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

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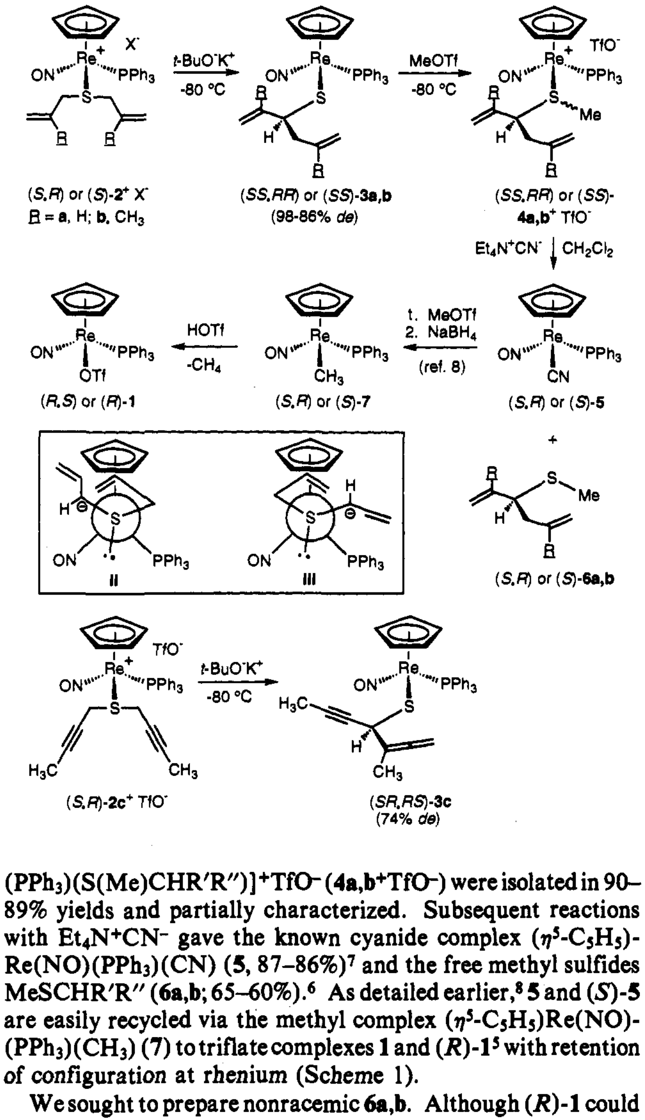
The [2,3] sigmatropic rearrangement of allyl and propargyl sulfur ylides is a powerful and extensively utilized carbon–carbon bond construct.[1] However, to our knowledge there are only two examples of chiral products forming enantioselectively from precursors lacking carbon stereocenters.[2] One features an ylide with a resolved sulfur stereocenter (≥94% ee), and the other a chiral base (5–12% ee). Surprisingly, approaches involving chiral auxiliaries do not appear to have been investigated.[3] In this communication, we report that the chiral rhenium Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (**I**) serves as an easily resolved and recycled auxiliary for transforming di(allyl) and di(propargyl) sulfides to rearrangement products of high enantiomeric purities. These data further suggest that chiral transition-metal reagents or catalysts might be able to control absolute stereochemistry in other sigmatropic rearrangements involving heteroatom donor groups.

Dialkyl sulfide complexes of **I** have been prepared previously.[4] In similar procedures, the triflate complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OTf)$ (**1**)[5] and di(allyl) or di(propargyl) sulfides SR_2 (1.5 equiv; R = **a**, $CH_2CH{=}CH_2$; **b**, $CH_2C(CH_3){=}CH_2$; **c**, $CH_2C{\equiv}CCH_3$) were reacted. Workups gave the sulfonium salts $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(SR_2)]^+TfO^-$ (**2a–c**$^+$TfO$^-$; 86–79%), which were characterized by microanalysis and IR and NMR (^{1}H, ^{13}C, ^{31}P) spectroscopy.[6] The diastereotopic SR_2 groups gave only one set of NMR signals at ambient temperature. Exchange requires both sulfur inversion and rhenium–sulfur bond rotation, and $\Delta G^\ddagger$ is only 9.6–9.7 kcal/mol (205–213 K) when R = methyl.[4]

THF solutions of **2a–c**$^+$TfO$^-$ and *t*-BuO$^-$K$^+$ (1.0 equiv) were combined at −80 °C. Reactions were complete within a few minutes as assayed in separate NMR experiments. Workups gave the rearranged thiolate complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(SCHR'R'')$ (**3**; R′/R″ = **a**, $CH{=}CH_2/CH_2CH{=}CH_2$; **b**, $C(CH_3){=}CH_2/CH_2C(CH_3){=}CH_2$; **c**, $C{\equiv}CCH_3/C(CH_3){=}C{=}CH_2$) in 95–92% yields as 93:7, 98:2, and 87:13 mixtures of Re,C configurational diastereomers (Scheme 1). Hence, there is efficient transfer of chirality from rhenium to the new carbon stereocenter, presumably via intermediate ylides (e.g., **II**, **III**). Complexes **3a–c** were characterized analogously to **2a–c**$^+$TfO$^-$.[6]

Attention was turned to detaching the thiolate ligands from rhenium. First, **3a,b** were treated with MeOTf. The corresponding methyl sulfide complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(S(Me)CHR'R'')]^+TfO^-$ (**4a,b**$^+$TfO$^-$) were isolated in 90–89% yields and partially characterized. Subsequent reactions with $Et_4N^+CN^-$ gave the known cyanide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CN)$ (**5**, 87–86%)[7] and the free methyl sulfides MeSCHR′R″ (**6a,b**; 65–60%).[6] As detailed earlier,[8] **5** and (*S*)-**5** are easily recycled via the methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**7**) to triflate complexes **1** and (*R*)-**1**[5] with retention of configuration at rhenium (Scheme 1).

Scheme 1. Rearrangement, Methylation, and Displacement of Sulfur Donor Ligands



We sought to prepare nonracemic **6a,b**. Although (*R*)-**1** could be converted to (*S*)-**2a,b**$^+$TfO$^-$, these were—like many compounds in this series—more difficult to crystallize and purify than the racemates. For this initial study, analytically pure reactants were desired. Thus, the substitution-labile chlorobenzene complex (*S*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClC_6H_5)]^+BF_4^-$ (**8**) was generated *in situ* from methyl complex (*S*)-**7** as previously described.[9] Additions of sulfides **a,b** gave the tetrafluoroborate salts (*S*)-**2a,b**$^+$BF$_4^-$ (80–70%).[5] Configurations (retention) were assigned by analogy to other substitution reactions of **1**, **8**, and related compounds.[5,7–11]

Reactions of (*S*)-**2a,b**$^+$BF$_4^-$ and *t*-BuO$^-$K$^+$ gave thiolates **3a,b** (79%) as 93:7 and >99.5:0.5 *SS*/*SR* mixtures.[5] Before workup, **3b** was a 99.3:0.7 *SS*/*RR* mixture. Thus, (*S*)-**2b**$^+$BF$_4^-$ gives higher diastereoselectivity than the racemic triflate salt. Carbon configurations were assigned as described below. Subsequent reactions with MeOTf gave **4a,b**$^+$TfO$^-$ (95–89%; 92:8, >99.5:0.5

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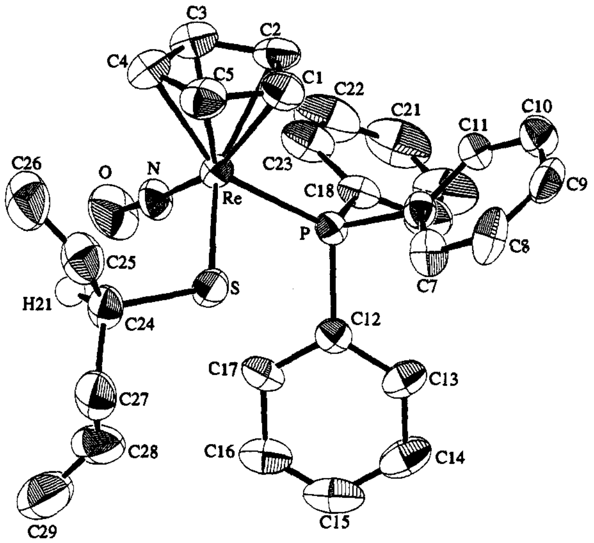

Figure 1. Structure of (*SS*)-**3a** with a calculated proton position. Selected bond lengths (Å) and angles (deg): Re–S 2.348(1), S–C24 1.849(6), C24–C27 1.517(9), C27–C28 1.46(1), C28–C29 1.29(1), C24–C25 1.48(1), C26–C25 1.33(1), Re–P 2.384(1), Re–N 1.741(5), N–O 1.209(6); Re–S–C24 109.5(2), S–C24–C25 111.3(5), S–C24–C27 108.3(4), C24–C25–C26 125.9(8), C24–C27–C28 115.2(6), C27–C28–C29 127.3(8), S–Re–N 100.7(2), S–Re–P 86.00(5), P–Re–N 93.2(2), Re–N–O 174.3(5).

SS/*SR*), which were treated with $Et_4N^+CN^-$ to give the cyanide complex (*S*)-**5** (93–92%; >98% ee, $Eu(hfc)_3$) and (*S*)-**6a**,**b** (67–58%; 84% ee, >98% ee, $Ag(fod)/Eu(hfc)_3$). The enantiomeric purity of (*S*)-**5** shows that there is no loss of configuration at rhenium during the preceding sequence, and retention has been established for closely related cyanide ion substitutions.[8]

Complex (*SS*)-**3a** was crystallized to diastereomeric purity, and an X-ray structure established the relative and absolute Re,C configurations (Figure 1). The conformations about the Re–S–C bonds were similar to those about the Re–O–C bonds of an analogous 1-phenylethoxide complex.[11] The major diastereomers of **3a**–**c** exhibited ^{31}P and cyclopentadienyl ^1H and ^{13}C NMR signals upfield from those of the minor diastereomers. Hence, configurations were assigned to **3b** (*SS*,*RR* or *SS* major) and **3c** (*SR*,*RS* major) accordingly. This establishes, in conjunction with the precedents cited above, retention at rhenium throughout Scheme 1—as would be intuitively expected for the ligand-based transformations that convert $\mathbf{2}^+X^-$ to **3** and then $\mathbf{4}^+TfO^-$.

Mechanisms of [2,3] sigmatropic rearrangements of sulfur ylides have been studied in detail.[12] The stereochemistry of **3a** is consistent with transition-state models **II** and **III**, in which the *si* face of the ylide carbanion is alkylated when the rhenium configuration is *S*. Models **II** and **III** also show the sulfur lone pair in the presumably favored position with respect to (1) the allyl moiety in the cyclic transition state ("exo")[12] and (2) the rhenium fragment (the interstice between the PPh_3 and NO ligands).[4] However, these features are not demanded by the data. In fact, in our present view neither **II** nor **III** offers an obvious energetic advantage over S–C conformers that would present the carbanion *re* face to alkylation. Hence, transition states with alternative geometries—particularly about the labile sulfur stereocenter—must remain in consideration.

All of the preceding reactions are spectroscopically quantitative. Thus, there is much potential for yield optimization, including the combination of consecutive steps. The methyl complex **7** can be accessed in four steps from commercial $Re_2(CO)_{10}$ (57%), and resolution is easily effected in two steps en route.[8,13] All compounds are air-stable as solids. Finally, it should be noted that sulfur donor ligands undergo numerous other types of base-promoted rearrangements.[14] Many extensions of the above chemistry are readily envisioned and are under active investigation.

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Supplementary Material Available: Syntheses and characterization data for new compounds, and tables of crystallographic data (15 pages); observed and calculated structure factors (13 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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