfO$^-$. A similar workup gave **7c**$^+$TfO$^-$ as an orange powder (0.624 g, 0.712 mmol, 89%; 93:7 *SS,RR/SR,RS*).[44a] **B.** Complex **5c** (1.06 g, 1.48 mmol; 97:3 *SS/SR*), CH_2Cl_2 (35 mL), and MeOTf (168 μL, 1.48 mmol) were combined in a procedure analogous to that for **7a**$^+$TfO$^-$. After 30 min, the solution was filtered through a 3 cm silica gel plug on a frit, which was rinsed with CH_2Cl_2 (20 mL) and THF (100 mL). Solvent was removed from the THF rinse by rotary evaporation. The orange foam was dried under oil pump vacuum (12 h) and dissolved in CH_2Cl_2 (10 mL). Solvent was removed under oil pump vacuum (12 h) to give **7c**$^+$TfO$^-$ as an orange powder (1.20 g, 1.37 mmol, 93%; 97:3 *SS,SR*).

NMR, (*SS*)-7c$^+$TfO$^-$ ($CDCl_3$):[42] ^1H 7.37−7.07 (m, 3 Ph), 5.64 (dd, J_{HH} = 17, 11, C*H*=CH_2), 5.37 (s, C_5H_5), 5.01 (br d, J_{HH} = 12, SCHC*H*=), 4.95−4.85 (m, =CH_2), 3.34 (d, J_{HH} = 11, SCH), 1.92 (s, SCH_3), 1.75, 1.61 (2 s, 2 =CCH_3), 0.92, 0.85 (2 s, 2 SCHCC*H*$_3$); $^{13}C\{^1H\}$ 132.7 (d, J_{CP} = 11, *o*-Ph), 131.4 (d, J_{CP} = 56, *i*-Ph), 131.0 (d, J_{CP} = 3, *p*-Ph), 128.6 (d, J_{CP} = 11, *m*-Ph), 142.8, 140.8 (2 s, 2 CH=), 120.3 (q, J_{CF} = 321, CF_3), 115.8, 113.9 (2 s, =*C*$(CH_3)_2$, =CH_2), 91.5 (s, C_5H_5), 71.8 (d, J_{CP} = 1, SCH), 67.3 (s, *C*$(CH_3)_2$), 25.7, 25.3, 23.3, 23.2, 18.5 (5 s, 5 CH_3); $^{31}P\{^1H\}$ 11.9 (s). (*SR*)-7c$^+$TfO$^-$ (partial): ^1H 5.35 (s, C_5H_5); $^{13}C\{^1H\}$ 92.3 (s, C_5H_5).

[(η^5-C_5H_5)Re(NO)(PPh_3)(S(Me)CH(CH(CH_3)-CH=CH_2)CH=CHCH_3)]$^+$TfO$^-$ (7e$^+$TfO$^-$). Complex **5e** (0.302 g, 0.441 mmol; 52:45:2:1 *SRS,RSR/SRR,RSS/SSS,RRR* or *SSR,RRS*), CH_2Cl_2 (25 mL), and MeOTf (49.9 μL, 0.441 mmol) were combined in a procedure analogous to that for **7a**$^+$TfO$^-$. After 10 min, the cold bath was removed. After 30 min, the mixture was filtered through a 3 cm silica gel plug on a frit, which was rinsed with CH_2Cl_2 (20 mL) and THF (100 mL). Solvent was removed from the THF rinse under aspirator and oil pump vacuum (24 h) to give **7e**$^+$TfO$^-$ as an orange

powder (0.317 g, 0.374 mmol, 85%; 50:47.5:1.5:1 *SRS,RSR/SRR,RSS/SSS,RRR* or *SSR,RRS*).

NMR, (*SRS,RSR*)- and (*SRR,RSS*)-7e$^+$TfO$^-$ ($CDCl_3$):[42] ^{1}H 7.49–7.19 (m, 6 Ph), 6.05–5.60 (m, 2 C*H*=CH_2), 5.77–5.49 (m, 2 =C*H*CH_3), 5.64, 5.62 (2 s, 2 C_5H_5), 5.27–5.02 (m, 2 =CH_2, 2 CHC*H*=), 3.33–3.24 (m, 2 SCH), 2.83–2.59 (m, 2 C*H*CH=CH_2), 2.07, 1.99 (2 s, 2 SCH_3), 1.72 (m, 2 =CHC*H*$_3$), 1.12, 1.02 (2 d, J_{HH} = 7, 2 C(C*H*$_3$)CH=); ^{13}C{^{1}H} 133.1 (d, J_{CP} = 11, 2 *o*-Ph), 132.05, 132.00 (2 d, J_{CP} = 57, 2 *i*-Ph), 131.6 (s, 2 *p*-Ph), 129.2 (d, J_{CP} = 10, 2 *m*-Ph), 139.9, 137.0, 136.7, 136.5, 122.6, 122.5 (6 s, 6 CH=), 117.4, 115.5 (2 s, 2 =CH_2), 92.7 (s, 2 C_5H_5), 68.4, 66.8 (2 d, J_{CP} = 1, 2 SCH), 40.1, 39.5 (2 s, 2 *C*HCH=CH_2), 25.5, 24.7, 18.6, 18.08, 18.06, 14.4 (6 s, 6 CH_3); ^{31}P{^{1}H} 10.8, 10.4 (2 s). (*SSS,RRR*)- and (*SSR,RRS*)-7e$^+$TfO$^-$ (partial): ^{1}H 2.14, 2.04 (2 s, 2 SCH_3), 1.18, 1.06 (2 d, J_{HH} = 7, 2 C(C*H*$_3$)CH=); ^{31}P{^{1}H} 11.7, 11.5 (2 s).

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(S(Me)CH(CH(C(CH$_3$)$_3$)CH=CH_2)-CH=CHC(CH$_3$)$_3$)]$^+$TfO$^-$ (7f$^+$TfO$^-$). Complex **5f** (0.369 g, 0.480 mmol; 88:11:1:<0.5 *SRR,RSS/SRS,RSR*/other), CH_2Cl_2 (20 mL), and MeOTf (54.3 μL, 0.40 mmol) were combined in a procedure analogous to that for **7a**$^+$TfO$^-$. After 30 min, heptane (20 mL) was added. The mixture was concentrated by rotary evaporation. The yellow powder was collected by filtration, washed with pentane (10 mL), and dried under oil pump vacuum to give **7f**$^+$TfO$^-$ (0.410 g, 0.440 mmol, 92%; 94:6 *SRR,RSS/SRS,RSR*).

NMR, (*SRR,RSS*)-7f$^+$TfO$^-$ ($CDCl_3$):[42] ^{1}H 7.57–7.23 (m, 3 Ph), 5.83 (d, J_{HH} = 16, CHCH=C*H*), 5.62 (s + m, C_5H_5, C*H*=CH_2), 5.36 (dd, J_{HH} = 15, 10, CHC*H*=CH), 5.16 (dd, J_{HH} = 10, 1, =C*H*H′), 5.02 (dd, J_{HH} = 17, 1, =CH*H*′), 3.99 (dd, J_{HH} = 10, 4, SCH), 2.20 (dd, J_{HH} = 10, 4, C*H*CH=CH_2), 2.12 (s, SCH_3), 1.08, 0.93 (2 s, 6 CH_3); ^{13}C{^{1}H} 133.4 (d, J_{CP} = 10, *o*-Ph), 132.3 (d, J_{CP} = 54, *i*-Ph), 131.8 (d, J_{CP} = 2, *p*-Ph), 129.4 (d, J_{CP} = 11, *m*-Ph), 149.4 (s, *C*H=CH_2), 136.4 (s, =*C*HC(CH$_3$)$_3$), 119.9 (s, CH*C*H=CH), 118.3 (s, =CH_2), 92.5 (s, C_5H_5), 66.2 (s, SCH), 57.6 (s, *C*HCH=CH_2), 34.1, 33.9 (2 s, 2 *C*(CH$_3$)$_3$), 29.12, 29.10 (2 s, 2 C*C*H$_3$), 24.7 (s, SCH_3); ^{31}P{^{1}H} 11.4 (s). (*SRS,RSR*)-7f$^+$TfO$^-$ (partial): ^{13}C{^{1}H} 93.1 (s, C_5H_5), 29.0, 28.7 (2 s, 2 CH_3); ^{31}P{^{1}H} 9.9 (s).

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(S(CH$_2$Ph)CH(CH=CH$_2$)CH$_2$-CH=CH$_2$)]$^+$I$^-$ (10a$^+$I$^-$). A. A Schlenk flask was charged with **5a** (0.816 g, 1.24 mmol; 93:7 *SS,RR/SR,RS*) and CH_2Cl_2 (30 mL). Then $PhCH_2I$ (0.404 g, 1.85 mmol) was added with stirring. After 12 h, the solution was concentrated to ca. 10 mL, and ether (30 mL) was added dropwise. The yellow powder was collected by filtration, washed with ether (3 × 20 mL) and pentane (20 mL), and dried under oil pump vacuum to give **10a**$^+$I$^-$ (1.056 g, 1.210 mmol, 97%; 93:7 *SS,RR/SR,RS*). **B.** Complex **5a** (0.524 g, 0.796 mmol; 93:7 *SS/SR*), CH_2Cl_2 (25 mL) and $PhCH_2I$ (0.260 g, 1.19 mmol) were combined in a procedure analogous to **A**. An identical workup gave **10a**$^+$I$^-$ (0.570 g, 0.653 mmol, 82%; 93:7 *SS/SR*).[44a]

NMR, (*SS,RR*)-10a$^+$I$^-$ ($CDCl_3$):[42] ^{1}H 7.50–7.18 (m, 3 PPh), 7.17–6.96 (m, CPh), 5.76 (s, C_5H_5), 5.65–5.51 (m, 2 CH=), 5.34–5.27, 5.06–5.02 (2 m, 2 =CH_2), 4.24, 3.56 (2 d, J = 14, C*H*H′Ph, CH*H*′Ph), 3.50 (m, SCH), 2.39, 2.32 (2 m, SCHC*H*H′, SCHCH*H*′); ^{13}C{^{1}H} 133.3 (d, J_{CP} = 11, *o*-PPh), 132.2 (d, J_{CP} = 56, *i*-PPh), 131.7 (d, J_{CP} = 2, *p*-PPh), 129.4 (d, J_{CP} = 11, *m*-PPh), 134.7, 133.9 (2 s, 2 CH=), 132.8, 129.6, 129.4, 128.0 (4 s, C*Ph*), 122.4, 118.8 (2 s, =CH_2), 92.8 (s, C_5H_5), 59.2 (s, SCH), 47.2, 37.4 (2 s, *C*Ph, SCH*C*H$_2$); ^{31}P{^{1}H} 12.0 (s). (*SR,RS*)-10a$^+$I$^-$ (partial): ^{1}H 5.77 (s, C_5H_5); ^{13}C{^{1}H} 92.5 (s, C_5H_5); ^{31}P{^{1}H} 11.3 (s).

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(S(CH$_2$Ph)CH(C(CH$_3$)=CH$_2$)CH$_2$C-(CH$_3$)=CH$_2$)]$^+$I$^-$ (10b$^+$I$^-$). A. A Schlenk flask was charged with (*SS*)-**5b** (0.631 g, 0.920 mmol; >99.5:<0.5 *SS/SR*) and CH_2Cl_2 (30 mL). Then $PhCH_2I$ (0.301 g, 1.38 mmol) was added with stirring. After 16 h, the solution was concentrated to ca. 10 mL, and ether (30 mL) was added dropwise. The precipitate was collected by filtration, washed with ether (3 × 20 mL) and pentane (20 mL), and chromatographed on silica gel (20 × 2 cm column) with 2:1 (v/v) THF/CH_2Cl_2. Solvent was removed from a yellow fraction by rotary evaporation. The residue was dissolved in CH_2Cl_2 (10 mL), and ether (40 mL) was added dropwise. The yellow powder was collected by filtration, washed with ether (2 × 25 mL) and pentane (30 mL), and dried under oil pump vacuum to give (*SS*)-**10b**$^+$I$^-$ (0.657 g, 0.727 mmol, 79%; >99.5:<0.5 *SS/SR*). **B.** Complex **5b** (0.780 g, 1.14 mmol; 98:2 *SS,RR/SR,RS*), CH_2Cl_2 (30 mL), and $PhCH_2I$ (0.373 g, 1.1 mmol) were combined in a procedure analogous to **A**. An identical workup gave **10b**$^+$I$^-$ (0.865 g, 0.958 mmol, 84%; 98:2 *SS,RR/SR,RS*).[44d]

NMR, (*SS*)-10b$^+$I$^-$ ($CDCl_3$):[42] ^{1}H 7.76–7.45 (m, 3 PPh), 7.39–6.80 (m, CPh), 6.08 (s, C_5H_5), 5.79, 5.00, 4.86 (3 s, 1:2:1, 2 =CHH′), 5.16, 3.93 (2 d, J = 15, C*H*H′Ph, CH*H*′Ph), 4.26 (apparent dd, J = 13, 4, SCH), 2.80, 2.55 (2 m, SCHC*H*H′, SCHCH*H*′), 1.99, 1.45 (2 s, 2 CH_3); ^{13}C{^{1}H} NMR 133.0 (d, J_{CP} = 11, *o*-PPh), 131.8 (d, J_{CP} = 57, *i*-PPh), 131.4 (d, J_{CP} = 1, *p*-PPh), 129.1 (d, J_{CP} = 11, *m*-PPh), 140.4, 137.7 (2 s, 2 *C*(CH$_3$)=), 135.0, 129.0, 127.8, 127.3 (4 s, C*Ph*), 121.1, 113.5 (2 s, 2 =CH_2), 92.6 (s, C_5H_5), 62.1 (d, J_{CP} = 1, SCH), 49.6 (s, *C*Ph), 40.2 (s, SCH*C*H$_2$), 22.3 (2 s, 2 CH_3); ^{31}P{^{1}H} 12.2 (s). (*SR,RS*)-10b$^+$I$^-$: ^{31}P{^{1}H} 11.6 (s).

MeSCH(CH=CH$_2$)CH$_2$CH=CH$_2$ (8a). A. A Schlenk flask was charged with **7a**$^+$TfO$^-$ (1.375 g, 1.675 mmol; 92:8 *SS,RR/SR,RS*) and CH_2Cl_2 (20 mL). Then $Et_4N^+CN^-$ (0.392 g, 2.51 mmol) was added with stirring. After 30 min, the sample was concentrated to an oily residue under oil pump vacuum,[47] which was triturated with ether (100 mL). The yellow suspension was filtered through a 4 cm silica gel plug on a frit. The plug was rinsed with ether (10 × 25 mL). The filtrate was concentrated to ca. 0.5 mL and distilled under oil pump vacuum (25–50 °C) into a liquid N_2-cooled receiver. This gave previously reported[19] **8a** as a colorless liquid (0.129 g, 1.01 mmol, 60%). The plug was rinsed with THF (7 × 50 mL), and the rinses were concentrated to 50 mL. Heptane (50 mL) was added, and the mixture was concentrated to ca. 15 mL. The yellow powder was collected by filtration, washed with pentane (30 mL), and dried under oil pump vacuum to give (η^5-C_5H_5)Re(NO)(PPh$_3$)(CN) (**9**;[17] 0.828 g, 1.45 mmol, 87%). **B.** Complex **7a**$^+$TfO$^-$ (1.11 g, 1.35 mmol; 92:8 *SS/SR*), CH_2Cl_2 (25 mL), and $Et_4N^+CN^-$ (0.316 g, 2.03 mmol) were combined in a procedure analogous to **A**. An identical workup gave (*S*)-**9** (0.716 g, 1.26 mmol, 93%; >98% *ee*, Eu(hfc)$_3$) and (*S*)-**8a** (0.117 g, 0.911 mmol, 67%; 84% *ee*, Ag(fod)/Eu(hfc)$_3$ analysis[21] of 115.4 ppm ^{13}C NMR signal). Calcd for $C_7H_{12}S$: C, 65.57; H, 9.43. Found: C, 65.44; H, 9.38.[44c]

NMR, 8a ($CDCl_3$):[42] ^{1}H 5.81 (ddt, J_{HH} = 17, 10, 7, CH_2CH=), 5.60 (ddd, J_{HH} = 17, 10, 9, CHC*H*=), 5.12–4.95 (m, 2 =CH_2), 3.10 (m, SCH), 2.37 (apparent tq, J_{HH} = 7, 1, SCHC*H*$_2$), 1.99 (s, SCH_3); ^{13}C-{^{1}H} 138.2, 135.2 (2 s, 2 CH=), 116.8, 115.4 (2 s, 2 =CH_2), 49.9 (s, SCH), 38.4 (s, SCH*C*H$_2$), 13.7 (s, SCH_3).

MeSCH(C(CH$_3$)=CH$_2$)CH$_2$C(CH$_3$)=CH$_2$ (8b). A. Complex **7b**$^+$TfO$^-$ (1.022 g, 1.203 mmol; 98:2 *SS,RR/SR,RS*), CH_2Cl_2 (25 mL), and Et_4N^+ CN^- (0.292 g, 1.87 mmol) were combined in a procedure analogous to that for **8a**. An identical workup gave **9** (0.589 g, 1.04 mmol, 86%) and **8b** (0.122 g, 0.781 mmol, 65%) as a colorless liquid. Calcd for $C_9H_{16}S$: C, 69.17; H, 10.32. Found: C, 69.30; H, 10.41. **B.** Complex (*SS*)-**7b**$^+$TfO$^-$ (1.21 g, 1.41 mmol; >99.5:<0.5 *SS/SR*), CH_2Cl_2 (25 mL), and $Et_4N^+CN^-$ (0.285 g, 1.83 mmol) were combined in a procedure analogous to **A**. An identical workup gave (*S*)-**9** (0.735 g, 1.30 mmol, 92%; >98% *ee*) and (*S*)-**8b** (0.142 g, 0.82 mmol, 58%; >98% *ee*, Ag(fod)/Eu(hfc)$_3$ analysis[21] of 112.6 ppm ^{13}C NMR signal). Anal. Found: C, 69.28; H, 10.38.[44c]

NMR, 8b ($CDCl_3$):[42] ^{1}H 4.85–4.73 (m, 2 =CH_2), 3.37 (t, J_{HH} = 8, SCH), 2.32 (d, J_{HH} = 8, SCHC*H*$_2$), 1.92 (s, SCH_3), 1.73 (m, 2 CH_3); ^{13}C{^{1}H} 143.2, 142.7 (2 s, 2 *C*(CH$_3$)=), 113.4, 112.6 (2 s, 2 =CH_2), 52.0 (s, SCH), 40.8 (s, SCH*C*H$_2$), 21.8 (s, SCH_3), 16.8, 14.2 (2 s, 2 CH_3).

MeSCH(C(CH$_3$)$_2$CH=CH$_2$)CH=C(CH$_3$)$_2$ (8c). A. Complex **7c**$^+$TfO$^-$ (0.570 g, 0.650 mmol, 93:7 *SS,RR/SR,RS*), CH_2Cl_2 (20 mL), and $Et_4N^+CN^-$ (0.156 g, 1.00 mmol) were combined in a procedure analogous to that for **8a**. Similar workup and distillation (Kugelrohr, 50 °C, 0.2 Torr) gave previously reported[2b,20] **8c** as a colorless liquid (0.072 g, 0.39 mmol, 60%; **9**, 0.330 g, 0.579 mmol, 89%). **B.** Complex **7c**$^+$TfO$^-$ (1.19 g, 1.36 mmol; 97:3 *SS/SR*), CH_2Cl_2 (30 mL), and $Et_4N^+CN^-$ (0.276 g, 1.77 mmol) were combined in a procedure identical to **A**. A similar workup gave (*S*)-**8c** (0.163 g, 0.886 mmol, 65%; 92% *ee*, Ag(fod)Eu(hfc)$_3$ analysis[21] of 123.3 ppm ^{13}C NMR signal; (*S*)-**9**, 0.604 g, 1.06 mmol, 78%; >98% *ee*). Calcd for $C_{11}H_{20}S$: C, 71.67; H, 10.94. Found: C, 71.43; H, 10.87.[44c]

NMR, 8c ($CDCl_3$):[42] ^{1}H 5.92 (dd, J_{HH} = 17, 11, C*H*=CH_2), 5.07 (d sept, J_{HH} = 11, 1, SCHC*H*=), 5.00 (dd, J_{HH} = 11, 1, =C*H*H′), 4.97 (dd, J_{HH} = 17, 1, =CH*H*′), 3.28 (d, J_{HH} = 11, SCH), 1.91 (s, SCH_3),

1.78, 1.62 (2 d, J_{HH} = 1, 2 =CCH$_3$), 1.09, 1.06 (2 s, 2 SCHCCH_3); ^{13}C{^{1}H} 145.8, 123.3 (2 s, 2 CH=), 133.8 (s, =C(CH$_3$)$_2$), 111.8 (s, =CH$_2$), 55.5 (s, SCH), 40.7 (s, C(CH$_3$)$_2$), 26.1, 25.8, 23.9, 18.2, 14.2 (5 s, 5 CH$_3$).

MeSCH(CH(CH$_3$)CH=CH$_2$)CH=CHCH$_3$ (8e). Complex **7e**$^+$TfO$^-$ (0.317 g, 0.374 mmol; 50:47.5:1.5:1 diastereomer mixture), CH_2Cl_2 (25 mL), and $Et_4N^+CN^-$ (0.087 g, 0.56 mmol) were combined in a procedure analogous to that for **8a**. The oily residue was triturated with 1:1 pentane/ether (v/v, 40 mL). The bright yellow suspension was filtered through a 4 cm silica gel plug on a frit. The plug was rinsed with 9:1 pentane/ether (v/v, 70 mL). Further workup and distillation (Kugelrohr, ca. 100 °C, 0.1 Torr) as with **8a** gave **8e** as a colorless liquid (0.040 g, 0.30 mmol, 79%; 52:48 *RS,SR/RR,SS*; **9**, 0.189 g, 0.331 mmol, 89%). Calcd for $C_9H_{16}S$: C, 69.17; H, 10.32. Found: C, 69.04; H, 10.24.

NMR, (*RS,SR*)- and (*RR,SS*)-8e (CDCl$_3$):[42] ^{1}H 5.87−5.69 (m, 2 CH=CH$_2$), 5.42 (apparent dq, J_{HH} = 6, 15, 2 =CHCH$_3$), 5.29−5.18 (m, 2 CHCH=), 5.06−4.98 (m, 2 =CH$_2$), 2.97−2.88 (m, 2 SCH), 2.48−2.26 (m, 2 CHCH=CH$_2$), 1.95, 1.94 (2 s, 2 SCH$_3$), 1.719, 1.715 (2 dd, J_{HH} = 6, 2, 2 =CHCH_3), 1.07, 1.06 (2 d, J_{HH} = 7, 2 CHCH_3); ^{13}C{^{1}H} 141.6, 140.7, 129.9, 129.4, 127.4, 127.3 (6 s, 6 CH=), 114.6, 114.3 (2 s, 2 =CH$_2$), 55.8, 55.6 (2 s, 2 SCH), 42.2, 41.6 (2 s, 2 CHCH=CH$_2$), 18.1, 17.9, 17.5, 14.3, 14.2 (5 s, 6 CH$_3$).

MeSCH(CH(C(CH$_3$)$_3$)CH=CH$_2$)CH=CHC(CH$_3$)$_3$ (8f). Complex **7f**$^+$TfO$^-$ (0.410 g, 0.440 mmol; 94:6 diastereomer mixture), CH_2Cl_2 (20 mL), and $Et_4N^+CN^-$ (0.0721 g, 0.462 mmol) were combined in a procedure analogous to that for **8a**. The oily residue was dissolved in ether and filtered through a 5 cm silica gel plug on a frit. The plug was rinsed with ether (200 mL), and solvent was removed from the filtrate by rotary evaporation. Distillation (Kugelrohr, 100 °C, 0.05 torr) gave **8f** as a colorless liquid (0.055 g, 0.240 mmol, 54%; 94:6 *RR,SS/SR,RS*; **9**, 0.212 g, 0.370 mmol, 84%). Calcd exact mass, $C_{15}H_{28}S$: 240.19116; Found: 240.19276.

NMR, (*RR,SS*)-8f (CDCl$_3$):[42] ^{1}H 5.82 (dt, J_{HH} = 17, 10, CH=CH$_2$), 5.33 (d, J_{HH} = 15, =CHC(CH$_3$)$_3$), 5.22 (dd, J_{HH} = 15, 9, CHCH=CH), 5.13 (dd, J_{HH} = 10, 2, =CHH'), 4.98 (dd, J_{HH} = 17, 2, =CHH'), 3.20 (dd, J_{HH} = 9, 5, SCH), 1.98 (dd, J_{HH} = 11, 5, CHC(CH$_3$)$_3$), 1.88 (s, SCH$_3$), 1.03, 0.97 (2 s, 6 CH$_3$); ^{13}C{^{1}H} 141.4 (s, CH=CH$_2$), 137.0 (s, =CHC(CH$_3$)$_3$), 126.2 (s, =CHCHS), 117.8 (s, =CH$_2$), 59.4 (s, SCH), 51.5 (s, CHCH=CH$_2$), 33.9, 33.2 (2 s, 2 C(CH$_3$)$_3$), 30.1, 29.1 (2 s, 2 CCH$_3$), 14.6 (SCH$_3$). (*SR,RS*)-**8f** (partial): ^{1}H 3.37 (dd, J_{HH} = 10, 3, SCH), 2.07 (dd, J_{HH} = 11, 3, CHC(CH$_3$)$_3$), 1.90 (s, SCH$_3$), 1.04, 0.91 (2 s, 6 CCH$_3$); ^{13}C{^{1}H} 143.6 (s, CH=CH$_2$), 135.4 (s, =CHC(CH$_3$)$_3$), 122.9 (s, CHCH=CH), 118.8 (s, =CH$_2$), 58.9 (s, SCH), 51.2 (s, CHCH=CH$_2$), 29.9, 28.5 (2 s, 2 CH$_3$), 14.3 (SCH$_3$).

PhCH$_2$SCH(CH=CH$_2$)CH$_2$CH=CH$_2$ (11a). A. A Schlenk flask was charged with **10a**$^+$I$^-$ (0.954 g, 1.09 mmol; 93:7 *SS,RR/SR,RS*) and CH_2Cl_2 (30 mL). Then $Et_4N^+CN^-$ (0.204 g, 1.31 mmol) was added with stirring. After 1 h, the solution was concentrated to an oily residue (ca. 2 mL) under oil pump vacuum, which was triturated with ether (50 mL). The yellow suspension was filtered through a 3 cm silica gel plug on a frit, which was rinsed with ether (5 × 50 mL). The filtrate was concentrated to ca. 20 mL and transferred to a tared flask. Solvent was removed under oil pump vacuum to give **11a** as a faint yellow oil (0.208 g, 1.02 mmol, 84%). Calcd for $C_{13}H_{16}S$: C, 76.42; H, 7.89. Found: C, 76.32; H, 8.12. Complex **9** (0.520 g, 0.913 mmol, 84%) was isolated as in the preparation of **8a**. **B.** Complex **10a**$^+$I$^-$ (0.480 g, 0.550 mmol; 93:7 *SS/SR*), CH_2Cl_2 (25 mL), and $Et_4N^+CN^-$ (0.129 g, 0.824 mmol) were combined in a procedure analogous to **A**. An identical workup gave a red liquid, which was chromatographed on silica gel (26 × 2.5 cm column) with 9:1 (v/v) hexane/ether to give (*S*)-**11a** as a faint yellow liquid (0.087 g, 0.42 mmol, 77%; 86% *ee*, Ag(fod)/Eu(hfc)$_3$ analysis[21] of 134.9 ppm ^{13}C NMR signal; (*S*)-**9**, 0.291 g, 0.512 mmol, 93%; >98% *ee*).[44c] Anal. Found: C, 76.31; H, 7.92.

NMR, 11a (CDCl$_3$):[42] ^{1}H 7.24−7.10 (m, Ph), 5.73−5.51 (m, 2 CH=), 5.12−4.95 (m, 2 =CH$_2$), 3.60, 3.53 (2 d, J = 14, CHH$'$Ph, CHH'Ph), 3.04 (m, SCH), 2.27 (m, SCHCH_2); ^{13}C{^{1}H} 138.5, 134.9 (2 s, 2 CH=), 138.4 (s, *i*-Ph), 128.9, 128.4 (2 s, *o*, *m*-Ph), 126.8 (s, *p*-Ph), 116.9, 115.8 (2 s, 2 =CH$_2$), 47.7 (s, SCH), 38.5, 34.9 (2 s, CPh, SCHCH$_2$).

PhCH$_2$SCH(C(CH$_3$)=CH$_2$)CH$_2$C(CH$_3$)=CH$_2$ (11b). A. **10b**$^+$I$^-$ (0.761 g, 0.843 mmol; 98:2 *SS,RR/SR,RS*), CH_2Cl_2 (30 mL), and $Et_4N^+CN^-$ (0.198 g, 1.26 mmol) were combined in a procedure analogous to that for **11a**. An identical workup gave **11b** as a faint yellow liquid (0.167 g, 0.717 mmol, 85%; **9**, 0.437 g, 0.767 mmol, 91%). Calcd for $C_{15}H_{20}S$: C, 77.53; H, 8.67. Found: C, 77.43; H, 8.64. **B.** Complex (*SS*)-**10b**$^+$I$^-$ (0.592 g, 0.655 mmol; >99.5:<0.5 *SS/SR*), CH_2Cl_2 (25 mL), and $Et_4N^+CN^-$ (0.123 g, 0.786 mmol) were combined in a procedure analogous to that given for (*S*)-**11a**. An identical workup gave (*S*)-**11b** as a faint yellow liquid (0.125 g, 0.537 mmol, 82%; >98% *ee*, Ag(fod)/Eu(hfc)$_3$ analysis[21] of 112.6 ppm ^{13}C NMR signal; (*S*)-**9**, 0.339 g, 0.596 mmol, 91%; >98% *ee*). Anal. Found: C, 77.48; H, 8.74.[44c]

NMR, 11b (CDCl$_3$):[42] ^{1}H 7.31−7.20 (m, Ph), 4.92−4.68 (m, 2 =CH$_2$), 3.60, 3.56 (2 d, J_{HH} = 17, CHH$'$Ph, CHH'Ph), 3.40 (t, J_{HH} = 8, SCH), 2.30 (d, J_{HH} = 8, SCHCH_2), 1.78, 1.64 (2 s, 2 CH$_3$); ^{13}C{^{1}H} 143.5, 142.4 (2 s, 2 C(CH$_3$)=), 138.4, 128.9, 128.3, 126.7 (4 s, Ph), 113.7, 112.6 (2 s, 2 =CH$_2$), 49.8 (s, SCH), 40.8 (s, CPh), 35.3 (s, SCHCH$_2$), 21.7, 16.8 (s, 2 CH$_3$).

Crystallography. Data were collected as outlined in Table 1. Cell constants were obtained from reflections ((*S*)-**4a**$^+$SbF$_6^-$, 25 with 25° < 2θ < 30°; (*SS*)-**5a**, 25 with 30° < 2θ < 35°; (*SR,RSS*)-**5f**, 21 with 14° < 2θ <30°; (*SR,RS*)-**5a**-Me$_5$, 30 with 10° < 2θ <15°). Space groups were determined from systematic absences ((*S*)-**4a**$^+$SbF$_6^-$ and (*SRR,RSS*)-**5f**, none; (*SS*)-**5a**, 0*k*0 *k*=2*n*; (*SR,RS*)-**5a**-Me$_5$, 0*kl* *h*+*k* = 2*n*+1, *h*0*l* *h* = 2*n*+1) and subsequent least-squares refinements. Lorentz, polarization, and empirical absorption (ψ scans) corrections were applied. The structures were solved by standard heavy-atom techniques with the SDP-VAX package.[48] The absolute configurations of (*S*)-**4a**$^+$SbF$_6^-$ and (*SS*)-**5a** were established by two independent methods (Roger's η parameters, 1.029(9) and 0.998(2);[49] Flack's *x* parameters, 0.005(5) and 0.012(10)[50]). Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms positions were calculated and added to the structure factor calculations but were not refined, except for H21 in (*SRR,RSS*)-**5f**, which was located and refined. Scattering factors, and $\Delta f'$ and $\Delta f''$ values, were taken from the literature.[51]

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Supporting Information Available: General procedures, syntheses of sulfide ligands, experiments with deuterated compounds, and tables of crystallographic data (18 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(47) Extended pumping may volatilize the product and lower yields.

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