Reactions of *t*-BuOK and Dibenzyl, Benzyl Allyl, and Allyl *β*-Keto Sulfide Complexes of the Chiral Rhenium Lewis Acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$: Highly Diastereoselective or Chemoselective [2,3]-Sigmatropic Rearrangements

Phillip C. Cagle, Oliver Meyer, Dominique Vichard, Konrad Weickhardt, Atta M. Arif, and J. A. Gladysz*

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

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Reaction of the dibenzyl sulfide complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(S(CH_2Ph)_2)]^+TfO^-$ (**4a**$^+TfO^-$) and *t*-BuOK (THF, −80 °C) gives the thiolate $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(SCH(o\text{-}C_6H_4CH_3)Ph)$ (**5a**; 99%) as a 96:4 mixture of *SR*,*RS*/*SS*,*RR* Re:C diastereomers. This transformation involves initial deprotonation of a benzyl group to give an ylide, followed by [2,3]- and [1,3]-rearrangements. A crystal structure of (*SR*,*RS*)-**5a** establishes the configuration. Similar reactions of the benzyl allyl sulfide complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(S(CH_2CR{=}CH_2)CH_2Ph)]^+TfO^-$ (R = H, CH_3) give mainly the thiolates (*SS*,*RR*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(SCH(CH_2CR{=}CH_2)Ph)$, derived from benzyl group deprotonation. Some thiolates derived from allyl group deprotonation also form. Similar reactions of the allyl *β*-keto sulfide complexes $[(\eta^5\text{-}C_5R_5)Re(NO)(PPh_3)(S(CH_2CR'{=}CR''_2)CH_2COPh)]^+X^-$ (R/R′/R″ = H/H/H, H/H/CH_3, H/CH_3/H, CH_3/H/H) give the thiolates $(\eta^5\text{-}C_5R_5)Re(NO)(PPh_3)(SCH(CR''_2CR'{=}CH_2)COPh)$, derived from CH_2COPh group deprotonation, as >96:<4 to 68:32 diastereomer mixtures. Reactions of **4a**$^+TfO^-$ with MeLi give mainly the [1,2]-rearrangement product $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(SCH(CH_2Ph)Ph)$ ((35−70):(65−30) diastereomer mixtures), which has been independently synthesized. The thiolate ligands are easily converted to free methyl sulfides. Mechanisms of diastereoselection, and similar reactions of organic sulfonium salts, are discussed.

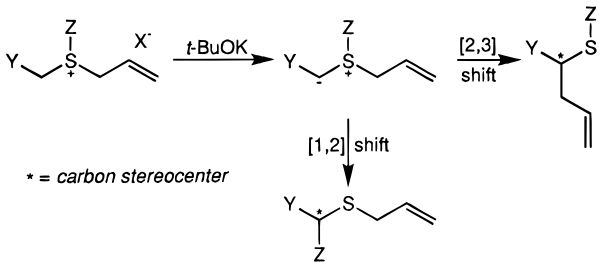
Sulfur ylides are extensively utilized in organic synthesis.[1] They can be generated, among other methods, by the deprotonation of sulfonium salts. When allyl or benzyl substituents are present, rapid bond migrations ensue.[1] In most cases, [2,3]-sigmatropic rearrangements occur. However, [1,2]-rearrangements also have precedent. These possibilities are diagrammed in Scheme 1.

We wondered if analogous transformations could be effected with cationic transition-metal complexes of unsaturated organic sulfides. Indeed, sulfur donor ligands have been found to undergo a variety of deprotonation reactions.[2] Furthermore, the types of rearrangements in Scheme 1 usually afford new carbon stereocenters. Hence, chiral metal fragments might be able to control the carbon configurations of the products. All enantioselective versions of these reactions reported to date are of limited generality or effectiveness.[3,4]

We recently discovered that adducts of the chiral rhenium Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (**I**) and symmetrical diallyl or dipropargyl sulfides rapidly react with *t*-BuOK in THF at −80 °C.[5] As exemplified in Scheme 2 with the parent diallyl sulfide complex, air-stable thiolate complexes rapidly form. These are derived from [2,3]-rearrangements of intermediate ylides and are isolated in high yields and diastereomeric purities. The thiolate complexes are easily converted to free, desymmetrized methyl or benzyl sulfides of high enantiomeric purities. The rhenium Lewis acid **I** can be conveniently recycled without loss of configuration.

We sought to extend the chemistry in Scheme 2 to other types of sulfide ligands. Three classes were

Scheme 1. Generation and Rearrangements of Allyl-Substituted Sulfur Ylides



[⊗] Abstract published in *Advance ACS Abstracts*, December 1, 1995.

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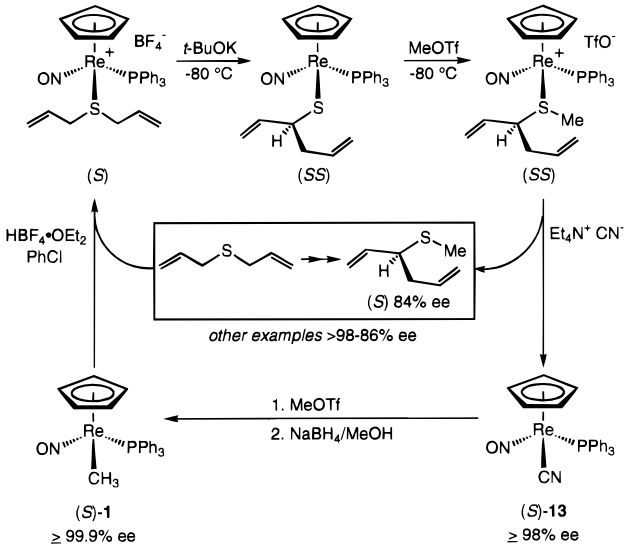
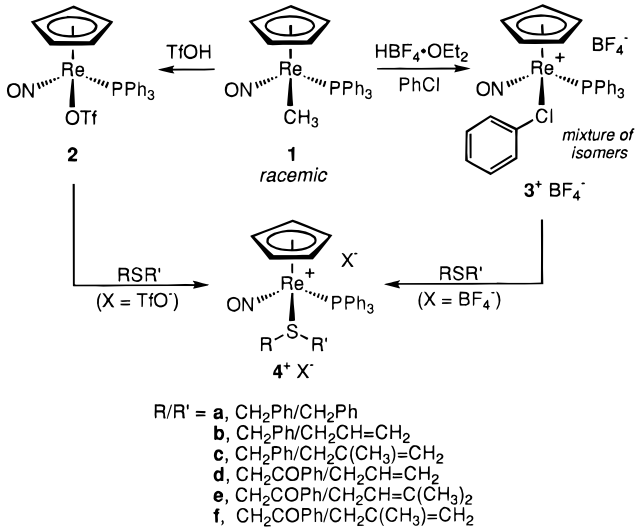
Scheme 2. Enantioselective Conversion of Achiral Diallyl Sulfides to Rearranged Chiral Sulfides Mediated by the Recyclable Chiral Rhenium Auxiliary I



Scheme 3. Syntheses of New Sulfide Complexes



R/R' = **a**, CH_2Ph/CH_2Ph
b, $CH_2Ph/CH_2CH{=}CH_2$
c, $CH_2Ph/CH_2C(CH_3){=}CH_2$
d, $CH_2COPh/CH_2CH{=}CH_2$
e, $CH_2COPh/CH_2CH{=}C(CH_3)_2$
f, $CH_2COPh/CH_2C(CH_3){=}CH_2$

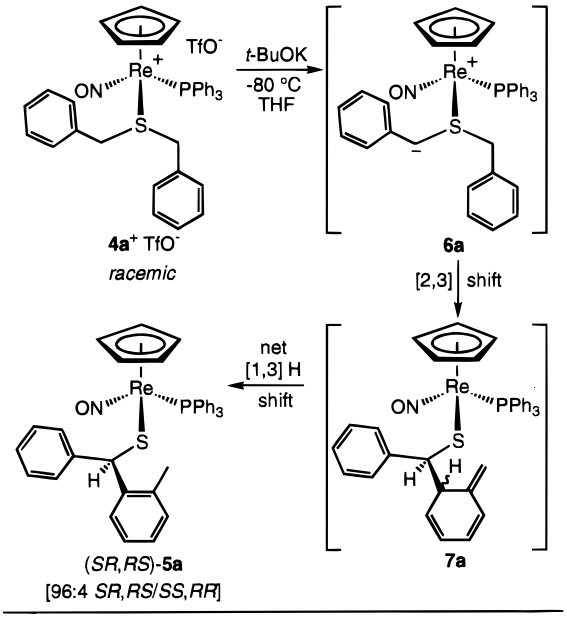
targeted: (1) dibenzyl sulfides, (2) benzyl allyl sulfides, and (3) allyl β-keto sulfides. As detailed below, the corresponding adducts of **I** react similarly with *t*-BuOK. However, a greater range of diastereoselectivities is observed. Also, in certain cases products derived from other rearrangement pathways, such as the [1,2]-shift in Scheme 1, can be detected.

Results

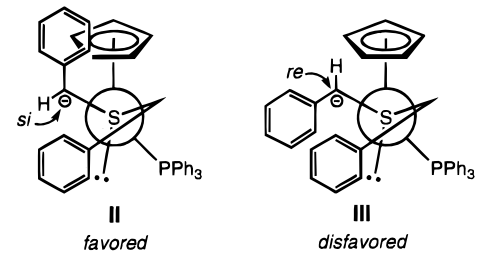
1. Syntheses of Sulfide Complexes. Functional equivalents of the chiral Lewis acid **I** were generated as summarized in Scheme 3. First, the easily prepared air-stable racemic methyl complex (η^5-C_5H_5)Re(NO)(PPh_3)(CH_3O) (**1**)[6] and triflic acid (TfOH) were combined to give the triflate complex (η^5-C_5H_5)Re(NO)(PPh_3)(OTf) (**2**).[7] Alternatively, **1** and HBF_4·OEt_2 were reacted in chlorobenzene (−45 °C) to generate labile adducts of formal composition [(η^5-C_5H_5)Re(NO)(PPh_3)(ClPh)]$^+BF_4^-$ (**3**$^+BF_4^-$).[8] Subsequent additions of the unsaturated sulfides shown in Scheme 3 gave the air-stable sulfide complexes [(η^5-C_5H_5)Re(NO)(PPh_3)(SRR′)]$^+X^-$ (**4a**−**f**$^+X^-$) in 92−53% unoptimized yields.

Complexes **4**$^+X^-$, and other new compounds below, were characterized by IR, NMR (^{1}H, ^{13}C, ^{31}P), and microanalysis. Data are summarized in the Experimental Section. IR and NMR properties indicated free, as opposed to coordinated, O═C and C═C moieties. The diastereotopic benzyl groups in **4a**$^+$TfO$^-$ gave only one set of NMR signals at room temperature, consistent with the low sulfur inversion/rotation barriers found earlier in this class of compounds (ca. 10 kcal/mol).[5,9] Similarly, **4b**−**f**$^+X^-$, which can exist as mixtures of Re:S configurational diastereomers, gave only a single set of resonances at room temperature.

Scheme 4. Reaction of Dibenzyl Sulfide Complex 4a$^+$TfO$^-$



transition state model:



2. Reactions of the Dibenzyl Sulfide Complex and *t*-BuOK. As shown in Scheme 4, THF solutions of the dibenzyl sulfide complex **4a**$^+$TfO$^-$ and *t*-BuOK were combined at −80 °C. Workup gave the air-stable, analytically pure thiolate complex (η^5-C_5H_5)Re(NO)-(PPh_3)(SCH(*o*-$C_6H_4CH_3$)Ph) (**5a**) in 99% yield as a 96:4 mixture of *SR,RS*/*SS,RR* Re:C configurational diastereomers.[10,11] Configurations were assigned crystallo-

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Table 1. Effects of Solvent and Temperature on the Conversion of 4a$^+$TfO$^-$ to 5a[a]

solvent	temp (°C)	(*SR*,*RS*)-**5a**/(*SS*,*RR*)-**5a**
THF	−80	96:04
CH_2Cl_2	−80	92:08
toluene[b]	−80	90:10
ethyl acetate[c]	−80	70:30
THF	−60	95:05
CH_2Cl_2	−60	92:08
acetonitrile	−60	86:14
THF	ambient	90:10
CH_2Cl_2	ambient	75:25

[a] Reactions were conducted in NMR tubes utilizing *t*-BuOK in THF as described in the Experimental Section. [b] **4a**$^+$TfO$^-$ is slightly soluble in toluene. [c] **4a**$^+$TfO$^-$ is insoluble in ethyl acetate.

graphically (below). This transformation was presumed to involve the initial formation of ylide **6a** (Scheme 4), followed by a [2,3]-sigmatropic rearrangement. This would yield an intermediate with a dearomatized ring (**7a**), which could then undergo a net [1,3]-hydrogen migration to give **5a**. Organic benzyl sulfonium salts are well known to undergo similar transformations.[3c,12]

The diastereoselectivity of the related reaction of the diallyl sulfide complex in Scheme 2 was solvent- and temperature-dependent. Thus, **4a**$^+$TfO$^-$ and *t*-BuOK were combined under additional conditions as summarized in Table 1. All reactions were quantitative by NMR. The original solvent, THF, gave the greatest **5a** diastereomer ratio. As would be intuitively expected, diastereoselectivities decreased at higher reaction temperatures.

A sample of **5a** was crystallized to diastereomeric purity. NMR spectra of the macroscopic sample showed that only the major diastereomer was present. The crystal structure was determined as summarized in Table 2 and the Experimental Section. Refinement gave the structure shown in Figure 1. The unit cell contained equal amounts of *SR* and *RS* enantiomers.[9] Key bond lengths, bond angles, and torsion angles are listed in Table 4. The metal−sulfur conformation is similar to those in four related rhenium and ruthenium thiolate complexes.[5,13] In all cases, the carbon substituent is directed into the least congested interstice between the two smallest ligands (rhenium, cyclopentadienyl and NO; ruthenium, cyclopentadienyl and CO).

The relative rhenium:carbon configuration of the major diastereomer of **5a** is identical with those of thiolate complexes generated from the corresponding diallyl sulfide complexes (Scheme 2).[5] Hence, we presume that the dominant diastereomers of thiolate complexes formed from sulfide complexes **4b**−**f**$^+$X$^-$ below have analogous configurations. However, these assignments should be viewed as provisional. The formation of (*SR*,*RS*)-**5a** is consistent with the transition state model **II** (Scheme 4), as further elaborated in the Discussion.

3. Reactions of Benzyl Allyl Sulfide Complexes. As shown in Scheme 5, the benzyl allyl sulfide complexes **4b**,**c**$^+$TfO$^-$ could potentially give two types of ylides: **6b**,**c**, from benzyl group deprotonation, or **8b**,**c**

Table 2. Summary of Crystallographic Data for (*SR*,*RS*)-(η^5-C_5H_5)Re(NO)(PPh_3)(SCH(*o*-$C_6H_4CH_3$)Ph) ((*SR*,*RS*)-5a)

mol formula	$C_{37}H_{33}NOPReS$
mol wt	756.920
cryst syst	monoclinic
space group	$P2_1/c$
cell dimens (16 °C)	
a, Å	12.667(2)
b, Å	8.069(1)
c, Å	31.960(5)
β, deg	90.3783(5)
V, Å^3	3266.32
Z	4
d_{calc}, g/cm^3	1.539
d_{obs}, g/cm^3 (ether/CH_2I_2)	1.50
cryst dimens, mm	0.43 × 0.33 × 0.25
diffractometer	CAD4
radiation, Å	λ(Mo Kα), 0.710 73
data collection method	θ−2θ
scan speed, deg/min	variable
no. of reflns measd	6480
scan width, deg	0.80 + 0.34 tan θ
2θ limit, deg	4.00−50.00
total no. of unique data	5734
no. of obs data, $I > 3\sigma(I)$	4460
abs coeff, cm^{-1}	39.079
min transmissn, %	78.97
max transmissn, %	99.95
no. of variables	383
goodness of fit	1.5850
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.0297
$R_w = \sum\|\|F_o\| - \|F_c\|\|w^{1/2}/\sum\|F_o\|w^{1/2}$	0.0442
weighting scheme	non-Poisson contribn
ignorance factor *P*	0.04
Δ/σ (max)	0.003
$\Delta\rho$ (max), e/Å^3	0.928 (ca. 1.123 Å from Re)

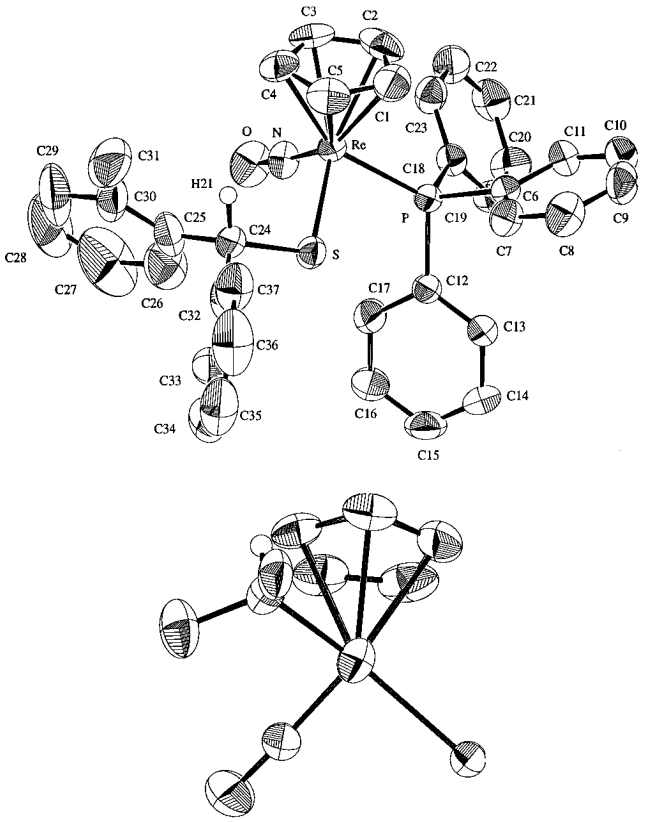

Figure 1. Structure of the *SR* enantiomer of (*SR*,*RS*)-(η^5-C_5H_5)Re(NO)(PPh_3)(SCH(*o*-$C_6H_4CH_3$)Ph) ((*SR*,*RS*)-**5a**): (top) numbering diagram; (bottom) Newman-type projection down the sulfur−rhenium bond with phenyl rings omitted.

(10) The configuration at rhenium is specified first (and according to conventions described previously).[9]

(11) All product ratios are normalized to 100. Error limits on each integer are generally ±2. Diastereomer ratios were determined by integration of the following NMR signals: **5a**, η^5-C_5H_5 ^{1}H; **5d** and **5d**-Me_5, SCH ^{1}H; **5e**, η^5-C_5H_5 and SCH ^{1}H and ^{31}P; **5f**, η^5-C_5H_5 ^{1}H; **11f**$^+$TfO$^-$ and **17**, ^{31}P.

(12) Reference 1, pp 922−923, 967−971.

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Table 3. Atomic Coordinates and Equivalent Isotropic Thermal Parameters of Located Atoms of (*SR,RS*)-5a[a]

atom	*x*	*y*	*z*	*B* (Å^2)
Re	0.02926(2)	0.20448(3)	0.41544(1)	2.674(4)
S	0.1259(1)	0.2364(2)	0.35220(5)	3.34(3)
P	−0.1057(1)	0.0701(2)	0.37749(5)	2.60(3)
O	0.1116(4)	−0.1108(6)	0.4492(2)	5.3(1)
N	0.0792(4)	0.0142(6)	0.4342(2)	3.5(1)
C1	−0.0582(6)	0.4587(9)	0.4212(2)	4.8(2)
C2	−0.0809(6)	0.3518(9)	0.4563(3)	5.3(2)
C3	0.0139(6)	0.3260(8)	0.4776(2)	4.5(2)
C4	0.0935(6)	0.4139(8)	0.4577(2)	4.2(1)
C5	0.0496(6)	0.4927(8)	0.4225(2)	4.5(2)
C6	−0.2037(5)	0.2118(7)	0.3550(2)	3.0(1)
C7	−0.1696(5)	0.3337(8)	0.3270(2)	3.8(1)
C8	−0.2424(6)	0.4388(9)	0.3084(3)	5.0(2)
C9	−0.3480(6)	0.4241(9)	0.3177(3)	5.0(2)
C10	−0.3813(5)	0.3078(9)	0.3453(3)	4.8(2)
C11	−0.3110(5)	0.2009(8)	0.3641(2)	3.9(1)
C12	−0.0716(4)	−0.0603(7)	0.3332(2)	2.8(1)
C13	−0.1298(5)	−0.0598(8)	0.2964(2)	3.3(1)
C14	−0.1054(5)	−0.1670(8)	0.2634(2)	3.9(1)
C15	−0.0244(6)	−0.276(1)	0.2683(2)	5.1(2)
C16	0.0345(6)	−0.274(1)	0.3045(3)	5.8(2)
C17	0.0117(5)	−0.1701(9)	0.3371(2)	4.6(2)
C18	−0.1853(4)	−0.0733(7)	0.4092(2)	3.0(1)
C19	−0.2439(5)	−0.2004(8)	0.3900(2)	3.8(1)
C20	−0.3058(6)	−0.3049(9)	0.4143(2)	4.6(2)
C21	−0.3112(5)	−0.2820(9)	0.4567(3)	4.7(2)
C22	−0.2535(6)	−0.160(1)	0.4758(2)	4.6(2)
C23	−0.1896(5)	−0.0576(8)	0.4519(2)	3.8(1)
C24	0.2545(5)	0.3287(8)	0.3664(2)	3.4(1)
C25	0.3252(5)	0.219(1)	0.3930(3)	4.9(2)
C26	0.3221(7)	0.050(1)	0.3896(3)	6.8(2)
C27	0.3909(9)	−0.052(1)	0.4118(4)	11.7(3)
C28	0.4661(8)	0.021(2)	0.4394(3)	13.0(4)
C29	0.4666(7)	0.183(2)	0.4428(3)	11.4(4)
C30	0.4000(6)	0.285(1)	0.4202(3)	6.3(2)
C31	0.4105(7)	0.465(2)	0.4268(3)	8.8(3)
C32	0.3073(5)	0.3880(9)	0.3275(2)	4.1(1)
C33	0.3490(6)	0.277(1)	0.2984(2)	5.1(2)
C34	0.3924(6)	0.333(1)	0.2611(3)	7.6(3)
C35	0.3933(6)	0.499(1)	0.2522(3)	8.2(3)
C36	0.3528(7)	0.608(1)	0.2794(3)	8.0(2)
C37	0.3102(6)	0.553(1)	0.3178(3)	5.7(2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3$ [$a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)$].

Table 4. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) in (*SR,RS*)-5a

Re−P	2.354(2)	Re−C4	2.309(6)
Re−S	2.384(2)	Re−C5	2.351(7)
Re−N	1.764(5)	S−C24	1.845(6)
N−O	1.189(7)	C24−C25	1.48(1)
Re−C1	2.339(7)	C24−C32	1.493(9)
Re−C2	2.256(7)	C30−C31	1.48(2)
Re−C3	2.226(6)		
P−Re−N	91.8(2)	S−Re−N	101.3(2)
S−Re−P	89.31(5)	Re−S−C24	107.0(2)
C1−C2−C3	107.1(7)	Re−N−O	176.0(6)
C3−C4−C5	108.2(7)	C2−C3−C4	109.0(7)
C2−C1−C5	107.2(7)	C4−C5−C1	108.5(7)
S−C24−C25	114.8(5)	C24−C25−C32	112.8(6)
S−C24−C32	108.9(5)	C25−C30−C31	121.8(9)
P−Re−S−C24	−175.3(2)	Re−S−C24−C25	65.7(5)
N−Re−S−C24	−83.6(3)	Re−S−C24−C32	−166.7(4)

from allyl group deprotonation. These would lead to different thiolate complexes. Thus, THF solutions of **4b**$^+$TfO$^-$ and *t*-BuOK were reacted at −80 °C. Workups gave slightly varying mixtures of three or four products. In one typical case (Experimental Section), a 43:37:20 mixture of three thiolate complexes was obtained in 95% yield. Crystallization gave samples enriched in the major product, which ^{1}H and ^{13}C NMR data clearly indicated to be (*SS,RR*)-(η^5-C_5H_5)Re(NO)(PPh_3)(SCH(CH_2-CH=CH_2)Ph) ((*SS,RR*)-**5b**)—derived from rearrangement of ylide **6b**.

A similar reaction of **4c**$^+$TfO$^-$ and *t*-BuOK gave a 72:15:13 mixture of three thiolate complexes. The major product was isolated by crystallization, and ^{1}H and ^{13}C NMR data showed the structure to be (*SS,RR*)-(η^5-C_5H_5)Re(NO)(PPh_3)(SCH($CH_2C(CH_3)$=CH_2)Ph) ((*SS,RR*)-**5c**). The NMR data also established that the minor products in both reactions were constitutional isomers, as opposed to diastereomers. Hence, allowing for detection limits, **5b**,**c** are generated as ≥96:≤4 mixtures of *SS,RR*/*SR,RS* diastereomers.

We sought to identify at least some of the minor isomeric products. In the case of **4b**$^+$TfO$^-$, NMR data were consistent with the structures (η^5-C_5H_5)Re(NO)(PPh_3)(SCH=$CHCH_2$(*p*-$C_6H_4CH_3$)) (**9**) and (η^5-C_5H_5)Re(NO)(PPh_3)(SCH=$CHCH_2CH_2$Ph) (**10**), shown in Scheme 5. Importantly, the corresponding free methyl sulfides had been characterized previously.[14] Thus, following the protocol in Scheme 2, the reaction mixture from **4b**$^+$TfO$^-$ was treated with MeOTf. Workup gave a mixture of [(η^5-C_5H_5)Re(NO)(PPh_3)(S(Me)CH(CH_2-CH=CH_2)Ph)]$^+$TfO$^-$ (**11b**$^+$TfO$^-$; from **5b**) and two isomeric methyl sulfide complexes. These were only partially characterized. Subsequent reaction with $Et_4N^+CN^-$ gave a 47:34:19 mixture of MeSCH(CH_2-CH=CH_2)Ph (**12b**) and two isomeric methyl sulfides.

The mixture was carefully characterized by ^{1}H and ^{13}C NMR. COSY, HETCOR, and APT experiments enabled complete assignments of the nonaromatic protons and carbons for each isomer. The chemical shifts and coupling constants ($CDCl_3$) closely matched those previously reported (CCl_4)[14] for **12b**, MeSCH=$CHCH_2$(*p*-$C_6H_4CH_3$), and MeSCH=$CHCH_2CH_2$Ph. In particular, diagnostic features associated with the MeSCH=CH moieties of the last two were evident.

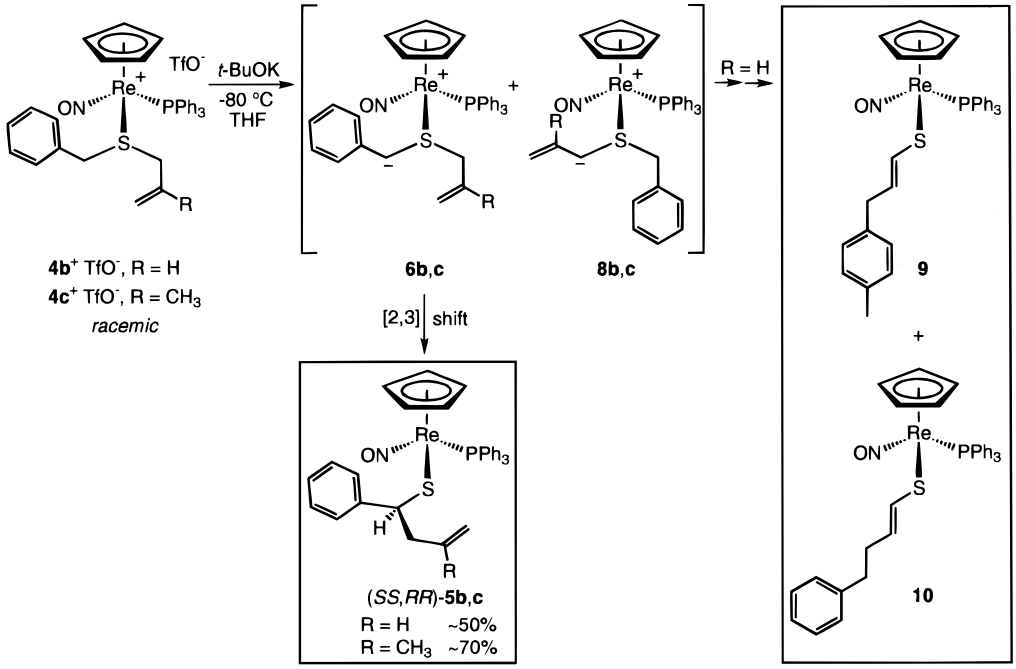
Both **9** and **10** are derived from the ylide **8b** (Scheme 5). Formally, **10** can form by a [1,4]-shift. Complex **9** can be viewed as arising from a [4,5]-shift to give a dearomatized intermediate (cf. **7a**, Scheme 4), followed by a net [1,5]-hydrogen shift. However, other mechanistic possibilities exist. Interestingly, organic benzyl allyl sulfides undergo similar transformations when treated with *n*-BuLi.[14]

4. Reactions of Allyl *β*-Keto Sulfide Complexes. As summarized in Scheme 6, similar reactions of the allyl *β*-keto sulfide complexes **4d**−**f**$^+$X$^-$ and *t*-BuOK were investigated.[15] Analytically pure thiolate complexes **5d**−**f** were isolated in 98−66% yields. These are derived from ylides **6d**−**f**, formed by deprotonations of the *β*-keto moieties. Diastereoselectivities depended upon the nature of the allyl group. Furthermore, solvent trends did not follow those found with the dibenzyl sulfide complex **4a**$^+$TfO$^-$ in Table 1. For example, under the standard conditions in THF, **5d** was obtained as a 68:32 mixture of diastereomers. In CH_2Cl_2, the ratio improved to 74:26. In CH_2Cl_2, **5e** was obtained as a ≥96:≤4 mixture of diastereomers (^{31}P NMR, 96:4; ^{1}H NMR, (98−99):(2−1)).[10]

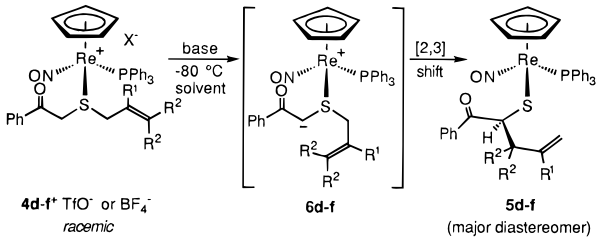
(14) Biellmann, J. F.; Ducep, J. B.; Schirlin, D. *Tetrahedron* **1980**, *36*, 1249.

(15) For similar reactions of related organic sulfonium salts, see reference 1, pp 919, 922−924, 941.

Scheme 5. Reactions of Benzyl Allyl Sulfide Complexes 4b,c$^+$TfO$^-$

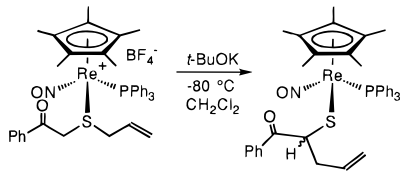


Scheme 6. Reactions of Allyl β-Keto Sulfide Complexes 4d−f$^+$X$^-$



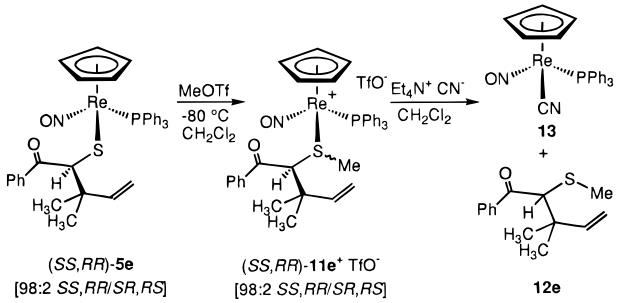
Reactant	R^1	R^2	Base	Solvent	Products[a]	Ratio	Yield (%)
4d$^+$ TfO$^-$	H	H	*t*-BuOK	THF	(*SS*,*RR*)/(*SR*,*RS*)-**5d**	68:32	82
4f$^+$ BF_4^-	CH_3	H	*t*-BuOK	THF	(*SS*,*RR*)/(*SR*,*RS*)-**5f**	76:24	66
4d$^+$ TfO$^-$	H	H	*t*-BuOK	CH_2Cl_2	(*SS*,*RR*)/(*SR*,*RS*)-**5d**	74:26	88
4e$^+$ TfO$^-$	H	CH_3	*t*-BuOK	CH_2Cl_2	(*SS*,*RR*)/(*SR*,*RS*)-**5e**	≥96:≤4	98
4f$^+$ BF_4^-	CH_3	H	*t*-BuOK	CH_2Cl_2	(*SS*,*RR*)/(*SR*,*RS*)-**5f**	84:16	69
4d$^+$ TfO$^-$	H	H	LDA	THF	(*SS*,*RR*)/(*SR*,*RS*)-**5d**	71:29	92

[a] provisional assignments



Complex **5f** also formed in a higher diastereomer ratio in CH_2Cl_2 than in THF (84:16 vs 76:24). However, a tetrafluoroborate salt, **4f**$^+BF_4^-$, was employed as the precursor, precluding exact comparisons with **4d**,**e**$^+$TfO$^-$. The triflate salt **4f**$^+$TfO$^-$ could not be prepared by the route in Scheme 3. We also wondered whether different bases might give improved diastereoselectivities. It has been previously shown that amides can be substituted for *t*-BuOK in Scheme 2.[5b] However, a reaction of **4d**$^+$TfO$^-$ and LDA in THF gave **5d** as only a 71:29 mixture of diastereomers.

Scheme 7. Detachment of Thiolate Ligands



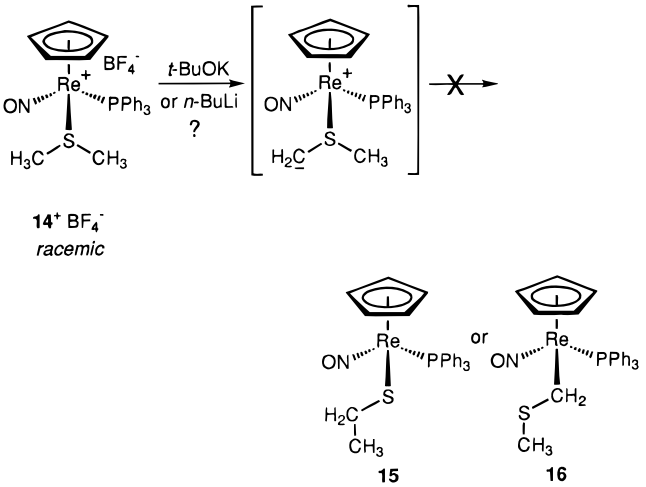
It was also hoped that *pentamethyl*cyclopentadienyl complexes might give improved diastereoselectivities. Thus, **4d**$^+$-$Me_5BF_4^-$ was prepared via a chlorobenzene complex similar to that shown in Scheme 3. However, reaction with *t*-BuOK in CH_2Cl_2 gave **5d**-Me_5 in a diastereomer ratio only slightly higher than that of **5d** (Scheme 6). Interestingly, pentamethylcyclopentadienyl analogs were found to give *reversed* selectivities in Scheme 2.[5b] Hence, configurations are not assigned to the diastereomers of **5d**-Me_5.

We sought to verify that the thiolate ligand detachment protocol in Scheme 2 would also apply to the functionalized thiolate complexes in Scheme 6. Thus, **5e** (98:2 *SS*,*RR*/*SR*,*RS*) and MeOTf were combined in CH_2Cl_2 at −80 °C. As shown in Scheme 7, the cationic methyl sulfide complex [(η^5-C_5H_5)Re(NO)(PPh_3)(S(Me)-CH(C(CH_3)$_2$CH=CH_2)COPh)]$^+$TfO$^-$ (**11e**$^+$TfO$^-$; 98:2 *SS*,*RR*/*SR*,*RS*) was isolated in 85% yield. Subsequent reaction with $Et_4N^+CN^-$ gave the analytically pure methyl sulfide MeSCH(CH_2CH=C(CH_3)$_2$)COPh (**12e**) in 98% yield and the cyanide complex (η^5-C_5H_5)Re(NO)-(PPh_3)(CN) (**13**)[16] in 85% yield.

5. Other Types of Rearrangements. We wondered whether complexes of **I** and saturated sulfide ligands would give base-induced rearrangements. As

(16) (a) Fernández, J. M.; Gladysz, J. A. *Organometallics* **1989**, *8*, 207. (b) Dewey, M. A.; Knight, D. A.; Klein, D. P.; Arif, A. M.; Gladysz, J. A. *Inorg. Chem.* **1991**, *30*, 4995.

Scheme 8. Attempted Reactions of Dimethyl Sulfide Complex $14^+BF_4^-$



sketched in Scheme 8, the previously reported dimethyl sulfide complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(S(CH_3)_2)]^+BF_4^-$ (**14**$^+BF_4^-$)[9] might give an ylide that could undergo a [1,2]-methyl shift to give the thiolate complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(SCH_2CH_3)$ (**15**) or a [1,2]-rhenium shift to give the alkyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2SCH_3)$ (**16**). The latter has been independently synthesized and characterized.[17]

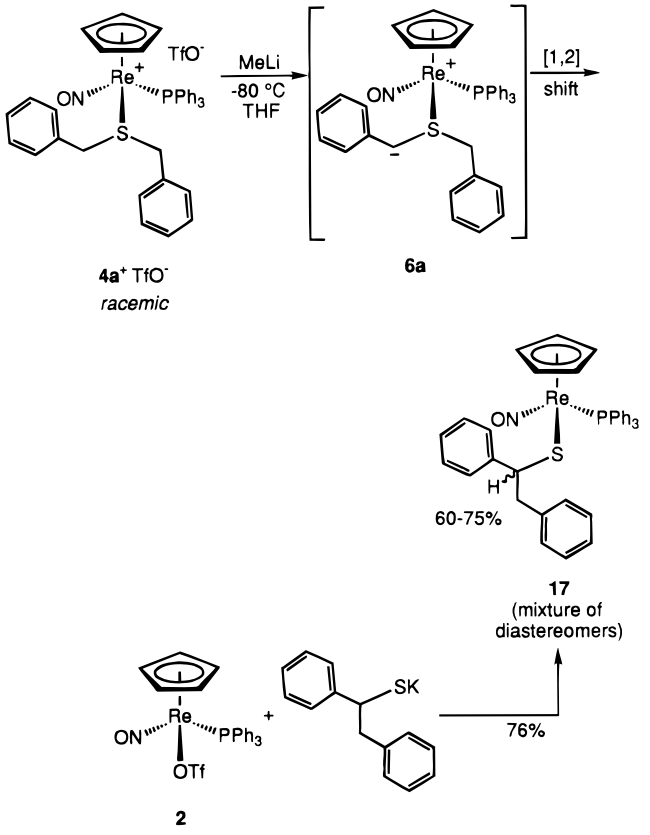
Thus, a THF suspension of **14**$^+BF_4^-$ and a THF solution of *t*-BuOK were combined in an NMR tube at −95 °C (Scheme 8). The sample became homogeneous, but a ^{31}P NMR spectrum (−95 °C) showed many products (major at 28.2 ppm). A similar reaction under homogeneous conditions in CH_2Cl_2 gave a comparable mixture. In each case, significant amounts of starting material remained. When **14**$^+BF_4^-$ and *n*-BuLi were combined in THF at −95 °C, a multitude of products formed. In all of these experiments, the chemical shifts of the resonances of **15** or **16** can be confidently predicted. In no case was an appreciable amount of either species present.

We also examined reactions of the dibenzyl sulfide complex **4a**$^+$TfO$^-$ and stronger bases. In certain cases, evidence for the [1,2]-rearrangement product $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(SCH(CH_2Ph)Ph)$ (**17**) was obtained. In order to help verify the formation of **17**, an authentic sample was synthesized from the triflate complex **2** and the corresponding potassium thiolate, as shown in Scheme 9. Workup gave a 61:39 mixture of Re:C diastereomers in 76% yield. Since there was not an obvious basis for assigning configurations, the diastereomers were simply termed "A" and "B".

Next, THF solutions of **4a**$^+$TfO$^-$ and ether solutions of MeLi were combined under slightly differing conditions in NMR tubes at −80 °C (Scheme 9). Reactions were complete at −80 °C, and workups gave samples (ca. 63−78%) that contained 60−75% of **17**. Two minor products were present that appeared to be thiolate complexes but were distinct from **5a**. As the **4a**$^+$TfO$^-$:MeLi stoichiometries were varied from 1:1.1 to 1:1.6 to 1:2.0 to 1:2.5, the diastereomer ratios (A:B) increased from 35:65 to 45:55 to 60:40 to 70:30. Yields of **17** were comparable when toluene suspensions of **4a**$^+$TfO$^-$ were utilized but were somewhat higher when MeLi/LiBr was employed.

(17) McCormick, F. B.; Gleason, W. B.; Zhao, X.; Heah, P. C.; Gladysz, J. A. *Organometallics* **1986**, *5*, 1778.

Scheme 9. Generation and Independent Synthesis of a [1,2]-Rearrangement Product



Dichloromethane solutions of **4a**$^+$TfO$^-$ and ether solutions of MeLi were similarly combined at −95 °C. At 1:1.1 and 1:2.0 stoichiometries, diastereomer ratios (A/B) were 44:56 and 86:14, respectively. Workup of the latter gave a sample (ca. 98%) that contained 78% of **17**. Interestingly, reactions of organic benzyl sulfonium salts and bases often give greater proportions of [1,2]-rearrangement products under aprotic conditions.[18] With the procedure in Scheme 4, some *t*-BuOH is present. Marked effects upon the base concentration have also been demonstrated.[18]

Discussion

Schemes 4−6 establish, together with earlier work (Scheme 2),[5] that a variety of types of cationic unsaturated sulfide complexes of the chiral rhenium Lewis acid **I** can react with *t*-BuOK to give ylides. Most of these rapidly undergo subsequent [2,3]-sigmatropic rearrangements. One of the most striking aspects of this chemistry is the degree to which it parallels that of *organic* sulfonium salts. As noted above, the minor products in Scheme 5, and the conditions required for the [1,2]-rearrangement in Scheme 9, all have close analogy in purely organic systems. Hence, the rhenium fragment appears to act as a chemically innocent auxiliary.

Of course, the rhenium is not a stereochemically innocent auxiliary. It efficiently controls the configuration of the new carbon stereocenter in **5a** (Scheme 4). As discussed at length elsewhere,[5b] we presently analyze diastereoselection in terms of two types of competing transition states, exemplified by **II** and **III** in Scheme

(18) Reference 1, pp 921−922.

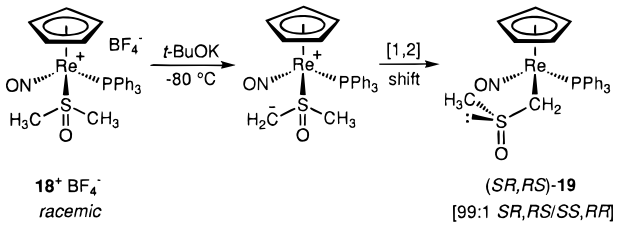
4. Both of these would give thiolate complex **5a** in the most stable rhenium−sulfur conformation,[5b] similar to that in the crystal structure (Figure 1). Both are in turn derived from the most stable rhenium−sulfur conformation of precursor **4a**$^+$TfO$^-$. However, the carbon configuration of the major diastereomer of **5a** requires that the *si* face of the ylide carbanion be alkylated (when the configuration at rhenium is *S*). This feature is unique to **II**.

We had originally thought that **II** might be disfavored due to steric interactions between the cyclopentadienyl ligand and the phenyl substituent on the ylide carbon. However, **5a** is formed in a diastereomer ratio that matches or exceeds those of thiolates derived from most diallyl sulfide complexes (Scheme 2).[5] These reactions involve ylides with smaller vinyl substituents. Therefore, we suspect there is some type of attractive interaction between the cyclopentadienyl ligand and the unsaturated ylide carbanion substituents. Evidence for a variety of related phenomena has been reported.[19,20] Regardless, our "standard conditions" in THF give high *Re*:S*C* diastereomer ratios for all symmetrical diallyl, dipropargyl, and dibenzyl sulfide complexes of **I** examined to date.

The conversions of the unsymmetrically substituted benzyl allyl sulfide complexes **4b**,**c**$^+$TfO$^-$ to **5b**,**c** (Scheme 5) are also highly diastereoselective. The dominant diastereomers would logically arise from transition states very closely related to **II**. However, these reactions are not very chemoselective, presumably due to the modest stability differences between the benzyl- and allyl-stabilized ylides **6b**,**c** and **8b**,**c**. In contrast, reactions of the allyl β-keto sulfide complexes **4d**−**f**$^+$X$^-$ (Scheme 6) are highly chemoselective but less diastereoselective. Here, the carbanion-stabilizing β-keto group controls the ylide that is generated. However, the transition states that would correspond to II and III—in which PhCO would replace Ph, introducing additional degrees of freedom—are apparently closer in energy. Nonetheless, we believe it should be possible to empirically optimize the results for both classes of reactions.

The conversion of **4a**$^+$TfO$^-$ to **17** in Scheme 9 shows that, under appropriate conditions, the preceding types of ylides can undergo [1,2]-shifts. Such rearrangements are frequently associated with radical pathways.[1] However, this mechanistic issue is beyond the scope of this study. The failure of the dimethyl sulfide complex **14**$^+$BF$_4^-$ to give the similar [1,2]-shift product **15** (Scheme 8) may be due to either (1) the inaccessibility of the corresponding ylide, which would lack carbanion-stabilizing substituents, or (2) the lower migratory aptitude of a methyl group. In this context, it is instructive to contrast the reactivity of **14**$^+$BF$_4^-$ with that of the analogous DMSO complex **18**$^+$BF$_4^-$. As shown in Scheme 10, the electron-withdrawing oxo group now allows an ylide to be accessed with *t*-BuOK, as evidenced by the quantitative and highly diastereoselective formation of the [1,2]-shift product **19**.[21] In this case, but not Scheme 9, the rhenium has a higher migratory aptitude than the S-alkyl group.

Scheme 10. Reaction of DMSO Complex 18$^+$BF$_4^-$



18$^+$ BF$_4^-$ *racemic*

(*SR,RS*)-**19** [99:1 *SR,RS*/*SS,RR*]

For convenience, all of the exploratory reactions in Schemes 3−9 employed racemic complexes. However, on the basis of our experience with Scheme 2,[5] equally selective transformations should occur with enantiomerically pure complexes, thereby allowing access to nonracemic organosulfur compounds by procedures such as those in Scheme 7. Furthermore, no difficulties have been encountered with gram-scale syntheses, and much larger reactions should be feasible. Finally, we also anticipate that it will be possible to realize similar processes with a variety of other cationic metal sulfide complexes. Indeed, enantioselective syntheses involving cyclopentadienyl iron or ruthenium diallyl sulfide complexes will be featured in forthcoming reports from this laboratory.[22]

Experimental Section[23,24]

[(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(S(CH$_2$Ph)$_2$)]$^+$TfO$^-$ (4a$^+$TfO$^-$). A Schlenk flask was charged with (η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(OTf) (**2**;[7] 0.383 g, 0.553 mmol) and PhCl (10 mL). Then S(CH$_2$Ph)$_2$ (0.178 g, 0.830 mmol) was added with stirring. After 18 h, a yellow precipitate was collected by filtration and washed with ether (10 mL). The filtrate was stirred an additional 6 h, and volatiles were removed by oil pump vacuum (12 h). The residue was dissolved in acetone (2 mL). The solution was added dropwise to rapidly stirred ether (50 mL). The precipitate was collected by filtration and washed with ether (10 mL). The crops were combined, washed with pentane (50 mL), and dried by oil pump vacuum to give **4a**$^+$TfO$^-$ (0.432 g, 0.476 mmol, 86%) as a yellow powder, mp 232 °C dec. Anal. Calcd for C$_{38}$H$_{34}$F$_3$NO$_4$PReS$_2$: C, 50.32; H, 3.78. Found: C, 50.42; H, 3.86. IR: ν_{NO} 1712 vs.[24]

NMR ($CDCl_3$):[24] ^{1}H, 7.54−7.04 (m, 5 Ph), 5.53 (s, C$_5$H$_5$), 4.15 (d, J_{HH} = 13, 2 SC*H*H′), 3.82 (d, J_{HH} = 13, 2 SCH*H*′); ^{13}C{^{1}H}, 133.2 (d, J_{CP} = 11, *o*-PPh), 132.3 (d, J_{CP} = 56, *i*-PPh), 131.7 (d, J_{CP} = 2, *p*-PPh), 129.3 (d, J_{CP} = 11, *m*-PPh), 134.1 (s, *i*−C*Ph*), 129.4, 129.3 (2 s, *o*-, *m*-C*Ph*), 128.3 (s, *p*-C*Ph*), 92.6 (s, C$_5$H$_5$), 48.6 (s, SCH$_2$); ^{31}P{^{1}H}, 13.0 (s).

[(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(S(CH$_2$CH=CH$_2$)CH$_2$Ph)]$^+$TfO$^-$ (4b$^+$TfO$^-$). Complex **2** (0.51 g, 0.74 mmol), PhCl (15 mL), and S(CH$_2$CH=CH$_2$)CH$_2$Ph (0.241 g, 1.46 mmol) were combined in a procedure analogous to that for **4a**$^+$TfO$^-$. After 24 h, the mixture was refluxed for 45 min and cooled. Volatiles were removed under oil pump vacuum. The residue was dissolved in acetone (5−6 mL). The solution was added dropwise to rapidly stirred ether (100 mL). The precipitate was collected by filtration, washed with ether (10 mL), and dried by oil pump vacuum to give **4b**$^+$TfO$^-$ (0.58 g, 0.68 mmol, 92%) as a yellow powder, mp 122 °C dec. Anal. Calcd for C$_{33}$H$_{32}$F$_3$NO$_4$PReS$_2$: C, 47.66; H, 3.76. Found: C, 47.38; H, 3.89. IR: ν_{NO} 1698 vs.[24]

(19) Brunner, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 897 (see sections 6−8).
(20) Nishio, M.; Umezawa, Y.; Hirota, M.; Takeuchi, Y. *Tetrahedron* **1995**, *51*, 8665.
(21) Meyer, O.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1995**, *14*, 1844.
(22) Bell, P. T.; Cagle, P. C.; Vichard, D.; Gladysz, J. A. Manuscript in preparation.
(23) Most instrumental procedures, reagent purifications, and reactant syntheses are routine. Details are given in the Supporting Information.
(24) 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).

NMR ($CDCl_3$):[24] ^{1}H, 7.57−7.04 (m, 5 Ph), 5.64 (s, C_5H_5), 5.48−5.38 (m, CH═), 5.34−5.28 (2 m, ═CH_2), 4.18 (d, J_{HH} = 13, C*H*H′Ph), 3.87 (d, J_{HH} = 13, CH*H*′Ph), 3.61 (dd, J_{HH} = 13, 7, C*H*H′CH═), 3.26 (d, J_{HH} = 13, 7, CH*H*′CH═); ^{13}C{^{1}H}, 133.0 (d, J_{CP} = 11, *o*-PPh), 132.4 (d, J_{CP} = 56, *i*-PPh), 131.7 (d, J_{CP} = 2, *p*-PPh), 129.4 (d, J_{CP} = 11, *m*-PPh), 134.1 (s, *i*-C*Ph*), 130.3 (s, CH═), 129.8, 128.9 (2 s, *o*-, *m*-C*Ph*), 128.3 (s, *p*-C*Ph*), 122.7 (s, ═CH_2), 93.1 (s, C_5H_5), 48.5, 47.1 (2 s, *C*H_2CH═, *C*H_2Ph); ^{31}P{^{1}H}, 12.7 (s).

[(η^5-C_5H_5)Re(NO)(PPh_3)(S($CH_2C(CH_3)$═CH_2)CH_2Ph)]$^+$ TfO$^-$ (4c$^+$TfO$^-$). Complex **2** (0.171 g, 0.247 mmol), PhCl (15 mL), and S($CH_2C(CH_3)$═CH_2)CH_2Ph (0.080 g, 0.45 mmol) were combined in a procedure analogous to that for **4a**$^+$TfO$^-$. After 14 h, volatiles were removed by oil pump vacuum. The residue was dissolved in acetone (3 mL). The solution was added dropwise to rapidly stirred ether/pentane (1:1 v/v, 80 mL). The precipitate was collected by filtration and washed with ether (10 mL). The filtrate was concentrated to ca. 10 mL. Pentane (30 mL) was added, and the precipitate was collected by filtration. The crops were combined, washed with ether (2 × 10 mL), and dried by oil pump vacuum to give **4c**$^+$TfO$^-$ (0.197 g, 0.227 mmol, 92%) as a yellow powder, mp 181−182 °C dec. Anal. Calcd for $C_{35}H_{36}F_3NO_4PReS_2$: C, 48.18; H, 3.93. Found: C, 48.27; H, 3.93. IR: ν_{NO} 1713 vs.[24]

NMR ($CDCl_3$):[24] ^{1}H, 7.55−7.08 (m, 5 Ph), 5.64 (s, C_5H_5), 5.20 (s, ═C*H*H′), 5.06 (s, ═CH*H*′), 4.16 (d, J_{HH} = 13, C*H*H′Ph), 3.99 (d, J_{HH} = 13, CH*H*′Ph), 3.71 (d, J_{HH} = 12, C*H*H′C(CH_3)═), 3.18 (d, J_{HH} = 12, CH*H*′C(CH_3)═), 1.41 (s, CH_3); ^{13}C{^{1}H}, 133.0 (d, J_{CP} = 11, *o*-PPh), 132.3 (d, J_{CP} = 56, *i*-PPh), 131.7 (d, J_{CP} = 2, *p*-PPh), 129.4 (d, J_{CP} = 11, *m*-PPh), 137.3 (s, *i*-C*Ph*), 134.1 (s, *C*(CH_3)═), 129.8, 128.9 (2 s, *o*-, *m*-C*Ph*), 128.3 (s, *p*-C*Ph*), 119.3 (s, ═CH_2), 92.7 (s, C_5H_5), 52.4, 49.0 (2 s, *C*H_2C(CH_3)═, *C*H_2-Ph), 20.4 (CH_3); ^{31}P{^{1}H}, 13.0 (s).

[(η^5-C_5H_5)Re(NO)(PPh_3)(S(CH_2CH═CH_2)CH_2COPh)]$^+$ TfO$^-$ (4d$^+$TfO$^-$). Complex **2** (0.267 g, 0.385 mmol), PhCl (20 mL), and S(CH_2CH═CH_2)CH_2COPh (0.111 g, 0.578 mmol) were combined in a procedure analogous to that for **4a**$^+$TfO$^-$. After 18 h, the mixture was filtered through a 5 cm silica gel plug on a frit. The plug was rinsed with ether (200 mL) and acetone (100 mL; to elute **4d**$^+$TfO$^-$). Solvent was removed from the acetone rinse by rotary evaporation. The residue was dissolved in acetone (10 mL). The solution was added dropwise to rapidly stirred heptane (500 mL). The yellow powder was collected by filtration, washed with ether (50 mL) and pentane (100 mL), and dried by oil pump vacuum to give **4d**$^+$TfO$^-$ (0.228 g, 0.258 mmol, 67%). A portion was dissolved in CH_2Cl_2 and layered with heptane. After 3 days, orange prisms of **4d**$^+$TfO$^-$ were collected by filtration, washed with pentane (10 mL), and dried by oil pump vacuum; mp 156 °C dec. Anal. Calcd for $C_{35}H_{32}F_3NO_5PReS_2$: C, 47.50; H, 3.64. Found: C, 47.43; H, 3.64. IR: ν_{NO} 1719 vs, ν_{CO} 1681 m.[24]

NMR (CD_2Cl_2):[24] ^{1}H, 7.93−7.90, 7.66−7.62, 7.53−7.28, 7.35−7.28 (4 m, 4 Ph), 5.64 (s, C_5H_5), 5.58−5.44 (m, CH═), 5.36−5.29 (m, ═CH_2), 4.45 (s, CH_2CO), 3.54 (dd, J_{HH} = 13, 8, C*H*H′CH═), 3.27 (dd, J_{HH} = 13, 7, CH*H*′CH═); ^{13}C{^{1}H}, 133.8 (d, J_{CP} = 11, *o*-PPh), 132.8 (d, J_{CP} = 56, *i*-PPh), 132.3 (d, J_{CP} = 2, *p*-PPh), 129.9 (d, J_{CP} = 11, *m*-PPh), 192.8 (s, CO), 135.5 (s, *i*-C*Ph*), 134.9 (s, *p*-C*Ph*), 130.7 (s, CH═), 129.4, 129.1 (2 s, *o*-, *m*-C*Ph*), 124.0 (s, ═CH_2), 93.4 (d, J_{CP} = 1, C_5H_5), 51.3, 48.7 (d/s, J_{CP} = 2, *C*H_2CH═, *C*H_2CO); ^{31}P{^{1}H}, 11.9 (s).

[(η^5-C_5H_5)Re(NO)(PPh_3)(S(CH_2CH═$C(CH_3)_2$)CH_2COPh)]$^+$TfO$^-$ (4e$^+$TfO$^-$). Complex **2** (0.096 g, 0.139 mmol), PhCl (20 mL), and S(CH_2CH═$C(CH_3)_2$)CH_2COPh (0.046 g, 0.208 mmol) were combined in a procedure analogous to that for **4a**$^+$TfO$^-$. After 18 h, the mixture was filtered through a 5 cm silica gel plug on a frit. The plug was rinsed with ether (200 mL) and acetone (100 mL; to elute **4e**$^+$TfO$^-$). Solvent was removed from the acetone rinse by rotary evaporation. The residue was dissolved in acetone (10 mL). The solution was added dropwise to rapidly stirred heptane (500 mL). The yellow powder was collected by filtration, washed with ether (50 mL) and pentane (100 mL), and dried by oil pump vacuum to give **4e**$^+$TfO$^-$ (0.067 g, 0.073 mmol, 53%), mp 169 °C dec. Anal. Calcd for $C_{37}H_{36}F_3NO_5PReS_2$: C, 48.68; H, 3.97. Found: C, 48.51; H, 4.00. IR: ν_{NO} 1709 vs, ν_{CO} 1685 m.[24]

NMR (CD_2Cl_2):[24] ^{1}H, 7.86−7.83, 7.66−7.26 (2 m, 4 Ph), 5.64 (s, C_5H_5), 5.04 (m, CH═), 4.30 (d, J_{HH} = 17, C*H*H′CO), 4.14 (d, J_{HH} = 17, CH*H*′CO), 3.56 (dd, J_{HH} = 13, 8, C*H*H′CH═), 3.38 (dd, J_{HH} = 13, 8, CH*H*′CH═), 1.66, 1.52 (2 s, 2 CH_3); ^{13}C-{^{1}H}, 133.7 (d, J_{CP} = 11, *o*-PPh), 133.0 (d, J_{CP} = 56, *i*-PPh), 132.3 (d, J_{CP} = 2, *p*-PPh), 129.9 (d, J_{CP} = 11, *m*-PPh), 192.8 (s, CO), 143.7 (s, ═*C*(CH_3)$_2$), 135.4 (s, *i*-C*Ph*), 134.9 (s, *p*-C*Ph*), 129.4, 129.1 (2 s, *o*-, *m*-C*Ph*), 116.8 (s, CH═), 93.3 (br s, C_5H_5), 50.3, 45.0 (2 s, *C*H_2CH═, *C*H_2CO), 26.1, 18.6 (2 s, 2 CH_3); ^{31}P-{^{1}H}, 11.0 (s).

[(η^5-C_5H_5)Re(NO)(PPh_3)(S($CH_2C(CH_3)$═CH_2)CH_2CO-Ph)]$^+$BF$_4^-$ (4f$^+$BF$_4^-$). A Schlenk flask was charged with (η^5-C_5H_5)Re(NO)(PPh_3)(CH_3) (**1**;[6] 0.244 g, 0.436 mmol) and PhCl (20 mL) and cooled to −45 °C (CH_3CN/CO_2). Then HBF_4·OEt_2 (5.5 M in ether; 79.4 μL, 0.436 mmol) was added with stirring.[7] After 5 min, S($CH_2C(CH_3)$═CH_2)CH_2COPh (0.135 g, 0.655 mmol) was added. The cold bath was allowed to warm to room temperature. After 16 h, the sample was filtered through a 5 cm silica gel plug on a frit. The plug was rinsed with ether (200 mL) and acetone/CH_2Cl_2 (1:1 v/v, 100 mL; to elute **4f**$^+$BF$_4^-$). Solvent was removed from the acetone/CH_2Cl_2 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 pentane (100 mL), and dried by oil pump vacuum to give **4f**$^+$BF$_4^-$ (0.259 g, 0.309 mmol, 71%), mp 114−116 °C dec. Anal. Calcd for $C_{35}H_{34}BF_4NO_2PReS$: C, 50.24; H, 4.10. Found: C, 49.98; H, 4.23. IR: ν_{NO} 1705 vs.[24]

NMR (CD_2Cl_2):[24] ^{1}H, 7.96−7.93, 7.68−7.25 (m, 4 Ph), 5.61 (s, C_5H_5), 5.18, 5.02 (2 br m, ═CH_2), 4.60 (d, J_{HH} = 17, C*H*H′CO), 4.38 (d, J_{HH} = 17, CH*H*′CO), 3.52 (d, J_{HH} = 12, C*H*H′C(CH_3)═), 3.15 (d, J_{HH} = 12, CH*H*′C(CH_3)═), 1.41 (s, CH_3); ^{13}C{^{1}H}, 133.8 (d, J_{CP} = 11, *o*-PPh), 132.8 (d, J_{CP} = 56, *i*-PPh), 132.2 (d, J_{CP} = 2, *p*-PPh), 129.9 (d, J_{CP} = 11, *m*-PPh), 192.7 (s, CO), 138.2 (s, *C*(CH_3)═), 135.6 (s, *i*-C*Ph*), 134.9 (s, *p*-C*Ph*), 129.5, 129.1 (2 s, *o*-, *m*-C*Ph*), 120.4 (s, ═CH_2), 93.3 (d, J_{CP} = 1, C_5H_5), 53.5, 52.4 (s/d, J_{CP} = 2, *C*H_2C(CH_3)═, *C*H_2-CO), 20.5 (s, CH_3); ^{31}P{^{1}H}, 11.5 (s).

[(η^5-C_5Me_5)Re(NO)(PPh_3)(S(CH_2CH═CH_2)CH_2CO-Ph)]$^+$BF$_4^-$ (4d$^+$-Me$_5$BF$_4^-$). A Schlenk flask was charged with (η^5-C_5Me_5)Re(NO)(PPh_3)(CH_3) (1-Me$_5$;[25] 0.330 g, 0.524 mmol) and PhCl (20 mL) and cooled to −45 °C (CH_3CN/CO_2). Then HBF_4·OEt_2 (5.5 M in ether; 95.3 μL, 0.524 mmol) was added with stirring.[26] After 5 min, S(CH_2CH═CH_2)CH_2COPh (0.152 g, 0.524 mmol) was added. The cold bath was warmed to room temperature. After 16 h, the mixture was filtered through a 5 cm silica gel plug on a frit. The plug was rinsed with ether (200 mL) and acetone/CH_2Cl_2 (1:1 v/v, 100 mL; to elute **4d**$^+$-Me$_5$BF$_4^-$). Solvent was removed from the acetone/CH_2Cl_2 rinse by rotary evaporation. The residue was dissolved in acetone (10 mL). The solution was added dropwise to rapidly stirred ether (500 mL). The tan powder was collected by filtration, washed with pentane (100 mL), and dried by oil pump vacuum to give **4d**$^+$-Me$_5$BF$_4^-$ (0.311 g, 0.348 mmol, 67%), mp 108−110 °C dec. Anal. Calcd for $C_{39}H_{42}BF_4NO_2$-PReS: C, 52.47; H, 4.74. Found: C, 51.75; H, 4.89. IR: ν_{NO} 1680 vs.[24]

NMR (CD_2Cl_2):[24] ^{1}H, 7.64−7.26 (m, 4 Ph), 5.88 (m, CH═), 5.41 (br d, J_{HH} = 10, ═C*H*H′), 5.20 (br d, J_{HH} = 17, ═CH*H*′), 4.05 (dd, J_{HH} = 13, 9, C*H*H′CH═), 3.94 (d, J_{HH} = 17, C*H*H′CO), 3.41 (dd, J_{HH} = 13, 7, CH*H*′CH═), 3.38 (d, J_{HH} = 17, CH*H*′CO), 1.77 (s, 5 CH_3); ^{13}C{^{1}H}, 133.9 (d, J_{CP} = 11, *o*-PPh), 132.4 (d, J_{CP} = 2, *p*-PPh), 130.1 (d, J_{CP} = 11, *m*-PPh), 192.1 (s, CO), 135.1 (s, *i*-C*Ph*), 130.2 (s, CH═), 129.3, 128.7 (2 s, *o*-, *m*-C*Ph*), 124.8 (s, ═CH_2), 103.9 (d, J_{CP} = 1, C_5Me_5), 51.4, 46.9 (2 s, *C*H_2-

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CH═, *C*H_2CO), 10.0 (s, CH_3), *i*-PPh/*p*-C*Ph* not observed/obscured; $^{31}P\{^1H\}$, 16.5 (s).

(η^5-C_5H_5)Re(NO)(PPh_3)(SCH(*o*-$C_6H_4CH_3$)Ph) (5a). A. An oven-dried NMR tube was charged with **4a**$^+$TfO$^-$ (0.0118 g, 0.0130 mmol) and THF (1 mL), capped with a septum, and cooled to −80 °C. Then *t*-BuOK (1.0 M in THF; 15.6 μL, 0.0156 mmol) was added and the tube shaken. After 5 min, the tube was removed from the cold bath. A ^{31}P NMR spectrum was recorded. Volatiles were removed by oil pump vacuum, and the residue was dissolved in benzene (2 mL). The solution was filtered through a 1 cm plug of silica gel on a frit. Volatiles were removed by oil pump vacuum to give **5a** as an orange powder (0.0100 g, 0.0130 mmol, 99%; 96:4 *SR*,*RS*/*SS*,*RR*).[10] A sample was dissolved in CH_2Cl_2 and layered with hexane. After 2 days, yellow prisms of (*SR*,*RS*)-**5a** (major isomer only by NMR) were collected by filtration and dried by oil pump vacuum, mp 214 °C dec. These were used for the crystal structure determination below. Anal. Calcd for $C_{37}H_{33}NOPReS$: C, 58.71; H, 4.36. Found: C, 58.57; H, 4.39. IR: ν_{NO} 1637 vs.[24]

B. Related experiments involving different solvents or temperatures are given in the Supporting Information.

NMR ($CDCl_3$)[24] for (*SR*,*RS*)-**5a**: ^1H, 7.53−7.09 (m, 5 Ph), 5.27 (s, SCH), 4.96 (s, C_5H_5), 2.51 (s, CH_3); $^{13}C\{^1H\}$, 134.8 (s, J_{CP} = 54, *i*-PPh), 133.8 (d, J_{CP} = 11, *o*-PPh), 130.2 (d, J_{CP} = 2, *p*-PPh), 128.1 (d, J_{CP} = 11, *m*-PPh), 146.6, 145.1, 135.5, 129.9, 129.0, 128.3, 125.8, 125.5 (8 s, *i*, *p*-C*Ph*, all $C_6H_4CH_3$), 129.1 (s, *o*-C*Ph*), 127.9 (s, *m*-C*Ph*), 90.8 (d, J_{CP} = 1, C_5H_5), 61.3 (d, J_{CP} = 7, SCH), 20.3 (s, CH_3); $^{31}P\{^1H\}$, 19.7 (s). NMR ($CDCl_3$)[24] for (*SS*,*RR*)-**5a** (partial): ^1H, 4.93 (s, C_5H_5), 2.35 (s, CH_3); $^{31}P\{^1H\}$, 20.0.

(η^5-C_5H_5)Re(NO)(PPh_3)(SCH($CH_2CH{=}CH_2$)Ph) (5b) and Isomeric Thiolates. An oven-dried Schlenk flask was charged with **4b**$^+$TfO$^-$ (0.9473 g, 1.105 mmol) and THF (40 mL) and cooled to −80 °C. Then *t*-BuOK (1.0 M in THF; 1.105 mL, 1.105 mmol) was added with stirring. After 10 min, the cold bath was removed. After 3 h, volatiles were removed by oil pump vacuum. The residue was extracted with benzene (100 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 yellow foam was dried by oil pump vacuum to give a 43:37:20 mixture of (*SS*,*RR*)-**5b**, (η^5-C_5H_5)Re(NO)(PPh_3)(SCH═CHCH$_2$(*p*-$C_6H_4CH_3$)) (**9**), and (η^5-C_5H_5)Re(NO)(PPh_3)(SCH═CHCH$_2$CH$_2$-Ph) (**10**) (0.7420 g, 1.0497 mmol, 95%), as assayed by integration of the η^5-C_5H_5 ^1H NMR signals. Crystallization from benzene/heptane gave samples enriched in (*SS*,*RR*)-**5b**.

NMR (C_6D_6)[24,27] for (*SS*,*RR*)-**5b**: ^1H, 7.69−6.95 (m, 5 Ph), 6.09 (br ddt, J_{HH} = 17, 10, 7, CH═), 5.17 (ddt, J_{HH} = 17, 2, 1, ═C*H*H′), 5.00 (ddt, J_{HH} = 10, 2, 1, ═CH*H*′), 4.76 (s, C_5H_5), 3.59 (dd, J_{HH} = 9, 6, SCH), 3.27 (dddm, J_{HH} = 13, 7, 6, C*H*H′CH═), 2.98 (dddm, J_{HH} = 14, 8, 7, CH*H*′CH═); $^{13}C\{^1H\}$, 136.4 (d, J_{CP} = 54, *i*-PPh), 134.7 (d, J_{CP} = 11, *o*-PPh), 130.7 (d, J_{CP} = 2, *p*-PPh), 148.6 (s, *i*-C*Ph*), 138.4 (s, CH═), 115.8 (s, ═CH_2), 91.3 (d, J_{CP} = 2, C_5H_5), 61.1 (d, J_{CP} = 7, SCH), 46.9 (s, *C*H_2CH═), *m*-PPh, *o*-, *m*-, *p*-C*Ph* obscured by solvent; $^{31}P\{^1H\}$, 19.9 (s). NMR (C_6D_6)[24,27] for **9**: ^1H, 7.69−6.95 (m, 5 Ph), 6.80 (dt, J_{HH} = 14, 1, SCH═), 5.86 (dt, J_{HH} = 15, 7, ═C*H*CH$_2$), 4.86 (s, C_5H_5), 3.50 (d, J_{HH} = 7, ═CHC*H*$_2$), 2.18 (s, CH_3); $^{13}C\{^1H\}$ (partial), 143.0 (s, SCH═), 126.4 (s, ═*C*HCH$_2$), 92.1 (d, J_{CP} = 2, C_5H_5), 39.9 (s, CH_2), 21.5 (s, CH_3); $^{31}P\{^1H\}$, 20.58 (s). NMR (C_6D_6)[24,27] for **10**: ^1H, 7.69−6.95 (m, 5 Ph), 6.69 (dm, J_{HH} = 15, SCH═), 5.78 (dt, J_{HH} = 15, 7, ═C*H*CH$_2$), 4.83 (s, C_5H_5), 2.63, 2.52, 2.31 (3 m, 2 CH_2); $^{13}C\{^1H\}$ (partial), 91.9 (d, J_{CP} = 2, C_5H_5), 37.0, 35.1 (2 s, 2 CH_2); $^{31}P\{^1H\}$, 20.65 (s).

(η^5-C_5H_5)Re(NO)(PPh_3)(SCH($CH_2C(CH_3){=}CH_2$)Ph) (5c). The complex **4c**$^+$TfO$^-$ (0.159 g, 0.183 mmol), THF (5 mL), and *t*-BuOK (1.0 M in THF; 183 μL, 0.183 mmol) were combined in a procedure analogous to that for **5b**. A similar workup (the silica gel plug was rinsed with ether) gave a 72:15:13 mixture of (*SS*,*RR*)-**5c** and two other thiolate complexes as a yellow foam (0.0693 g, 0.0960 mmol, 50%), as assayed by integration of the ^{31}P NMR signals. Benzene/heptane crystallization gave pure (*SS*,*RR*)-**5c**.

NMR (C_6D_6)[24] for (*SS*,*RR*)-**5c**: ^1H 7.69−6.95 (m, 5 Ph), 4.84, 4.79 (2 br s, ═C*H*H′, ═CH*H*′), 4.74 (s, C_5H_5), 4.04 (dd, J_{HH} = 9, 6, SCH), 3.24 (dd, J_{HH} = 14, 6, C*H*H′(CH$_3$)═), 2.88 (dd, J_{HH} = 14, 10, CH*H*′C(CH$_3$)═), 1.75 (s, CH_3); $^{13}C\{^1H\}$, 135.7 (d, J_{CP} = 54, *i*-PPh), 134.3 (d, J_{CP} = 11, *o*-PPh), 130.2 (d, J_{CP} = 2, *p*-PPh), 148.9, 144.6 (2 s, *C*(CH$_3$)═, *i*-C*Ph*), 112.3 (s, ═CH_2), 90.9 (d, J_{CP} = 1, C_5H_5), 59.2 (d, J_{CP} = 7, SCH), 50.6 (s, *C*H_2C-(CH$_3$)═), 23.0 (s, CH_3), *m*-PPh, *o*-, *m*-, *p*-C*Ph* obscured by solvent; $^{31}P\{^1H\}$, 20.5 (s).

(η^5-C_5H_5)Re(NO)(PPh_3)(SCH($CH_2CH{=}CH_2$)COPh) (5d). A. An oven-dried Schlenk flask was charged with **4d**$^+$TfO$^-$ (0.0137 g, 0.0155 mmol) and CH_2Cl_2 (0.5 mL) and cooled to −80 °C. Then *t*-BuOK (1.0 M in THF; 15.5 μL, 0.0155 mmol) was added with stirring. After 5 min, the cold bath was removed. After 30 min, the mixture was filtered through a 1 cm silica gel plug in a pipet. The plug was rinsed with pentane (10 mL) and then ether (10 mL; to elute **5d**). Solvent was removed from the ether rinse by rotary evaporation to give **5d** as an orange foam, which was dried by oil pump vacuum (0.0100 g, 0.0136 mmol, 88%; 74:26 *SS*,*RR*/*SR*,*RS*),[10] mp 204 °C dec. Anal. Calcd for $C_{34}H_{31}NO_2PReS$: C, 55.57; H, 4.25. Found: C, 55.40; H, 4.29. IR: ν_{CO} 1670 m, ν_{NO} 1639 vs.[24]

B. and C. Related reactions with different solvents or bases (Scheme 6) are given in the Supporting Information.

NMR (C_6D_6)[24] for (*SS*,*RR*)-**5d**: ^1H, 8.38−8.36, 7.58−7.43, 7.18−6.96 (3 m, 4 Ph), 6.03 (m, CH═), 5.18 (dm, J_{HH} = 17, ═C*H*H′), 5.02 (dm, J_{HH} = 11, ═CH*H*′), 4.95 (s, C_5H_5), 4.51 (ddd, J_{HH} = 8, 6, 1, SCH), 3.19, 2.86 (2 m, C*H*H′CH═, CH*H*′CH═); $^{13}C\{^1H\}$, 135.6 (d, J_{CP} = 54, *i*-PPh), 134.5 (d, J_{CP} = 11, *o*-PPh), 130.6 (d, J_{CP} = 2, *p*-PPh), 199.1 (s, CO), 138.6 (s, *i*-C*Ph*), 138.2 (s, CH═), 132.1 (s, *p*-C*Ph*), 130.2, 128.1 (2 s, *o*-, *m*-C*Ph*), 116.3 (s, ═CH_2), 91.4 (d, J_{CP} = 2, C_5H_5), 55.4 (d, J_{CP} = 8, SCH), 40.2 (s, *C*H_2CH═), *m*-PPh obscured by solvent; $^{31}P\{^1H\}$, 20.1 (s). NMR (C_6D_6)[24] for (*SR*,*RS*)-**5d** (partial): ^1H, 6.20 (m, CH═), 5.00 (s, C_5H_5), 5.29 (dm, J_{HH} = 17, ═CH*H*′), 5.02 (dm, J_{HH} = 10, ═C*H*H′), 4.31 (m, SCH), 3.39 (m, C*H*H′CH═), 3.02 (m, CH*H*′CH═); $^{13}C\{^1H\}$, 91.1 (d, J_{CP} = 2, C_5H_5); $^{31}P\{^1H\}$, 20.0 (s).

(η^5-C_5H_5)Re(NO)(PPh_3)(SCH(C(CH_3)$_2$CH═CH_2)COPh) (5e). The complex **4e**$^+$TfO$^-$ (0.0352 g, 0.0385 mmol), CH_2Cl_2 (1 mL), and *t*-BuOK (1.0 M in THF; 38.5 μL, 0.0385 mmol) were combined in a procedure analogous to that for **5d**. The mixture was filtered through a 1 cm silica gel plug in a pipet. The plug was rinsed with pentane (10 mL) and ether (10 mL; to elute **5e**). Solvent was removed from the ether rinse by rotary evaporation to give **5e** as an orange foam, which was dried by oil pump vacuum (0.0289 g, 0.0379 mmol, 98%; >96: <4 *SS*,*RR*/*SR*,*RS*),[10] mp 214−215 °C dec. Anal. Calcd for $C_{36}H_{35}NO_2PReS$: C, 56.68; H, 4.62. Found: C, 56.76; H, 4.67. IR: ν_{NO} 1642 vs.[24]

NMR (CD_2Cl_2)[24] for (*SS*,*RR*)-**5e**: ^1H, 7.94−7.91, 7.56−7.34 (2 m, 4 Ph), 6.15 (dd, J_{HH} = 17, 11, CH═), 4.95 (dd, J_{HH} = 18, 2, ═C*H*H′), 4.89 (dd, J_{HH} = 11, 2, ═CH*H*′), 4.82 (s, C_5H_5), 4.25 (s, SCH), 1.26, 1.23 (2 br s, 2 CH_3); $^{13}C\{^1H\}$, 135.0 (d, J_{CP} = 54, *i*-PPh), 134.4 (d, J_{CP} = 11, *o*−PPh), 130.9 (d, J_{CP} = 2, *p*-PPh), 128.7 (d, J_{CP} = 11, *m*-PPh), 202.5 (s, CO), 147.6 (s, CH═), 141.1 (s, *i*-C*Ph*), 132.4 (s, *p*-C*Ph*), 128.9 (br s, *o*-, *m*-C*Ph*), 111.1 (s, ═CH_2), 91.9 (s, C_5H_5), 71.1 (d, J_{CP} = 7, SCH), 41.9 (s, *C*(CH$_3$)$_2$), 26.5, 24.9 (2 s, 2 CH_3); $^{31}P\{^1H\}$, 19.8 (s). NMR (CD_2Cl_2)[24] for (*SR*,*RS*)-**5e** (partial): ^1H, 4.13 (s, SCH); $^{31}P\{^1H\}$, 19.2 (s).

(η^5-C_5H_5)Re(NO)(PPh_3)(SCH($CH_2C(CH_3){=}CH_2$)COPh) (5f). A. The complex **4f**$^+$$BF_4^-$ (0.0475 g, 0.0568 mmol), CH_2Cl_2 (1 mL), and *t*-BuOK (1.0 M in THF; 56.7 μL, 0.0568 mmol) were combined in a procedure analogous to that for **5d**. An identical workup gave **5f** as an orange foam (0.0294 g, 0.0393 mmol, 69%; 84:16 *SS*,*RR*/*SR*,*RS*),[10] mp 221 °C dec. Anal.

(27) The NMR signals were assigned to individual compounds through a combination of COSY, HETCOR, and APT experiments.

Calcd for $C_{35}H_{33}NO_2PReS$: C, 56.13; H, 4.44. Found: C, 55.92; H, 4.45. IR: ν_{CO} 1669 m, ν_{NO} 1637 vs.[24]

B. The complex **4f**$^+BF_4^-$ (0.0374 g, 0.0415 mmol), THF (1 mL), and *t*-BuOK (1.0 M in THF; 41.5 μL, 0.0415 mmol) were combined in a procedure analogous to that in A. An identical workup gave **5f** as an orange foam (0.0206 g, 0.0275 mmol, 66%; 76:24 *SS*,*RR*/*SR*,*RS*).

NMR (CD_2Cl_2)[24] for (*SS*,*RR*)-**5f**: ^{1}H, 8.22−8.16, 8.08−8.04, 7.58−7.32 (3 m, 4 Ph), 5.22 (s, C_5H_5), 4.68, 4.64 (2 m, =C*H*H′, =CH*H*′), 4.39 (ddd, J_{HH} = 10, 4, 1, SCH), 2.90 (dd, J_{HH} = 14, 10, C*H*H′C(CH$_3$)=), 2.54 (dd, J_{HH} = 15, 4, CH*H*′C(CH$_3$)=), 1.76 (br s, CH$_3$); ^{13}C{^{1}H}, 134.9 (d, J_{CP} = 54, *i*-PPh), 134.3 (d, J_{CP} = 11, *o*-PPh), 130.9 (d, J_{CP} = 2, *p*-PPh), 128.7 (d, J_{CP} = 10, *m*-PPh), 198.3 (s, CO), 147.6 (s, CH=), 145.2, 138.4 (2 s, *i*-C*Ph*, *C*(CH$_3$)=), 132.5 (s, *p*-C*Ph*), 129.4, 128.8 (2 s, *o*-, *m*-C*Ph*), 111.3 (s, =CH$_2$), 91.8 (d, J_{CP} = 1, C_5H_5), 54.2 (d, J_{CP} = 7, SCH), 43.4 (s, *C*H$_2$C(CH$_3$)=), 23.6 (s, CH$_3$); ^{31}P{^{1}H}, 18.9 (s). NMR (CD_2Cl_2)[24] for (*SR*,*RS*)-**5f** (partial): ^{1}H, 5.24 (s, C_5H_5); ^{13}C{^{1}H}, 91.5 (d, J_{CP} = 1, C_5H_5), 43.3 (s, *C*H$_2$C(CH$_3$)=), 23.8 (s, CH$_3$).

(η^5-C_5Me_5)Re(NO)(PPh$_3$)(SCH(CH$_2$CH=CH$_2$)COPh) (5d-Me$_5$). The complex **4d**$^+$-Me$_5BF_4^-$ (0.0258 g, 0.0289 mmol), CH_2Cl_2 (0.5 mL), and *t*-BuOK (1.0 M in THF; 28.9 μL, 0.0289 mmol) were combined in a procedure analogous to that for **5d**. The mixture was filtered through a 1 cm silica gel plug in a pipet. The plug was rinsed with pentane (10 mL) and ether (10 mL; to elute **5d**-Me$_5$). Solvent was removed from the ether rinse by rotary evaporation to give **5d**-Me$_5$ as an orange foam, which was dried by oil pump vacuum (0.0200 g, 0.0248 mmol, 86%; 82:18 mixture of diastereomers A/B),[10] mp 160−163 °C dec. Anal. Calcd for $C_{39}H_{41}NO_2PReS$: C, 58.19; H, 5.13. Found: C, 58.06; H, 5.17. IR: ν_{CO} 1663 m, ν_{NO} 1637 vs.[24]

NMR (CD_2Cl_2)[24] for diastereomer A of **5d**-Me$_5$: ^{1}H, 8.02−7.93, 7.11−7.52 (2 m, 4 Ph), 6.03 (dddd, J_{HH} = 17, 14, 11, 7, CH=), 4.95 (dq, J_{HH} = 17, 2, =C*H*H′), 4.86 (dm, J_{HH} = 10, =CH*H*′), 4.05 (dd, J_{HH} = 11, 4, SCH), 2.93, 2.63 (2 m, C*H*H′CH=, CH*H*′CH=), 1.72 (s, 5 CH$_3$); ^{13}C{^{1}H}, 134.5 (d, J_{CP} = 11, *o*-PPh), 129.7 (br s, *p*-PPh), 128.4 (d, J_{CP} = 14, *m*-PPh), 198.7 (s, CO), 138.2 (s, *i*-C*Ph*), 137.4 (s, CH=), 132.2 (s, *p*-C*Ph*), 129.7, 128.7 (2 s, *o*-, *m*-C*Ph*), 115.7 (s, =CH$_2$), 101.4 (d, J_{CP} = 2, C_5Me_5), 56.0 (br s, SCH), 42.1 (s, *C*H$_2$CH=), 10.5 (s, CH$_3$), *i*-PPh not observed; ^{31}P{^{1}H}, 17.5 (s). NMR (CD_2Cl_2)[24] for diastereomer B (partial): ^{1}H, 3.96 (dd, J_{HH} = 6, 1, SCH); ^{13}C-{^{1}H} 116.2 (s, =CH$_2$), 101.6 (d, J_{CP} = 2, C_5Me_5), 41.8 (s, SCH*C*H$_2$), 10.4 (s, CH$_3$); ^{31}P{^{1}H}, 18.1 (s).

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(S(Me)CH(CH$_2$CH=CH$_2$)Ph)]$^+$TfO$^-$ (11b$^+$TfO$^-$) and Isomeric Sulfide Complexes. A Schlenk flask was charged with a 43:37:20 **5b**/**9**/**10** mixture (0.7420 g, 1.050 mmol) and CH_2Cl_2 (30 mL) and cooled to −80 °C. Then MeOTf (118.8 μL, 1.050 mmol) was added dropwise with stirring. After 5 min, the cold bath was removed. After 30 min, volatiles were removed by oil pump vacuum. The oily residue was dissolved in CH_2Cl_2 (5 mL). The solution was filtered through a 2 cm silica gel plug on a frit. The plug was rinsed with CH_2Cl_2 (50 mL) and THF (100 mL). Solvent was removed from the THF rinse by rotary evaporation and the oily residue dried by oil pump vacuum to give a 43:37:20 mixture of **11b**$^+$TfO$^-$, [(η^5-C_5H_5)Re(NO)(PPh$_3$)(S(Me)CH=CHCH$_2$-(*p*-$C_6H_4CH_3$))]$^+$TfO$^-$, and [(η^5-C_5H_5)Re(NO)(PPh$_3$)(S(Me)-CH=CHCH$_2$CH$_2$Ph)]$^+$TfO$^-$ (0.8270 g, 0.9495 mmol, 90%), as assayed by integration of the η^5-C_5H_5 ^{1}H NMR signals.

NMR ($CDCl_3$)[24] for **11b**$^+$TfO$^-$: ^{1}H, 7.48−7.00 (m, 4 Ph), 5.60 (s, C_5H_5), 5.41 (m, CH=), 4.96 (dm, J_{HH} = 17, =CH*H*′), 4.92 (dm, J_{HH} = 10, =C*H*H′), 3.93 (dd, J_{HH} = 11. 4, SCH), 3.36, 3.23 (2 m, C*H*H′CH=, CH*H*′CH=), 1.84 (s, SCH$_3$); ^{31}P{^{1}H}, 10.5 (s). NMR ($CDCl_3$)[24] for [(η^5-C_5H_5)Re(NO)(PPh$_3$)(S(Me)-CH=CHCH$_2$(*p*-$C_6H_4CH_3$))]$^+$TfO$^-$: ^{1}H (partial), 6.06 (dt, J_{HH} = 15, 1, SCH=), 5.51 (s, C_5H_5); ^{31}P{^{1}H}, 12.24 (s). NMR ($CDCl_3$)[24] for [(η^5-C_5H_5)Re(NO)(PPh$_3$)(S(Me)CH=CHCH$_2$CH$_2$Ph)]$^+$TfO$^-$: ^{1}H (partial), 6.69 (dt, J_{HH} = 14, 1, SCH=), 5.44 (s, C_5H_5); ^{31}P{^{1}H}, 12.17 (s).

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(S(Me)CH(C(CH$_3$)$_2$CH=CH$_2$)-COPh)]$^+$TfO$^-$ (11e$^+$TfO$^-$). A Schlenk flask was charged with **5e** (0.7140 g, 0.9357 mmol; 98:2 *SS*,*RR*/*SR*,*RS*) and CH_2Cl_2 (20 mL) and cooled to −80 °C. Then MeOTf (105.9 μL, 0.9357 mmol) was added dropwise with stirring. After 5 min, the cold bath was removed. After 30 min, volatiles were removed by oil pump vacuum. The oily residue was dissolved in CH_2Cl_2 (5 mL). The solution was added dropwise to rapidly stirred heptane (500 mL). A yellow powder was collected by filtration, washed with ether (100 mL) and pentane (100 mL), and dried by oil pump vacuum to give **11e**$^+$TfO$^-$ (0.7344 g, 0.7921 mmol, 85%; 98:2 *SS*,*RR*/*SR*,*RS*),[10] mp 163−164 °C dec. Anal. Calcd for $C_{38}H_{38}F_3NO_5PReS_2$: C, 49.24; H, 4.13. Found: C, 49.07; H, 4.16. IR: ν_{NO} 1711 vs, ν_{CO} 1676 m.[24]

NMR (CD_2Cl_2)[24] for (*SS*,*RR*)-**11e**$^+$TfO$^-$: ^{1}H, 8.14−8.11, 7.81−7.50, 7.33−7.26 (3 m, 4 Ph), 6.02 (dd, J_{HH} = 17, 11, CH=), 5.12 (br d, J_{HH} = 11, =C*H*H′), 5.11 (br d, J_{HH} = 17, =CH*H*′), 5.05 (s, C_5H_5), 4.58 (s, SCH), 2.33 (s, SCH$_3$), 1.26, 1.19 (2 s, C(CH$_3$)$_2$); ^{13}C{^{1}H}, 133.7 (d, J_{CP} = 11, *o*-PPh), 132.3 (d, J_{CP} = 2, *p*-PPh), 132.2 (d, J_{CP} = 57, *i*-PPh), 129.8 (d, J_{CP} = 11, *m*-PPh), 196.3 (s, CO), 143.0 (s, CH=), 138.3 (s, *i*-C*Ph*), 135.6 (s, *p*-C*Ph*), 130.0, 129.2 (2 s, *o*-, *m*-C*Ph*), 115.4 (s, =CH$_2$), 93.2 (d, J_{CP} = 1, C_5H_5), 68.2 (d, J_{CP} = 4, SCH), 43.5 (s, *C*(CH$_3$)$_2$), 26.8, 26.5, 25.6 (3 s, 3 CH$_3$); ^{31}P{^{1}H}, 10.8 (s). NMR (CD_2Cl_2) for (*SR*,*RS*)-**11e**$^+$TfO$^-$ (partial): ^{1}H, 2.30 (s, SCH$_3$); ^{31}P{^{1}H}, 10.5 (s).

MeSCH(CH$_2$CH=CH$_2$)Ph (12b) and Isomeric Sulfides. A Schlenk flask was charged with CH_2Cl_2 (30 mL) and the mixture containing **11b**$^+$TfO$^-$ (0.8270 g, 0.9495 mmol). Then Et$_4$N$^+$CN$^-$ (0.223 g, 1.42 mmol) was added with stirring. After 30 min, the sample was concentrated to an oily residue by oil pump vacuum; this residue was then 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/pentane (1:1 v/v, 300 mL). The filtrate was concentrated and distilled under oil pump vacuum (100 °C) into a liquid-N_2-cooled receiver. This gave a 47:34:19 mixture of the known compounds **12b**, MeSCH=CHCH$_2$(*p*-$C_6H_4CH_3$), and MeSCH=CHCH$_2$CH$_2$-Ph,[14] as assayed by integration of the SCH$_3$ ^{1}H NMR signals.

NMR ($CDCl_3$)[24,27] for **12b**: ^{1}H, 7.24−7.05 (m, Ph), 5.76 (ddt, J_{HH} = 17, 10, 7, CH=), 5.08 (dm, J_{HH} = 17, =C*H*H′), 5.03 (dm, J_{HH} = 10, =CH*H*′), 3.76 (t, J_{HH} = 8, SCH), 2.64 (m, C*H*$_2$CH=), 1.90 (s, SCH$_3$); ^{13}C{^{1}H}, 135.4 (s, CH=), 141.8 (s, *i*-C*Ph*), 129.1−125.2 (*o*-, *m*-, *p*-C*Ph*), 116.8 (s, =CH$_2$), 51.3 (s, SCH), 40.4 (s, *C*H$_2$CH=), 14.2 (s, SCH$_3$). NMR ($CDCl_3$)[24,27] for MeSCH=CHCH$_2$(*p*-$C_6H_4CH_3$): ^{1}H, 7.24−7.05 (m, Ph), 6.07 (dt, J_{HH} = 15, 1, SCH=), 5.57 (dt, J_{HH} = 15, 7, =C*H*CH$_2$), 3.41 (d, J_{HH} = 7, =CHC*H*$_2$); ^{13}C{^{1}H}, 141.5 (s, *i*-C*Ph*), 125.2 (s, SCH=), 125.7 (s, =CH), 129.1−125.2 (*o*-, *m*-, *p*-C*Ph*), 38.9 (s, =CH*C*H$_2$), 20.9 ($C_6H_4CH_3$), 15.2 (s, SCH$_3$). NMR ($CDCl_3$)[24,27] for MeSCH=CHCH$_2$CH$_2$Ph: ^{1}H, 7.24−7.05 (m, Ph), 6.04 (dt, J_{HH} = 15, 1, SCH=), 5.50 (dt, J_{HH} = 15, 7, =C*H*CH$_2$), 2.72, 2.43 (2 m, 2 CH$_2$); ^{13}C{^{1}H}, 141.6 (s, *i*-C*Ph*), 124.6 (s, SCH=), 126.4 (s, =CH), 129.1−125.2 (*o*-, *m*-, *p*-C*Ph*), 36.0, 34.9 (2 s, 2 CH$_2$), 15.0 (s, SCH$_3$).

MeSCH(C(CH$_3$)$_2$C=CH$_2$)COPh (12e). A Schlenk flask was charged with **11e**$^+$TfO$^-$ (0.6023 g, 0.6497 mmol; 98:2 *SS*,*RR*/*SR*,*RS*) and CH_2Cl_2 (30 mL). Then Et$_4$N$^+$CN$^-$ (0.1134 g, 0.7257 mmol) was added with stirring. After 30 min, the sample was concentrated to an oily residue by oil pump vacuum, 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/pentane (1:1 v/v, 300 mL). Solvent was removed by rotary evaporation to give **12e** as a colorless liquid (0.1493 g, 0.6396 mmol, 98%). Anal. Calcd for $C_{14}H_{18}SO$: C, 71.75; H, 7.74. Found: C, 71.84; H, 7.76. The plug was rinsed with THF (200 mL), and heptane (50 mL) was added. The mixture was concentrated to ca. 100 mL. The yellow powder was collected by filtration, washed with pentane (30 mL), and dried by oil pump vacuum to give (η^5-C_5H_5)Re(NO)(PPh$_3$)(CN) (**13**;[16] 0.3148 g, 0.5488 mmol, 85%).

NMR (CD_2Cl_2)[24] for **12e**: ^{1}H, 8.03−7.96, 7.62−7.46 (2 m, Ph), 6.17 (dd, J_{HH} = 17, 11, CH=), 5.11 (dd, J_{HH} = 18, 1,

=C*H*H′), 5.03 (dd, J_{HH} = 11, 1, =CH*H*′), 4.18 (s, SCH), 2.08 (s, SCH_3), 1.32, 1.29 (2 s, $C(CH_3)_2$); $^{13}C\{^1H\}$, 197.0 (s, CO), 145.9 (s, CH=), 138.7 (s, *i*-C*Ph*), 133.4 (s, *p*-C*Ph*), 129.2, 128.6 (2 s, *o*-, *m*-C*Ph*), 112.9 (s, $=CH_2$), 58.1 (s, SCH), 41.7 (s, $C(CH_3)_2$), 26.0, 25.1 (2 s, 2 CCH_3), 17.0 (s, SCH_3).

(η^5-C_5H_5)Re(NO)(PPh_3)(SCH(CH_2Ph)Ph) (17). A. An oven-dried Schlenk flask was charged with HSCH(CH_2Ph)Ph[28] (0.2299 g, 1.0728 mmol) and THF (20 mL). Then *t*-BuOK (1.0 M in THF; 1.18 mL, 1.18 mmol) was added with stirring. After 10 min, the white suspension was cooled to −80 °C. A solution of **2** (0.4966 g, 0.7169 mmol) in THF (10 mL) was added by cannula with stirring. The cold bath was allowed to slowly warm. After 6 h, volatiles were removed by oil pump vacuum. The residue was dissolved in acetone (100 mL) and filtered through a 10 cm plug of silica gel on a frit. The plug was rinsed with ether (250 mL), and solvent was removed from the filtrate by rotary evaporation. The microcrystalline powder was collected on a frit, washed with pentane (100 mL), and dried by oil pump vacuum to give **17** as an orange powder (0.4095 g, 0.5410 mmol, 76%; 61:39 mixture of diastereomers A/B).[11] Anal. Calcd for $C_{37}H_{33}NOPReS$: C, 58.71; H, 4.39. Found: C, 58.61; H, 4.33.

B. An oven-dried NMR tube was charged with **4a**$^+$TfO$^-$ (0.0240 g, 0.0265 mmol) and THF (1 mL), capped with a septum, and cooled to −80 °C. Then MeLi (1.4 M in ether; 21 μL, 0.0294 mmol) was added and the tube shaken. A ^{31}P NMR spectrum (−80 °C) showed the reaction to be complete. The tube was kept for 12 h at room temperature. Volatiles were removed by oil pump vacuum. The residue was dissolved in benzene (2 mL). The solution was filtered through a 1 cm plug of silica gel on a frit. Volatiles were removed by oil pump vacuum to give a yellow powder (0.0133 g, ca. 0.0176 mmol, ca. 66%; contains 65% **17**, 35:65 diastereomer A/B).[11]

C.−K. Related experiments with other solvents or MeLi stoichiometries are given in the Supporting Information.

NMR ($CDCl_3$)[24] for diastereomer A of **17**: ^1H, 7.50−6.95 (m, 5 Ph), 4.88 (s, C_5H_5), 3.82 (br t, J_{HH} = 7, SCH), 3.28 (dd, J_{HH} = 14, 7, C*H*H′Ph), 3.19 (dd, J_{HH} = 14, 8, CH*H*′Ph); $^{13}C\{^1H\}$, 135.0 (d, J_{CP} = 54, *i*-PPh), 134.0 (d, J_{CP} = 11, *o*-PPh), 147.6, 141.8 (2 s, 2 *i*-C*Ph*), 91.3 (d, J_{CP} = 1, C_5H_5), 61.7 (s, SCH), 47.1 (s, CH_2Ph), *m*-, *p*-PPh, *o*-, *m*-, *p*-C*Ph* not resolved (130.4−125.5); $^{31}P\{^1H\}$, 20.1 (s). NMR ($CDCl_3$)[24] for diastereomer B: ^1H, 7.50−6.95 (m, 5 Ph), 4.94 (s, C_5H_5), 3.84 (dd, J_{HH} = 10, 6, SCH), 3.47 (dd, J_{HH} = 14, 6, C*H*H′Ph), 3.09 (dd, J_{HH} = 14, 10, CH*H*′Ph); $^{13}C\{^1H\}$, 134.0 (d, J_{CP} = 11, *o*-PPh), 147.8, 141.4 (2 s, 2 *i*-C*Ph*), 91.1 (d, J_{CP} = 1, C_5H_5), 61.6 (s, SCH), 48.2 (s, CH_2-Ph), *i*-, *m*-, *p*-PPh, *o*-, *m*-, *p*-C*Ph* not resolved (130.4−125.5); $^{31}P\{^1H\}$, 19.2 (s).

Crystallography. Data were collected on a prism of (*SR*,*RS*)-**5a** as outlined in Table 2. Cell constants were obtained from 30 reflections with 24° < 2θ < 30°. The space group was determined from systematic absences (*h*0*l*, *l* = 2*n* + 1; 0*k*0, *k* = 2*n* + 1) and subsequent least-squares refinement. Lorentz, polarization, and empirical absorption (ψ scans) corrections were applied. The structure was solved by standard heavy-atom techniques with the SDP/VAX package.[29] Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were calculated and added to the structure factor calculations but, except for H21, were not refined. Scattering factors and $\Delta f'$ and $\Delta f''$ values were taken from the literature.[30]

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Supporting Information Available: Text giving general procedures, syntheses of sulfide ligands, and additional reactivity data and a table of anisotropic thermal parameters for (*SR*,*RS*)-**5a** (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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