Diallyl Sulfide Complexes of Chiral Iron and Ruthenium Lewis Acids: Ylide Generation and Diastereoselective [2,3] Sigmatropic Rearrangements To Give Thiolate Complexes with New Carbon Stereocenters

Peter T. Bell, Phillip C. Cagle, Dominique Vichard, and J. A. Gladysz*

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

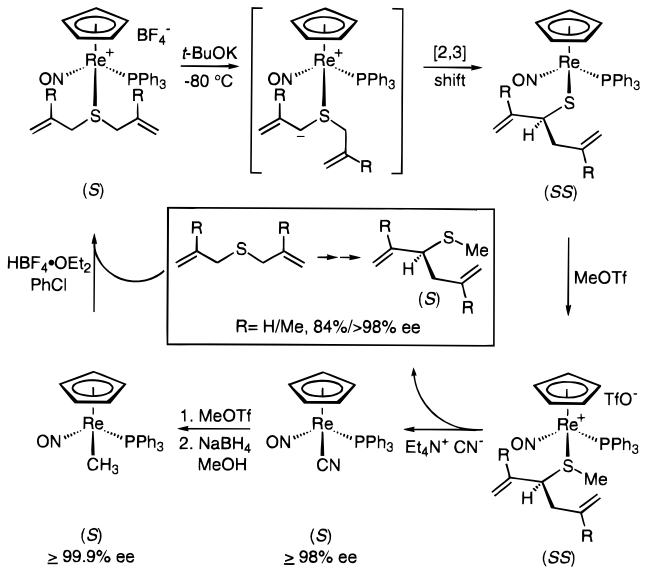
Received July 3, 1996[⊗]

Reactions of the racemic iron diallyl sulfide complex $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(S(CH_2\text{-}CH{=}CH_2)_2)]^+BF_4^-$ and *t*-BuOK (CH_2Cl_2 or THF, −80 to −60 °C) give the thiolate complex $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(SCH(CH{=}CH_2)CH_2CH{=}CH_2)$ (65−92%) as 77−68:23−32 mixtures of *SS*,*RR*/*SR*,*RS* Fe,S***C*** diastereomers. Reactions of the enantiomerically pure ruthenium diallyl sulfide complexes $[(\eta^5\text{-}C_5H_5)Ru(S,S\text{-chiraphos})(S(CH_2CR{=}CH_2)_2)]^+PF_6^-$ (**5**$^+PF_6^-$; R = **a**, H; R = **b**, CH_3) and *t*-BuOK (CH_2Cl_2, −98 °C) give the thiolate complexes $(\eta^5\text{-}C_5H_5)Ru(S,S\text{-chiraphos})(SCH(CR{=}CH_2)CH_2CR{=}CH_2)$ as 78:22 (**8a**, >99%) and 87:13 (**8b**, 97%) mixtures of chromatographically separable *SSS*/*SSR* P***C***,P′***C′***,S***C*** diastereomers. These transformations likely involve intermediate sulfur ylides as described in the title. Reactions of **8a**,**b** with CH_3I or $PhCH_2I$ and then NaI (acetone, reflux) give, via cationic methyl or benzyl sulfide complexes, enantiomerically enriched $R'SCH(CH_2CR{=}CH_2)CR{=}CH_2$ (R/R′ = H/CH_3, 75%; CH_3/CH_3, 71%; H/$PhCH_2$ and CH_3/$PhCH_2$, >99%) and $(\eta^5\text{-}C_5H_5)Ru(S,S\text{-chiraphos})(I)$ (**6**, ≥97%). Complex **6** is readily recycled to enantiomerically pure **5a**,**b**$^+PF_6^-$ ($NH_4^+PF_6^-$, CH_3OH, $S(CH_2CR{=}CH_2)_2$; 94−97%).

Chiral transition metal Lewis acids offer innumerable possibilities as control elements in enantioselective organic syntheses, and new methodologies are being discovered at an ever increasing pace.[1] We have reported, in a series of papers over the last 3 years, that the chiral rhenium Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (**I**)[2] readily binds diallyl, dipropargyl, and dibenzyl sulfides.[3−5] As exemplified in Scheme 1, subsequent additions of *t*-BuOK generate sulfur ylides that undergo highly diastereoselective [2,3] sigmatropic rearrangements. The rhenium fragment efficiently directs the configuration of the new carbon stereocenter in the resulting thiolate ligand. The thiolate can be detached as a thioether of high enantiomeric purity and the rhenium moiety recycled without racemization. There is currently no comparable means of controlling configuration in sigmatropic rearrangements of sulfur ylides or any type of desymmetrization of diallyl or related sulfides. Mechanisms that rationalize the observed stereochemistry have been proposed.[3]

The above results engender a number of questions regarding possible extensions. Can analogous deprotonations and rearrangements be effected in the coordination spheres of other chiral (or achiral) transition metal Lewis acids? Can even higher diastereoselectivities or thioether enantiomeric purities be achieved? Can the metal fragment be recycled more efficiently or other economies realized? Hence, we undertook a similar investigation of diallyl sulfide complexes of the readily available chiral iron and ruthenium Lewis acids $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)]^+$ (**II**) and $[(\eta^5\text{-}C_5H_5)Ru(S,S\text{-chiraphos})]^+$ (**III**). The former provides an environment that is approximately isosteric with **I**, whereas the latter features ligand-based instead of metal-based chirality. In this paper, we demonstrate that the answers to two of the preceding questions are "yes", an outcome that

Scheme 1. Enantioselective Conversion of Achiral Diallyl Sulfides to Rearranged Chiral Sulfides Mediated by the Chiral Rhenium Lewis Acid I



[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1996.

(1) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley: New York, 1994.

(2) Lead reference for functional equivalents and substitution mechanisms: Dewey, M. A.; Zhou, Y.; Liu, Y.; Gladysz, J. A. *Organometallics* **1993**, *12*, 3924.

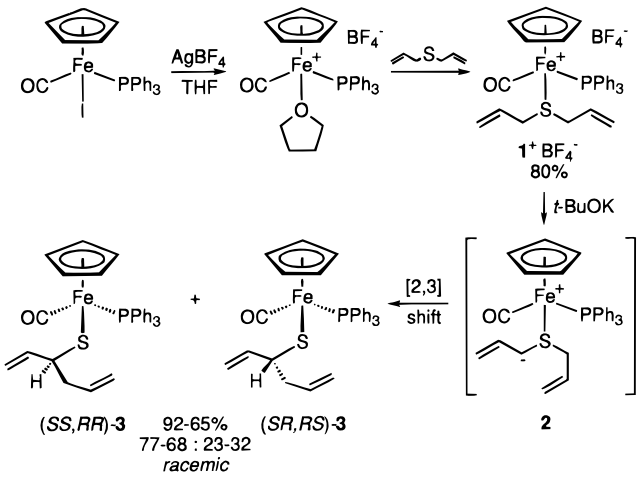
(3) (a) Cagle, P. C.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1994**, *116*, 3655. (b) Cagle, P. C.; Meyer, O.; Weickhardt, K.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1995**, *117*, 11730. (c) Cagle, P. C.; Meyer, O.; Vichard, D.; Weickhardt, K.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1996**, *15*, 194.

(4) Related papers: (a) Quirós Méndez, N.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1991**, *10*, 2199. (b) Meyer, O.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1995**, *14*, 1844.

(5) Brief review: Meyer, O.; Cagle, P. C.; Weickhardt, K.; Vichard, D.; Gladysz, J. A. *Pure Appl. Chem.* **1996**, *68*, 79.

S0276-7333(96)00541-9 CCC: $12.00

Scheme 2. Synthesis and Reaction of a Diallyl Sulfide Complex of a Chiral Iron Lewis Acid



augers well for the breadth, generality, and continued development of this new methodology.

Results

1. Iron Complexes. A racemic dimethyl sulfide complex of the iron Lewis acid **II** has been previously synthesized by thermal or photochemical reactions of PPh_3 and the achiral precursors $[(\eta^5\text{-}C_5H_5)Fe(CO)(SMe_2)_2]^+X^-$ or $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(SMe_2)]^+X^-$.[6,7] These are in turn prepared from substitution-labile cationic THF complexes, which are generated *in situ* from the corresponding neutral iodide complexes. We sought to similarly access a diallyl sulfide complex of **II**. Hence, $(\eta^5\text{-}C_5H_5)Fe(CO)_2(I)$ and $AgBF_4$ were combined in THF to generate the THF complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(THF)]^+BF_4^-$ as described earlier.[8] Subsequent addition of diallyl sulfide gave the substitution product $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(S(CH_2CH{=}CH_2)_2)]^+BF_4^-$ in moderate yield. However, photolysis with PPh_3 (5 equiv, CH_2Cl_2) gave numerous species.

Thus, the previously reported, chiral, racemic, PPh_3-substituted iodide complex $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(I)$[9] was similarly converted to the THF complex $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(THF)]^+BF_4^-$ as shown in Scheme 2. Reaction with diallyl sulfide (1.5 equiv, CH_2Cl_2) gave the blood red target complex $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(S(CH_2CH{=}CH_2)_2)]^+BF_4^-$ ($\mathbf{1}^+BF_4^-$) in 80% yield. Complex $\mathbf{1}^+BF_4^-$ was stable for prolonged periods as a solid but decomposed in aerobic solutions. It was characterized by microanalysis and IR and NMR (^1H, ^{13}C, ^{31}P) spectroscopy, as summarized in the Experimental Section. Properties were similar to those of the dimethyl sulfide complex of **II**.[6]

A CH_2Cl_2 solution of $\mathbf{1}^+BF_4^-$ and a THF solution of *t*-BuOK (1.0 equiv) were combined at −80 °C. The thiolate complex $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(SCH(CH{=}CH_2)CH_2CH{=}CH_2)$ (**3**) was isolated in 65% yield following column chromatography on alumina, consistent with the initial generation of ylide **2** as shown in Scheme 2. This dark green, analytically pure material was characterized as described for $\mathbf{1}^+BF_4^-$ (Experimental Section). NMR analyses showed that **3** was a 75:25 mixture of Fe,C configurational diastereomers (C_6D_6; cyclopentadienyl ^1H or PPh_3 ^{31}P signals).[10,11] The configuration of the major diastereomer was *tentatively* assigned by analogy to that obtained in the corresponding reaction involving the structurally related rhenium Lewis acid **I** (Scheme 1; *SS*,*RR*).

Complex $\mathbf{1}^+BF_4^-$ and *t*-BuOK (1.5 equiv) were similarly combined at −98 °C. A nonchromatographic workup gave spectroscopically pure **3** in 92% yield as a 68:32 mixture of diastereomers. THF solutions of $\mathbf{1}^+BF_4^-$ gave comparable diastereomer ratios, and NMR experiments (THF) did not show any appreciable reaction below −60 °C or detectable intermediates. Amide (R_2N^-) bases could also be used. In side-by-side reactions, CH_2Cl_2 solutions of $\mathbf{1}^+BF_4^-$ were treated with 0.6 equiv of *t*-BuOK, $(Me_2CH)_2NLi$, or $(Me_3Si)_2NLi$ in darkened rooms and foil shielded NMR tubes at −80 °C. In all cases, **3** formed as a 77:23 mixture of diastereomers. In contrast, the diallyl sulfide complex of **I** gave widely divergent diastereoselectivities with these bases.[3b] Some Lewis base adducts of **II** epimerize at iron under ambient light,[12] but the umbral conditions exclude this possibility here. The spread in diastereomer ratios (77−68:23−32; 65:35 in experiments not described) precludes any rapid thermal equilibration. Regardless, under none of the conditions investigated does **3** form with high diastereoselectivity.

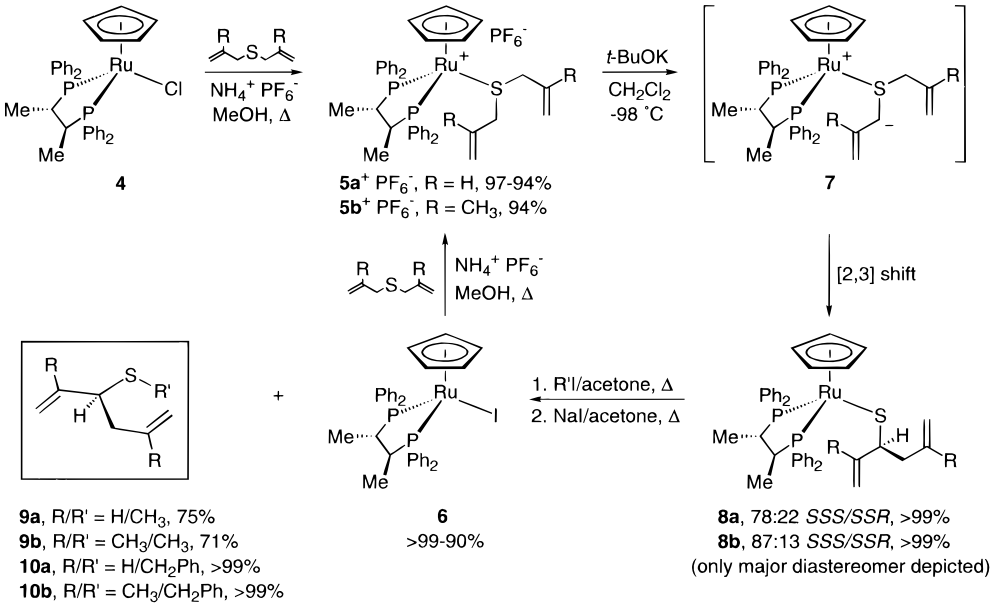
Complex **3** exhibited an IR ν_{CO} value close to that of the previously reported iron allyl thiolate complex $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(SCH_2CH{=}CH_2)$ (1936 vs 1932 cm^{-1}, KBr).[13] The NMR properties of the thiolate ligand were generally similar to those of the analogous adduct of **I**.[3b] However, **3** was much more air sensitive. Other compounds of the formula $(\eta^5\text{-}C_5R_5)Fe(CO)(PR'_3)(SR'')$ (R″ = alkyl, aryl) have been observed to undergo facile one electron oxidations,[14] as well as alkylation at sulfur (CH_3CH_2Br, 21 °C, $CHCl_3$).[15] However, in view of the modest diastereoselectivities, no elaboration of the thiolate ligand of **3** was attempted.

2. Ruthenium Complexes. The chiral, enantiomerically pure ruthenium chloride complex $(\eta^5\text{-}C_5H_5)Ru(S,S\text{-chiraphos})(Cl)$ (**4**) is easily prepared from $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2(Cl)$ and commercially available *S*,*S*-chiraphos.[16] However, when **4** was treated with $AgBF_4$, THF, and diallyl sulfides in procedures similar to that used for $\mathbf{1}^+BF_4^-$ in Scheme 2, much lower yields of sulfide complexes were obtained. Thus, a method reported by Schenk for the synthesis of the correspond-

(6) Kuhn, N.; Schumann, H.; Zauder, E. *J. Organomet. Chem.* **1987**, *327*, 17.
(7) Kuhn, N.; Schumann, H. *J. Organomet. Chem.* **1984**, *276*, 55.
(8) Reger, D. L.; Coleman, C. *J. Organomet. Chem.* **1977**, *131*, 153.
(9) Treichel, P. M.; Shubkin, R. L.; Barnett, K. W., Reichard, D. *Inorg. Chem.* **1966**, *5*, 1177.

(10) All diastereomer and enantiomer ratios are normalized to 100. The error limits on each component are ±2 for diastereomer ratios and ±4 for enantiomer ratios.
(11) The configuration of the chiral transition metal Lewis acid is specified first (rhenium, iron, or chiraphos ligand stereocenters), followed by that at carbon.
(12) (a) Davies, S. G.; Metzler, M. R.; Yanada, K.; Yanada, R. *J. Chem. Soc., Chem. Commun.* **1993**, 658. (b) Davies, S. G.; Watkins, W. C. *J. Chem. Soc., Chem. Commun.* **1994**, 491.
(13) Weigand, W. *Z. Naturforsch., B*: *Anorg. Chem., Org. Chem.* **1991**, *46b*, 1333.
(14) (a) Treichel, P. M.; Komar, D. A. *J. Organomet. Chem.* **1981**, *206*, 77. (b) Treichel, P. M.; Rosenhein, L. D. *J. Am. Chem. Soc.* **1981**, *103*, 691. (c) Treichel, P. M.; Rosenhein, L. D.; Schmidt, M. S. *Inorg. Chem.* **1983**, *22*, 3960.
(15) Treichel, P. M.; Schmidt, M. S.; Koehler, S. D. *J. Organomet. Chem.* **1983**, *258*, 209.
(16) Consiglio, G.; Morandini, F.; Bangerter, F. *Inorg. Chem.* **1982**, *21*, 455.

Scheme 3. Synthesis and Reactions of Diallyl Sulfide Complexes of a Chiral Ruthenium Lewis Acid



ing dialkyl sulfide complexes was investigated.[17] As shown in Scheme 3, reactions of **4** with $NH_4^+PF_6^-$ and then diallyl or dimethallyl sulfide in refluxing methanol gave the target complexes $[(\eta^5\text{-}C_5H_5)Ru(S,S\text{-chiraphos})(S(CH_2CR{=}CH_2)_2)]^+PF_6^-$ (**5**$^+PF_6^-$; R = **a**, H; R = **b**, CH_3) as analytically pure powders in >90% yields. Complexes **5a**,**b**$^+PF_6^-$ were characterized as described for **1**$^+BF_4^-$. They could also be isolated in similar yields from analogous reactions with the iodide complex (η^5-C_5H_5)Ru(*S*,*S*-chiraphos)(I) (**6**).[17,18]

A CH_2Cl_2 solution of **5a**$^+PF_6^-$ and a THF solution of *t*-BuOK were combined at −98 °C. A nonchromatographic workup gave the spectroscopically pure thiolate complex (η^5-C_5H_5)Ru(*S*,*S*-chiraphos)(SCH(CH=CH_2)CH_2-CH=CH_2) (**8a**) in >99% yield as a 78:22 mixture of *SSS*/*SSR* P***C***,P′***C***′,S***C*** diastereomers, as assayed by ^1H and ^{31}P NMR.[10] As illustrated in Scheme 3, this product is consistent with the intermediacy of ylide **7**, and configurations were assigned as described below. Pure samples of each diastereomer were sought—an objective for which less diastereoselective conditions can be advantageous. Thus, a THF solution of **5a**$^+PF_6^-$ was similarly reacted at −80 °C. Flash chromatography gave (*SSS*)-**8a** and (*SSR*)-**8b** in 52% and 44% yields (54:46), respectively. Both diastereomers were dextrorotatory ($[\alpha]^{25}_{589}$ 384° ± 2°, 257° ± 2°) and were characterized by ^1H, ^{13}C, and ^{31}P NMR. A combined sample gave a correct microanalysis.

The dimethallyl sulfide complex **5b**$^+PF_6^-$ behaved similarly. When CH_2Cl_2 solutions of **5b**$^+PF_6^-$ and THF solutions of *t*-BuOK were combined at −98 °C, the thiolate complex (η^5-C_5H_5)Ru(*S*,*S*-chiraphos)(SCH-(C(CH_3)=CH_2)CH_2C(CH_3)=CH_2) (**8b**) formed as a 87:13 mixture of *SSS*/*SSR* diastereomers. A nonchromatographic workup gave **8b** in >99% yield. When a similar reaction was conducted at −80 °C, the diastereomer ratio decreased to 68:32. Curiously, with **8a** the diastereomer ratio varied only slightly under comparable conditions. Complexes **8a**,**b** were much more robust than the iron analog **3** but did decompose upon prolonged exposure to air, chlorinated solvents, or silica gel.

A low-temperature NMR experiment showed that **5a**$^+PF_6^-$ and *t*-BuOK rapidly reacted in CH_2Cl_2 at −98 °C to give **8a** without any detectable intermediates. NMR experiments were also conducted in other solvents in hopes of enhancing diastereoselectivity. However, diastereomer ratios were always lower than those obtained in CH_2Cl_2 (CH_3CN, −45 °C, 67:33; DMF, −60 °C, 63:37; THF, −90 °C, 62:38; EtOAc, −90 °C, 59:41; diglyme, −66 °C, 57:43; acetone, −90 °C, 52:48).

Attention was turned to detaching the thiolate ligands from the ruthenium. Previous reports have shown that cyclopentadienylruthenium thiolate complexes are easily alkylated at sulfur to give cationic sulfide complexes,[19] analogous to the rhenium chemistry in Scheme 1. Furthermore, Schenk has shown that sulfoxide complexes of **III** and NaI react in refluxing acetone to give free sulfoxides and iodide complex **6**.[17] Accordingly, **8a** and CH_3I were combined in acetone or acetone-d_6. A ^{31}P NMR experiment showed the slow conversion of **8a** to a new compound (83.8 and 66.6 ppm, 2 d, J_{PP} = 40 Hz), presumably a cationic methyl allyl sulfide complex. For convenience, preparative reactions were refluxed for 1 h. With longer reflux times, another new compound could be detected. However, the addition of excess NaI greatly accelerated the formation of this species (complete within 5 h at 50 °C with 5 equiv). Chromatography gave the iodide complex **6** in 98% yield, and distillation gave the previously characterized free methyl sulfide $CH_3SCH(CH{=}CH_2)CH_2CH{=}CH_2$ (**9a**)[3a] in 75% yield. An analogous reaction sequence with **8b** afforded **6** (90%) and the known methyl sulfide $CH_3SCH(C(CH_3){=}CH_2)CH_2C(CH_3){=}CH_2$ (**9b**,[3a] 71%).

As is readily visualized from Scheme 3, the preceding reactions allow an extremely efficient recycling of the chiral ruthenium Lewis acid **III**. The formation of **6** and **9** was quantitative by NMR. Thus, we attributed the lower isolated yields of **9a**,**b** to volatility-related

(17) Schenk, W. A.; Frisch, J.; Adam, W.; Prechtl, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1609.

(18) For prior characterization of the ruthenium iodide complex **6**, see: Frisch, J. Ph.D. Thesis, University of Würzburg, 1994.

(19) (a) Hachgenei, J. W.; Angelici, R. J. *J. Organomet. Chem.* **1988**, *355*, 359. (b) Schenk, W. A.; Stur, T. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1990**, *45*, 1495. (c) Treichel, P. M.; Schmidt, M. S.; Crane, R. A. *Inorg. Chem.* **1991**, *30*, 379.

handling losses. Accordingly, an analogous sequence involving a heavier alkylating agent, $PhCH_2I$, was investigated. Preparative reactions were worked up chromatographically and gave **6** in >99−97% yields and the previously characterized free benzyl sulfides $PhCH_2SCH(C(R)=CH_2)CH_2C(R)=CH_2$ (**10a**,**b**)[3a] in >99% yields.

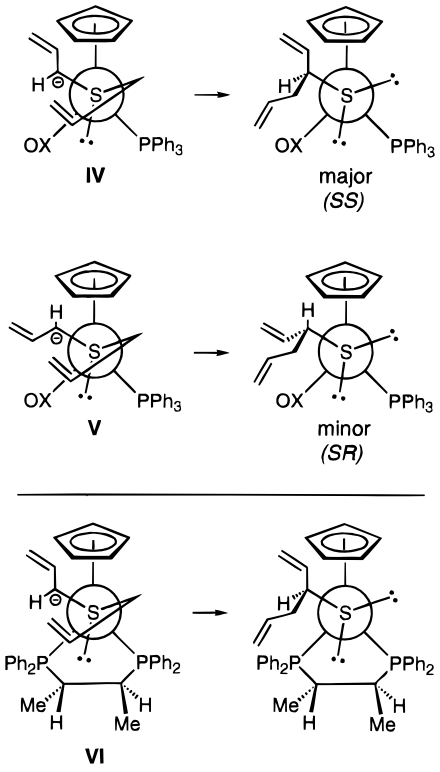
It has been previously shown that the enantiomeric purities of methyl and benzyl sulfides **9a**,**b** and **10a**,**b** can be assayed by ^{13}C NMR in the presence of Ag(fod) and $Eu(hfc)_3$.[3a,20] Also, the absolute configurations of **9a** and **10a** have been established by a crystal structure of the rhenium thiolate complex precursor shown in Scheme 1.[3a] Configurations were assigned to **9b** and **10b** by analogy this and two other structurally characterized rhenium thiolate complexes.[3a,b] A ^{13}C NMR assay of the sample of **9a** obtained in Scheme 3 established that the dominant configuration was *S*, identical with the result obtained with the rhenium Lewis acid **I** in Scheme 1 (71:29 *S*/*R*). The dominant configuration of **10b** was similarly shown to be *S* (88:12 *S*/*R*). Importantly, the enantiomer ratios are within experimental error of the **8a**,**b** diastereomer ratios.[10] Hence, the carbon stereocenter is not affected by the alkylation/substitution sequence.

Discussion

The above data establish that the deprotonation/rearrangement sequence shown for diallyl sulfide complexes of the chiral rhenium Lewis acid **I** in Scheme 1 can be extended to the chiral iron and ruthenium fragments $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)]^+$ (**II**; Scheme 2) and $[(\eta^5\text{-}C_5H_5)Ru(S,S\text{-chiraphos})]^+$ (**III**; Scheme 3). Thus, we believe that such transformations will prove general for d^6 cyclopentadienyl transition metal Lewis acids of the formula $[(\eta^5\text{-}C_5R_5)M(L)(L')]^+$. We also suggest that other types of formally octahedral d^6 metal fragments will behave similarly and would not be surprised to see this chemistry reduced to practice across the entire transition metal series. In this context, metal sulfide complexes are commonly air stable, thermally robust, and experimentally forgiving compounds.

However, we were disappointed that the iron Lewis acid **II** did not give higher diastereoselectivities than the rhenium Lewis acid **I**. Although these might at first glance seem to provide isosteric environments, metal−ligand bonds in iron complexes are typically 6−9% shorter than in rhenium homologs.[21] We had anticipated that the more congested iron coordination sphere would enhance the energy differences between the competing diastereomeric transition states. With **I**, diastereoselection has been previously analyzed in the context of transition state models **IV** (favored) and **V** (disfavored), as illustrated in Scheme 4.[3,5] In the former, a slight stabilizing interaction between the cyclopentadienyl ligand hydrogens and the C=C π cloud of the deprotonated allyl group has been proposed. Perhaps the attraction is diminished by the shorter contacts in **II**. It should also be emphasized that the configurations assigned to the resulting iron thiolate complexes (**3**, Scheme 2) are provisional, and **V** may in fact represent the dominant pathway.

Scheme 4. Possible Transition State Models for Competing [2,3] Sigmatropic Rearrangements



The ruthenium Lewis acid **III** gives somewhat higher diastereoselectivities than **II**, and the configurations of the resulting thiolate complexes (**8**, Scheme 3) have been rigorously established. However, only scant information is available concerning the preferred conformations of ruthenium−sulfur or sulfur−carbon bonds in sulfide or thiolate complexes of **III** or related compounds.[22] Hence, we feel that it is premature to propose a transition state model at this time. For the moment, we simply note that **VI** (Scheme 4), which is an arbitrary adaptation of the rhenium/iron model **IV**, would lead to the major diastereomer of the thiolate complex. It is nonetheless apparent from **VI** that the energy differences between the various competing transition states will largely depend upon the following two factors: (1) the PPh_2 phenyl ring orientations and (2) the $PCHCH_3$ methyl group that is directed toward the sulfide ligand.

Probably the most significant aspect of the ruthenium-based chemistry in Scheme 3 is the efficient recycle protocol. First, the thiolate ligand is easily detached in a one-flask alkylation/substitution sequence (R′I/NaI). Second, the starting ruthenium diallyl sulfide complex can then be regenerated in a single step, as opposed to the three steps required with the rhenium Lewis acid **I**. Third, all yields are essentially quantitative. Curiously, iodide ion does not readily displace sulfide ligands from the coordination sphere of **I**. Thus, the continued investigation of chiral cyclopentadienyl ruthenium Lewis acids would seem to hold particular promise. Although no fragments have yet been found that give diastereoselectivites as high as **I**, considerable structural diversity is clearly possible with Lewis acids of the formula $[(\eta^5\text{-}C_5R_5)M(L)(L')]^+$. Thus, it should be possible to develop an auxiliary that is optimized from both the diastereoselectivity and recycling standpoints.

(20) Offermann, W.; Mannschreck, A. *Tetrahedron Lett.* **1981**, *22*, 3227.

(21) For comparisons of iron and rhenium dimethyl sulfide complexes, see ref 4a.

(22) Ohkita, K.; Kurosawa, H.; Hirao, T.; Ikeda, I. *J. Organomet. Chem.* **1994**, *470*, 179.

Finally, this study adds to a growing body of data involving α carbon−hydrogen bond activation in neutral heteroatomic donor ligands. In the case of cationic transition metal Lewis acids, deprotonation will give reactive ylidic species. In our opinion, these have numerous potential applications in synthesis, as illustrated by the carbon−carbon bond-forming [2,3] sigmatropic rearrangements above. Although the literature examples cited in our previous papers have emphasized sulfide and sulfoxide ligands,[23] it is clear that ether[24] and phosphine[25] ligands can react similarly. Current efforts in our laboratory also include attempts to generate ylides of the types in Schemes 1−3 by alternative pathways that do not require base addition.

Experimental Section

General Procedures. IR and NMR spectra were recorded on Mattson Polaris and Varian FT spectrometers.[26] Microanalyses were conducted by Atlantic Microlab. Melting points were determined in evacuated capillaries using calibrated thermometers.[27] Reactions were conducted under dry N_2 atmospheres. Solvents were utilized as follows: CH_2Cl_2, CD_2Cl_2, distilled from CaH_2; THF, ether, hexanes, toluene, benzene, distilled from (Na or K)/benzophenone; pentane, distilled from activated 4 Å molecular sieves; C_6D_6, acetone, methanol, used as received. The following reagents were used as received (Aldrich unless noted): $S(CH_2CH{=}CH_2)_2$, *t*-BuOK (1.0 M in THF), $(Me_2CH)_2NLi{\cdot}$THF (1.5 M in cyclohexane), $(Me_3Si)_2NLi$ (1.0 M in THF), $AgBF_4$, Ag(fod), (+)-Eu(hfc)$_3$, CH_3I (Mallinckrodt), $PhCH_2I$ (AESAR), $NH_4{}^+PF_6{}^-$ (Strem), (*S*,*S*)-chiraphos (Strem), $S(CH_2C(CH_3){=}CH_2)_2$ (prepared as described earlier).[3b] Alumina (80−200 mesh, Fisher) was activated (300 °C, 0.05 Torr, 12 h) and silica gel (230−400 mesh, 60 Å, Aldrich) was degassed prior to use.

[(η⁵-C_5H_5)Fe(CO)(PPh_3)($S(CH_2CH{=}CH_2)_2$)]⁺$BF_4{}^-$ (1⁺$BF_4{}^-$). A Schlenk flask was charged with (η⁵-C_5H_5)Fe(CO)(PPh_3)(I)[9] (1.231 g, 2.287 mmol) and $AgBF_4$ (0.459 g, 2.36 mmol) and cooled to −80 °C (2-propanol/CO_2). Then THF (30 mL) was added with stirring. After 2 min, the cold bath was removed. After 30 min, volatiles were removed by oil pump vacuum. The residue was dissolved in CH_2Cl_2 (30 mL), and $S(CH_2CH{=}CH_2)_2$ (530 μL, 4.12 mmol) was added with stirring. After 6 h, volatiles were removed by oil pump vacuum (1 h). Then CH_2Cl_2 (80 mL) was added, and the mixture was filtered via cannula (no. 1 paper). The filtrate was concentrated by oil pump vacuum (*ca*. 20 mL), and ether (30 mL) was added dropwise (15 min), giving a red-brown solid. The supernatant was removed by cannula, and the solid was washed with ether (50 mL). Then CH_2Cl_2 (40 mL) was added, and the mixture was filtered via cannula (no. 1 paper). The filtrate was concentrated by oil pump vacuum (*ca*. 20 mL), and ether (50 mL) was added dropwise (15 min). This gave red microcrystals of 1⁺$BF_4{}^-$, which were washed with ether (30 mL) and pentane (30 mL) and dried by oil pump vacuum (1.12 g, 1.82 mmol, 80%), mp 180 °C dec. Calcd for $C_{30}H_{30}BF_4FeOPS$: C, 58.85; H, 4.94. Found: C, 58.67; H, 4.96. IR (cm^{-1}, CH_2Cl_2): ν_{CO} 1978 vs.

NMR (CD_2Cl_2):[26] ^1H 7.60−7.31 (m, 3 Ph), 5.56 (m, 2 CH═), 5.33 (m, 2 ═CH_2), 4.90 (d, J_{HP} = 2, C_5H_5), 3.23 (m, 2 SC***H***′), 2.81 (m, 2 SCH***H***′); $^{13}C\{^1H\}$ 133.4 (d, J_{CP} = 9, *o*-Ph), 132.4 (d, J_{CP} = 45, *i*-Ph), 132.1 (d, J_{CP} = 1, *p*-Ph), 129.8 (d, J_{CP} = 10, *m*-Ph), 130.6 (s, CH═), 123.3 (s, ═CH_2), 85.0 (s, C_5H_5), 43.0 (d, J_{CP} = 1, SCH_2), CO signal not observed; $^{31}P\{^1H\}$ 62.8 (s).

(η⁵-C_5H_5)Fe(CO)(PPh_3)(SCH($CH{=}CH_2$)$CH_2CH{=}CH_2$) (3). Method A. An oven-dried Schlenk flask was charged with 1⁺$BF_4{}^-$ (0.566 g, 0.924 mmol) and CH_2Cl_2 (30 mL) and cooled to −80 °C. Then *t*-BuOK (1.0 M in THF; 924 μL, 0.924 mmol) was added with stirring. After 5 min, the cold bath was removed. Volatiles were immediately removed by oil pump vacuum. Then ether/hexane (1:1 v/v, 40 mL) was added, and the mixture was filtered via cannula (no. 1 paper). The filtrate was chromatographed on an alumina column (14 × 2.5 cm) with hexane (100 mL) and ether (100 mL). The green band was concentrated by oil pump vacuum (30 mL), and hexane (30 mL) was added. The sample was slowly concentrated by oil pump vacuum. This gave green microcrystals of **3**, which were rapidly washed with hexane (5 mL) and dried by oil pump vacuum (0.315 g, 0.601 mmol, 65%; 75:25 *SS*,*RR*/*SR*,*RS*). Calcd for $C_{30}H_{29}FeOPS$: C, 68.71; H, 5.57. Found: C, 68.47; H, 5.62.[28] IR (cm^{-1}, KBr): ν_{CO} 1936 vs.

Method B. A flame-dried Schlenk flask was charged with 1⁺$BF_4{}^-$ (0.1080 g, 0.1765 mmol) and CH_2Cl_2 (20 mL) and cooled to −98 °C (CH_3OH/liquid N_2). Then *t*-BuOK (1.0 M in THF; 0.265 mL, 0.265 mmol) was added with stirring. After 1 h, volatiles were removed by oil pump vacuum as the cold bath was allowed to warm to room temperature. The residue was extracted with benzene (5 mL) and the extract passed through a frit. Volatiles were removed from the filtrate by oil pump vacuum to give **3** as a green syrup (0.0852 g, 0.163 mmol, 92% and >95% purity by ^1H NMR; 68:32 *SS*,*RR*/*SR*,*RS*).

NMR for (*SS*,*RR*)-**3**:[26] ^1H (CD_2Cl_2) 7.61−7.53 (m, 3 Ph), 5.78, 5.58 (2 m, 2 CH═), 4.90 (m, 2 ═CH_2), 4.50 (d, J_{HP} = 1, C_5H_5), 2.50 (m, SCH), 2.32 (m, SCHC***H***H′), 2.19 (m, SCHCH***H***′); ^1H (C_6D_6) 7.78−6.97 (m, 3 Ph), 6.14, 5.85 (2 m, 2 CH═), 5.28−4.90 (m, 2 ═CH_2), 4.35 (d, J_{HP} = 1, C_5H_5), 2.85 (m, SCHC***H***H′), 2.70−2.47 (m, SC***H***, SCHCH***H***′); $^{13}C\{^1H\}$ (CD_2Cl_2) 136.3 (d, J_{CP} = 43, *i*-Ph), 133.9 (d, J_{CP} = 9, *o*-Ph), 130.4 (d, J_{CP} = 3, *p*-Ph), 128.6 (d, J_{CP} = 10, *m*-Ph), 146.1, 138.5 (2 s, 2 CH═), 114.9, 111.0 (2 s, 2 ═CH_2), 84.6 (d, J_{CP} = 2, C_5H_5), 49.9 (d, J_{CP} = 4, SCH), 44.6 (s, SCH***C***H_2), CO signal not observed; $^{31}P\{^1H\}$ (CD_2Cl_2/C_6D_6) 68.1/71.2 (s). NMR for (*SR*,*RS*)-**3** (partial): ^1H (CD_2Cl_2/C_6D_6) 4.50/4.28 (d, J_{HP} = 1, C_5H_5); $^{13}C\{^1H\}$ (CD_2Cl_2) 136.1 (d, J_{CP} = 43, *i*-Ph), 134.0 (d, J_{CP} = 9, *o*-Ph), 144.8, 138.6 (2 s, 2 CH═), 115.1, 111.5 (2 s, 2 ═CH_2), 84.8 (d, J_{CP} = 2, C_5H_5), 49.4 (d, J_{CP} = 4, SCH), 44.3 (s, SCH***C***H_2); $^{31}P\{^1H\}$ (CD_2Cl_2/C_6D_6) 68.1/71.1 (s).

(η⁵-C_5H_5)Ru(*S*,*S*-chiraphos)(Cl) (4).[16] A flame-dried flask was charged with (η⁵-C_5H_5)Ru(PPh_3)$_2$(Cl) (1.79 g, 2.46 mmol),[29] (*S*,*S*)-chiraphos (1.16 g, 2.72 mmol), and benzene (200 mL) and fitted with a condenser. The mixture was refluxed for 4 h and cooled. Volatiles were removed by rotary evaporation. The residue was dissolved in a minimum of CH_2Cl_2 and chromatographed on a silica gel column (30 × 2.5 cm) with CH_2Cl_2 (until phosphine elution) and then acetone/CH_2Cl_2 (6:94 v/v). Volatiles were removed from the orange-red band by rotary evaporation and oil pump vacuum to give **4** as an orange powder (1.34 g, 2.13 mmol, 87%).

NMR ($CDCl_3$):[26] ^1H 7.60−6.50 (m, 4 Ph), 4.30 (s, C_5H_5), 2.66, 2.06 (2 m, 2 PCH), 1.02, 1.00 (2 dd, J_{HP} = 11, J_{HH} = 7; 2 PCHC***H***$_3$); $^{31}P\{^1H\}$ 85.7, 64.6 (2 d, J_{PP} = 40). These data matched literature values.[16]

[(η⁵-C_5H_5)Ru(*S*,*S*-chiraphos)($S(CH_2CH{=}CH_2)_2$)]⁺$PF_6{}^-$ (5a⁺$PF_6{}^-$). Method A. A flame-dried flask was charged with **4** (0.208 g, 0.331 mmol), $NH_4{}^+PF_6{}^-$ (0.360 g, 2.21 mmol), CH_3OH (20 mL), and $S(CH_2CH{=}CH_2)_2$ (0.170 mL, 1.32 mmol) and fitted with a condenser. The orange solution was refluxed and became a mustard yellow suspension (0.5 h). After 18 h, the mixture was cooled. Volatiles were removed by rotary

(23) Bennett, M. A.; Goh, L. Y.; Willis, A. C. *J. Am. Chem. Soc.* **1996**, *118*, 4984.
(24) Yi, C. S.; Wódka, D.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1996**, *15*, 2.
(25) Cagle, P. C. Unpublished results with diallylphosphine complexes of **I**, University of Utah, 1994.
(26) Chemical shift references: ^1H (300 MHz), TMS (δ 0.00); $^{13}C\{^1H\}$ (75.5 MHz), CD_2Cl_2 (53.8 ppm); $^{31}P\{^1H\}$ (121.5 MHz), external 85% H_3PO_4 (0.0 ppm). All *J* values are in Hz.
(27) Tiers, G. V. D. *J. Chem. Educ.* **1990**, *67*, 258.
(28) Melting points are not reported for mixtures of diastereomers.
(29) Bruce, M. I.; Hameister, C.; Swincer, A. G.; Wallis, R. C. *Inorg. Synth.* **1990**, *28*, 270.

evaporation. The residue was extracted with CH_2Cl_2 (10 mL). The extract was passed through a frit and added dropwise to ether (100 mL, 0 °C). The precipitate was collected on a frit, washed with ether (3 × 10 mL), and dried by oil pump vacuum over Drierite to give **5a**$^+PF_6^-$ as a bright yellow powder (0.265 g, 0.311 mmol, 94%), mp 216−220 °C dec, $[\alpha]^{25}_{589}$ 341° ± 3° (*c* 0.470 mg/mL, CH_2Cl_2).[30] Anal. Calcd for $C_{39}H_{43}F_6P_3RuS$: C, 54.99; H, 5.09. Found: C, 54.85; H, 5.31.

Method B. The iodide complex (η^5-C_5H_5)Ru(*S*,*S*-chiraphos)(I) (**6**, preparation below; 0.186 g, 0.258 mmol), $NH_4^+PF_6^-$ (0.233 g, 1.43 mmol), CH_3OH (25 mL), and $S(CH_2CH{=}CH_2)_2$ (68 μL, 0.53 mmol) were combined in an analogous procedure. An identical workup gave **5a**$^+PF_6^-$ as a bright yellow powder (0.213 g, 0.250 mmol, 97%)

NMR ($CDCl_3$):[26] ^{1}H 7.64−7.21, 7.01 (2 m, 4 Ph), 5.10 (ddt, J_{HH} = 17, 9, 7; 2 CH=), 4.96 (br d, J_{HH} = 9; 2 =C***H***H′), 4.75 (d, J_{HH} = 17; 2 =CH***H′***), 4.71 (s, C_5H_5), 2.58, 2.30 (2 m, 2 PCH), 2.54 (dd, J_{HH} = 14, 8; 2 SC***H***H′), 2.15 (dd, J_{HH} = 14, 5; 2 SCH***H′***), 0.78, 0.72 (2 dd, J_{HP} = 12, J_{HH} = 6; 2 PCHC***H***$_3$); ^{13}C{^{1}H} 134.1 (d, J_{CP} = 45, *i*-Ph), 133.8 (d, J_{CP} = 11, Ph), 132.4, 131.6 (2 d, J_{CP} = 9, Ph), 131.4 (d, J_{CP} = 4, Ph), 130.8 (br s, Ph), 129.8, 129.4, 129.1 (3 d, J_{CP} = 9, Ph), 128.7 (d, J_{CP} = 10, Ph), 132.0 (s, CH=), 121.0 (s, =CH_2), 84.1 (s, C_5H_5), 44.4 (t, J_{CP} = 6, SCH_2), 38.0, 36.7 (2 dd, J_{CP} = 32/31, 18/16; 2 PCH), 15.0, 14.6 (2 br d, J_{CP} = 20/19; 2 PCH***C***H_3), other Ph signals obscured; ^{31}P{^{1}H} 85.1, 63.2 (2 d, J_{PP} = 40).

[(η^5-C_5H_5)Ru(*S*,*S*-chiraphos)(S(CH$_2$C(CH$_3$)=CH$_2$)$_2$)]$^+PF_6^-$ (5b$^+PF_6^-$). Complex **6** (0.654 g, 0.909 mmol), $NH_4^+PF_6^-$ (1.16 g, 7.12 mmol), CH_3OH (70 mL), and $S(CH_2C(CH_3){=}CH_2)_2$ (0.517 g, 3.64 mmol) were combined in a procedure analogous to those for **5a**$^+PF_6^-$. The orange extract was passed through a frit and added dropwise to pentane (300 mL, 0 °C). The precipitate was collected on a frit, washed with pentane (3 × 30 mL), and dried by oil pump vacuum over Drierite to give **5b**$^+PF_6^-$ as a green powder (0.748 g, 0.850 mmol, 94%), mp 135−147 °C dec, $[\alpha]^{25}_{589}$ 294° ± 1° (*c* 0.470 mg/mL, CH_2Cl_2).[30] Anal. Calcd for $C_{41}H_{47}F_6P_3RuS$: C, 55.97; H, 5.38. Found: C, 54.65; H, 5.36.

NMR (CD_2Cl_2):[26] ^{1}H 7.74−7.55, 7.50−7.28, 7.02 (3 m, 4 Ph), 4.69 (s, 2 =C***H***H′), 4.67 (s, 2 =CH***H′***), 4.56 (s, C_5H_5), 2.81 (d, J_{HH} = 14; 2 SC***H***H′), 2.58 (d, J_{HH} = 14; 2 SCH***H′***), 2.62, 2.38 (2 m, 2 PCH), 1.31 (s, 2 =CCH_3), 0.85, 0.73 (2 dd, J_{HP} = 12/13, J_{HH} = 7/7; 2 PCHC***H***$_3$); ^{13}C{^{1}H} 134.5 (d, J_{CP} = 47, *i*-Ph), 133.8, 129.6, 128.8 (3 d, J_{CP} = 10, Ph), 132.9, 130.2, 129.4 (3 d, J_{CP} = 9, Ph), 131.4−130.9 (m, Ph), 139.5 (s, =***C***CH_3), 116.6 (s, =CH_2), 84.8 (s, C_5H_5), 38.6, 36.9 (2 dd, J_{CP} = 32/31, 18/17; 2 PCH), 21.6 (s, =C***C***H_3), 15.0, 14.5 (2 dd, J_{CP} = 17/18, 5/4; 2 PCH***C***H_3), other Ph and SCH_2 signals obscured; ^{31}P{^{1}H} 81.2, 66.2 (2 d, J_{PP} = 42).

(η^5-C_5H_5)Ru(*S*,*S*-chiraphos)(SCH(CH=CH$_2$)CH$_2$CH=CH$_2$) (8a). Method A. A flame-dried Schlenk flask was charged with **5a**$^+PF_6^-$ (0.0531 g, 0.0623 mmol) and CH_2Cl_2 (10 mL) and cooled to −98 °C (CH_3OH/liquid N_2). Then *t*-BuOK (1.0 M in THF; 0.10 mL, 0.10 mmol) was slowly added with stirring. After 1 h, volatiles were removed by oil pump vacuum as the cold bath was allowed to warm to room temperature. The residue was extracted with benzene (5 mL). The extract was passed through a frit. Volatiles were removed by oil pump vacuum to give **8a** as an orange syrup (0.0453 g, 0.0637 mmol, >99% and >95% purity by ^{1}H and ^{31}P NMR; 78:22 *SSS*/*SSR*).

Method B. A flame-dried Schlenk flask was charged with **5a**$^+PF_6^-$ (0.100 g, 0.117 mmol) and THF (10 mL) and cooled to −80 °C. Then *t*-BuOK (1.0 M in THF; 0.18 mL, 0.18 mmol) was slowly added with stirring. The cold bath was removed. After 1 h, volatiles were removed by rotary evaporation. The residue was dissolved in a minimum of toluene and flash chromatographed on a silica gel column (230−400 mesh, 30 × 1.0 cm) with hexanes/ether (4:1 v/v) and N_2 pressure. Two orange bands were collected. Volatiles were removed by rotary evaporation and oil pump vacuum to give (*SSS*)-**8a** (0.0430 g, $[\alpha]^{25}_{589}$ 384° ± 2° (*c* 0.860 mg/mL, toluene)[30]) and (*SSR*)-**8a** (0.0370 g, $[\alpha]^{25}_{589}$ 257° ± 2° (*c* 0.745 mg/mL, toluene)[30]) as orange syrups (combined yield 0.0800 g, 0.113 mmol, 97%; 54:46 *SSS*/*SSR*).

Method C. An analogous reaction was conducted in which both diastereomers of **8a** were collected as one fraction. Anal. Calcd for $C_{39}H_{42}P_2RuS$: C, 66.36; H, 6.00; exact mass 706.151 96. Found: C, 66.27; H, 6.05; exact mass 706.152 46.[28]

NMR for (*SSS*)-**8a** (C_6D_6):[26] ^{1}H 8.21, 7.62, 7.27, 7.30−7.00, 6.93 (5 m, 4 Ph), 5.98 (dt, J_{HH} = 17, 10, CHC***H***=), 5.72 (ddt, J_{HH} = 17, 10, 6, CH_2C***H***=), 5.00−4.91 (m, =C***HH′***), 4.82 (dd, J_{HH} = 10, 2, =C′***H***H′), 4.71 (s, C_5H_5), 4.64 (dd, J_{HH} = 17, 2, =C′H***H′***), 3.36, 1.98 (2 m, 2 PCH),[31] 2.42 (m, SCHC***HH′***),[31] 1.47 (td, J_{HH} = 9, 4, SCH),[31] 0.98, 0.87 (2 dd, J_{HP} = 11/12, J_{HH} = 7/7; 2 PCHC***H***$_3$); ^{13}C{^{1}H} 144.1 (d, J_{CP} = 45, *i*-Ph), 138.7 (d, J_{CP} = 43, *i*-Ph), 137.5, 136.7 (2 d, J_{CP} = 11, Ph), 133.1, 131.7, 127.6, 127.5 (4 d, J_{CP} = 9, Ph), 149.4, 139.6 (2 s, 2 CH=), 114.4, 111.4 (2 s, 2 =CH_2), 82.9 (s, C_5H_5), 49.4 (t, J_{CP} = 6, SCH), 47.7 (s, SCH***C***H_2), 38.0, 37.6 (2 dd, J_{CP} = 34/27, 19/17; 2 PCH), 17.5, 16.3 (2 dd, J_{CP} = 17/15, 3/5; 2 PCH***C***H_3), other Ph signals obscured; ^{31}P{^{1}H} 87.5, 74.7 (2 d, J_{PP} = 35). NMR for (*SSR*)-**8a** (C_6D_6):[26] ^{1}H 8.19, 7.65, 7.49, 7.30−6.88 (4 m, 4 Ph), 5.88 (ddt, J_{HH} = 18, 9, 7, CH_2C***H***=),[31] 5.67 (ddd, J_{HH} = 19, 10, 9, CHC***H***=),[31] 4.95−4.73 (m, 2 =C***HH′***), 4.62 (s, C_5H_5), 2.94, 2.06 (2 m, 2 PCH),[31] 2.62 (m, SCHC***H***H′),[31] 2.39 (m, SCHCH***H′***),[31] 2.22 (td, J_{HH} = 9, 4, SCH),[31] 0.87, 0.76 (2 dd, J_{HP} = 11, J_{HH} = 7; 2 PCHC***H***$_3$); ^{13}C{^{1}H} 142.1, 138.8, 138.7 (3 d, J_{CP} = 43, *i*-Ph), 136.2 (d, J_{CP} = 10, Ph), 135.4 (d, J_{CP} = 11, Ph), 133.4, 131.8 (2 d, J_{CP} = 9, Ph), 129.6, 129.3 (2 d, J_{CP} = 2, Ph), 127.7 (d, J_{CP} = 9, Ph), 147.9, 139.4 (2 s, 2 CH=), 114.4, 110.7 (2 s, 2 =CH_2), 83.6 (s, C_5H_5), 49.8 (t, J_{CP} = 4, SCH), 45.9 (s, SCH***C***H_2), 40.3, 37.5 (2 dd, J_{CP} = 29/32, 20/19; 2 PCH), 16.6, 16.4 (2 dd, J_{CP} = 12/12, 4/5; 2 PCH***C***H_3), other Ph signals obscured; ^{31}P{^{1}H} 89.4, 71.8 (2 d, J_{PP} = 40).

(η^5-C_5H_5)Ru(*S*,*S*-chiraphos)(SCH(C(CH$_3$)=CH$_2$)CH$_2$C(CH$_3$)=CH$_2$) (8b). Method A. Complex **5b**$^+PF_6^-$ (0.0771 g, 0.0876 mmol), CH_2Cl_2 (10 mL), and *t*-BuOK (1.0 M in THF; 0.10 mL, 0.10 mmol) were combined in a procedure analogous to method A for **8a**. An identical workup gave **8b** as a red-orange powder (0.0623 g, 0.0849 mmol, 97% and >95% purity by ^{1}H NMR; 87:13 *SSS*/*SSR*).

Method B. Complex **5b**$^+PF_6^-$ (0.100 g, 0.114 mmol), CH_2Cl_2 (20 mL), and *t*-BuOK (1.0 M in THF; 0.136 mL, 0.136 mmol) were combined in a procedure analogous to method B for **8a**. The residue was extracted with benzene (5 mL). The extract was passed through a frit, and volatiles were removed by oil pump vacuum to give **8b** as a red-orange powder (0.0830 g, 0.114 mmol, >99%; 68:32 *SSS*/*SSR*).

Method C. The preceding reaction and workup was repeated, and the sample was flash chromatographed as described in procedure C for **8a**. Anal. Calcd for $C_{41}H_{46}P_2RuS$: C, 67.09; H, 6.32. Found: C, 67.09; H, 6.60.[28]

NMR for (*SSS*)-**8b** (C_6D_6):[26] ^{1}H 8.31, 7.66, 7.27−7.00, 6.93 (4 m, 4 Ph), 4.75, 4.67, 4.57 (3 m, 2 =C***HH′***), 4.72 (s, C_5H_5), 3.40, 1.99 (2 m, 2 PCH), 2.55 (t, J_{HH} = 13, SCHC***H***H′), 2.27 (dd, J_{HH} = 14, 5, SCHCH***H′***), 2.21, 1.52 (2 s, 2 =CCH_3), 2.08 (dd, J_{HH} = 12, 5, SCH), 0.98, 0.90 (2 dd, J_{HP} = 11/12, J_{HH} = 7/7; 2 PCHC***H***$_3$); ^{13}C{^{1}H} 144.4 (d, J_{CP} = 43, *i*-Ph), 139.1, 139.0 (2 d, J_{CP} = 44; 2 *i*-Ph), 137.9, 136.7 (2 d, J_{CP} = 11, Ph), 133.1, 131.7 (2 d, J_{CP} = 9, Ph), 130.0, 129.9, 129.2 (3 d, J_{CP} = 2, Ph), 127.6, 127.4 (2 d, J_{CP} = 6, Ph), 152.4, 145.6 (2 s, 2 =***C***CH_3), 111.6, 111.0 (2 s, 2 =CH_2), 82.4 (s, C_5H_5), 51.1 (br d, J_{CP} = 6, SCH), 49.7 (s, SCH***C***H_2), 38.3, 37.8 (2 dd, J_{CP} = 39/27, 19/17; 2 PCH), 22.8, 18.3 (2 s, 2 =C***C***H_3), 17.8, 16.4 (2 dd, J_{CP} = 16/15, 2/4; 2 PCH***C***H_3), other Ph signals obscured; ^{31}P{^{1}H} 87.5, 76.2 (2 d, J_{PP} = 34). NMR for (*SSR*)-**8b** (C_6D_6):[26] ^{1}H 8.19, 7.70, 7.63, 7.30, 7.29−6.89 (5 m, 4 Ph), 4.77, 4.72, 4.66, 4.57 (4 m, 2 =C***HH′***), 4.61 (s, C_5H_5), 2.72, 2.15 (2 m, 2 PCH), 2.63 (dd,

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

(31) These ^{1}H NMR assignments were confirmed by COSY experiments.

J_{HH} = 10, 5, SCH), 2.42 (m, SCHC***HH′***), 0.81, 0.61 (2 dd, J_{HP} = 11, J_{HH} = 7; 2 PCHC***H***$_3$); ^{13}C{^{1}H} 135.4, 133.4 (2 d, J_{CP} = 9, Ph), 134.4 (d, J_{CP} = 10, Ph), 129.5, 129.1 (2 br s, Ph), 152.3, 145.7 (2 s, 2 =***C***CH$_3$), 111.2, 110.5 (2 s, 2 =CH$_2$), 83.9 (s, C_5H_5), 52.2 (dd, J_{CP} = 6, 4, SCH), 48.5 (s, SCH***C***H$_2$), 42.2, 36.6 (2 dd, J_{CP} = 31/30, 21/19; 2 PCH), 22.2, 18.2 (2 s, 2 =C***C***H$_3$), 16.6, 15.9 (2 dd, J_{CP} = 17/18, 5/3; 2 PCH***C***H$_3$), other Ph signals obscured; ^{31}P{^{1}H} 92.3, 72.1 (2 d, J_{PP} = 42).

CH$_3$SCH(CH=CH$_2$)CH$_2$CH=CH$_2$ (9a) and (η^5-C$_5$H$_5$)Ru-(*S*,*S*-chiraphos)(I) (6). A flask was charged with **8a** (0.8298 g, 1.175 mmol; 75:25 *SSS*/*SSR*), acetone (50 mL), and CH$_3$I (81 μL, 1.3 mmol) and fitted with a condenser. The orange solution turned yellow within 2 min and was refluxed for 1 h. Then NaI (3.5 g, 23 mmol) was added, and the mixture refluxed for 5 h. The sample was concentrated by rotary evaporation, and the volatiles were transferred (25−50 °C, oil pump vacuum) into a liquid N_2-cooled receiver. Residual solvent was removed by rotary evaporation to give previously characterized[3b] (*S*)-**9a** as a pale green-yellow liquid (0.1125 g, 0.8773 mmol, 75%; 71:29 *S*/*R*, Ag(fod)/Eu(hfc)$_3$ analysis[10,20] of the 117.0 ppm ^{13}C NMR signal). The residue from the vacuum transfer was dissolved in CH_2Cl_2 and flash chromatographed on a silica gel column (230−400 mesh, 30 × 1.0 cm) with CH_2Cl_2 and N_2 pressure. Volatiles were removed by rotary evaporation to give **6** (0.829 g, 1.15 mmol, 98%) as an orange syrup.[18]

NMR for **9a** ($CDCl_3$):[26] ^{1}H 5.82 (ddt, J_{HH} = 17, 10, 7, CH$_2$C***H***=), 5.61 (ddd, J_{HH} = 17, 10, 9, CHC***H***=), 5.14−4.96 (m, 2 =CH$_2$), 3.11 (m, SCH), 2.38 (apparent tq, J_{HH} = 7, 1, SCHC***HH′***), 2.00 (s, SCH$_3$); ^{13}C{^{1}H} 138.4, 135.4 (2 s, 2 CH=), 117.0, 115.6 (2 s, 2 =CH$_2$), 50.1 (s, SCH), 38.6 (s, SCH***C***H$_2$), 13.9 (s, SCH$_3$). These data matched literature values.[3b] NMR for **6** ($CDCl_3$):[26] ^{1}H 7.93, 7.58−7.17, 7.01 (3 m, 4 Ph), 4.45 (s, C_5H_5), 3.03, 2.14 (2 m, 2 PCH), 1.13, 1.04 (2 dd, J_{HP} = 11/11, J_{HH} = 7/7; 2 PCHC***H***$_3$); ^{31}P{^{1}H} 82.6, 74.0 (2 d, J_{PP} = 34). These data matched literature values.[18]

PhCH$_2$SCH(CH=CH$_2$)CH$_2$CH=CH$_2$ (10a) and 6. Complex **8a** (0.3429 g, 0.4858 mmol), PhCH$_2$I (0.1170 g, 0.5340 mmol), acetone (20 mL), and NaI (0.154 g, 1.03 mmol) were combined in a procedure analogous to that for **9a**. Volatiles were removed by rotary evaporation. The residue was dissolved in a minimum of CH_2Cl_2 and flash chromatographed on a silica gel column (230−400 mesh, 30 × 2.5 cm) with pentane/CH_2Cl_2 (9:1 v/v) and N_2 pressure. Volatiles from the first fraction were removed by rotary evaporation to give previously characterized[3b] **10a** as a faint yellow liquid (0.0993g, 0.486 mmol, >99%). The column was eluted with 6:94 acetone/CH_2Cl_2 (v/v) to give a red-orange fraction. Solvent was removed by rotary evaporation to give **6** (0.3507 g, 0.4874 mmol, >99%) as an orange syrup. NMR data were identical with those above.

NMR for **10a** (acetone-d_6):[26] ^{1}H 7.59−7.31 (m, Ph), 5.97−5.74 (m, 2 CH=), 5.28−5.10 (m, 2 =CH$_2$), 3.85 (d, J = 14, C***H***H′Ph), 3.77 (d, J = 14, CH***H′***Ph), 3.31 (m, SCH), 2.46 (SCHC***HH′***). These data matched literature values.[3b]

CH$_3$SCH(C(CH$_3$)=CH$_2$)CH$_2$C(CH$_3$)=CH$_2$ (9b) and 6. Complex **8b** (0.0291 g, 0.0397 mmol), CH$_3$I (3 μL, 0.05 mmol), acetone (10 mL), and NaI (0.119 g, 0.793 mmol) were combined in a procedure analogous to that for **9a**. An identical workup gave **9b** as a faint yellow liquid (0.0044 g, 0.028 mmol, 71%) and **6** (0.0257 g, 0.0357 mmol, 90%) as an orange syrup.

NMR for **9b** ($CDCl_3$):[26] ^{1}H 4.88−4.75 (m, 2 =CH$_2$), 3.31 (t, J_{HH} = 8, SCH), 2.34 (d, J_{HH} = 8, SCHC***HH′***), 1.95 (d, J_{HH} = 1, SCH$_3$), 1.76 (s, 2 CH$_3$). These data matched literature values.[3b]

PhCH$_2$SCH(C(CH$_3$)=CH$_2$)CH$_2$C(CH$_3$)=CH$_2$ (10b) and 6. Complex **8b** (0.0787 g, 0.107 mmol), PhCH$_2$I (0.0282 g, 0.129 mmol), acetone (20 mL), and NaI (0.321 g, 2.14 mmol) were combined in a procedure analogous to that for **10a**. An identical workup gave **10b** as a light yellow liquid (0.0248 g, 0.107 mmol, >99%; 88:12 *S*/*R*, Ag(fod)/Eu(hfc)$_3$ analysis[10,20] of 112.6 ppm ^{13}C NMR signal) and **6** (0.0749 g, 0.104 mmol, 97%) as an orange syrup.

NMR for **10b** ($CDCl_3$):[26] ^{1}H 7.31−7.20 (m, Ph), 4.93−4.69 (m, 2 =CH$_2$), 3.60 (d, J_{HH} = 13, C***H***H′Ph), 3.56 (d, J_{HH} = 13, CH***H′***Ph), 3.42 (t, J_{HH} = 8, SCH), 2.31 (d, J_{HH} = 8, SCHC***HH′***), 1.80, 1.65 (2 s, 2 CH$_3$). These data matched literature values.[3b]

Acknowledgment. We thank the NSF for financial support. Postdoctoral fellowships were generously provided by the NIH (P.T.B., P.C.C) and NATO (D.V.).

OM960541Q