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A New Reaction of Coordinated Sulfoxides: Facile and Highly Diastereoselective Deprotonation of a Chiral, Cationic Rhenium DMSO Complex to an Ylide and Subsequent [1,2] Migration of Rhenium from Sulfur to Carbon

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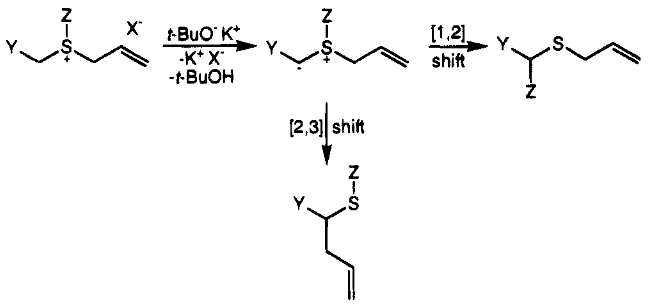
Reaction of the chiral, cationic sulfur-ligated DMSO complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(S(O)(CH_3)_2)]^+BF_4^-$ and $t\text{-}BuO^-K^+$ (CH_2Cl_2, −80 °C) gives the neutral alkyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2S(O)CH_3)$ (**2**) in 96% yield as a 99:1 mixture of *SR,RS/SS,RR* Re,S configurational diastereomers. An intermediate ylide with a $ReS(O)(CH_3)(CH_2^-)$ linkage is proposed. Subsequent [1,2] migration of rhenium from sulfur to carbon then gives **2**. In $CDCl_3$ at room temperature, **2** slowly equilibrates to a 4:96 *SR,RS/SS,RR* mixture. A mechanism involving epimerization at sulfur and the methylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CH_2)]^+X^-$ ($\mathbf{4}^+X^-$) is supported by (1) enhanced rates in the presence of catalytic amounts of HOTf, which presumably convert the $^-S(O)CH_3$ moieties to better leaving groups, $HOSCH_3$, (2) reduced rates in the presence of pyridine, and (3) trapping of $\mathbf{4}^+X^-$ with $P(p\text{-}tol)_3$. The crystal structure of (*SS,RR*)-**2** is determined, and possible origins of the kinetic and thermodynamic selectivities are discussed.

Carbanions adjacent to sulfoxide groups are easily generated and see abundant use in synthetic organic chemistry.[1] Such carbanions are also chiral, and can often be prepared—in some cases as S=NR derivatives—in nonracemic form. Accordingly, numerous applications in enantioselective syntheses have been developed.[2] Surprisingly, there do not appear to have been prior attempts to generate carbanions from metal-bound sulfoxides.[3] In view of the growing number of chiral metal complexes available in enantiomerically pure form and the facile binding and detachment of sulfur donor ligands from many metal fragments,[4] we thought that such species would have good prospects for applications in enantioselective syntheses.

In previous studies, we have shown that sulfide and sulfoxide ligands are easily coordinated to the chiral rhenium Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (**I**).[5-7] When diallyl sulfide complexes of **I** are treated with $t\text{-}BuO^-K^+$, sulfur ylides are generated that undergo rapid [2,3] sigmatropic rearrangements.[7] A generic version of this well-known reaction is sketched in Scheme 1. The resulting thiolate complexes contain new carbon stereocenters, and one configuration greatly dominates. Organic sulfides of high enantiomeric purities can subsequently be isolated. However, sulfur ylides sometimes undergo [1,2] sigmatropic rearrangements, an alternative also diagrammed in Scheme 1. In fact, the deprotonation of simple sulfoxide complexes of **I** leads to rapid [1,2] migrations of rhenium, as described in the new chemistry below.

Scheme 1. Representative Sulfur Ylide Rearrangements



Results

The sulfur-ligated DMSO complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(S(O)(CH_3)_2)]^+BF_4^-$ ($\mathbf{1}^+BF_4^-$)[5] was dissolved in CH_2Cl_2 at −80 °C and treated with 1.0 equiv of $t\text{-}BuO^-K^+$ in THF (Scheme 2). Workup gave an orange solid (**2**) in 96% yield, which was characterized by microanalysis and IR and NMR (^1H, ^{13}C, ^{31}P) spectroscopy (Experimental Section). Complex **2** exhibited spectroscopic features typical of neutral alkyl complexes

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[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1995.

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(7) (a) Cagle, P. C.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1994**, *116*, 3655. (b) Cagle, P. C.; Weickhardt, K.; Meyer, O.; Arif, A. M.; Gladysz, J. A. Manuscript in preparation.

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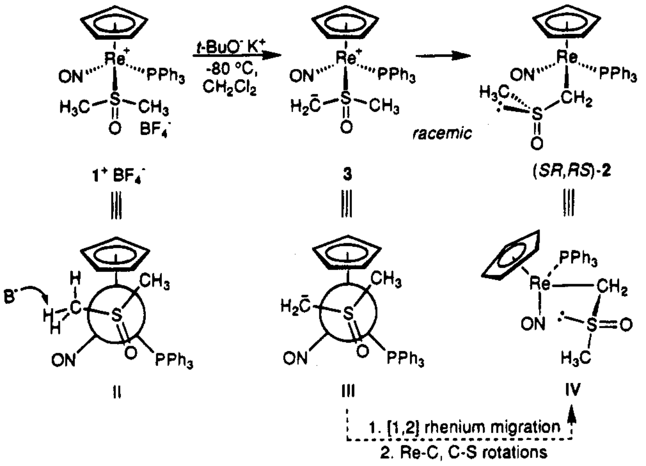
Scheme 2. Deprotonation and Rearrangement of DMSO Complex $1^+BF_4^-$

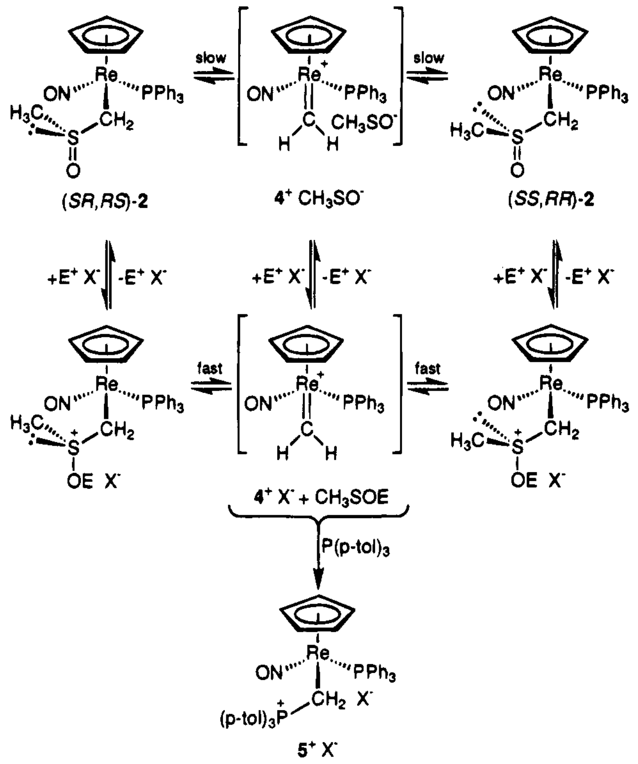


of the rhenium fragment I.[8] These included an IR ν_{NO} value much lower than that of $1^+BF_4^-$ (1638 vs 1718 cm^{-1}), a phosphorus-coupled ReC ^{13}C NMR signal (15.3 ppm, d, J_{CP} = 3.9 Hz), and phosphorus-coupled ReCHH′ ^1H NMR signals (δ 3.70, 3.25; 2 dd). Hence, **2** was formulated as the alkyl or α-sulfinyl complex (η^5-C_5H_5)-Re(NO)(PPh_3)($CH_2S(O)CH_3$). Free DMSO exhibits an IR ν_{SO} band at 1057 cm^{-1}, and **2** gave three absorptions in this region (1093 (m), 1015 (m), 998 (m sh)). A UV/visible spectrum showed, in addition to the intense band at ca. 234 nm characteristic of all adducts of I, a unique absorption at 306 nm (ϵ 2200 M^{-1} cm^{-1}, CH_2Cl_2).

As illustrated in Scheme 2, $1^+BF_4^-$ and t-BuO^-K^+ likely first react to give the ylide or zwitterion **3**, derived from deprotonation of a methyl group. The formal positive charge can be placed on either sulfur, phosphorus, nitrogen, or rhenium. A [1,2] migration of rhenium from sulfur to carbon would then give **2**. No trace of the species that would result from a [1,2] migration of the remaining methyl group, sulfenate complex (η^5-C_5H_5)Re(NO)(PPh_3)($S(O)CH_2CH_3$), was detected. Hence, the electropositive rhenium fragment I has a much higher migratory aptitude than a methyl group.

In contrast to precursor $1^+BF_4^-$, **2** contains two stereocenters—one at rhenium and one at sulfur. Accordingly, two diastereomers are possible. Indeed, **2** was isolated as a 99:1 mixture of *SR,RS/SS,RR* diastereomers,[9] the configurations of which were assigned from a crystal structure below. Thus, the reaction is highly diastereoselective. Furthermore, the 99:1 ratio constitutes only a lower boundary to the actual diastereoselectivity. When a sample was kept in $CDCl_3$ at room temperature, slow epimerization occurred. After 7 days, a 4:96 *SR,RS/SS,RR* mixture had formed, as assayed by ^{31}P NMR.[10] This ratio did not change after an additional 14 days. Hence, (*SR,RS*)-**2** is less stable than (*SS,RR*)-**2**, and the kinetic and thermodynamic diastereomer ratios diverge dramatically.

Scheme 3. Some Possible Mechanisms of Epimerization of 2



We sought to probe the mechanism of epimerization. In extensive studies to date, only alkoxide and amido complexes of I have been observed to lose configuration at rhenium near room temperature.[11,12] Thus, we suspected that the sulfur stereocenter of **2** was labile. Importantly, when a $CHCl_3$ solution of a 95:5 *SR,RS/SS,RR* mixture was treated with HOTf (ca. 0.5 mol %; OTf = $OS(O)_2CF_3$), epimerization was catalyzed. After 0.25 and 6.25 h, 56:64 and 5:95 *SR,RS/SS,RR* mixtures were present. Conversely, when a $CDCl_3$ solution of a 99:1 *SR,RS/SS,RR* mixture was treated with pyridine (1.5 equiv), epimerization was slowed. After 7 and 21 days, 25:75 and 4:96 *SR,RS/SS,RR* mixtures were present.

We envisioned, based upon the preceding data, the epimerization mechanism shown in Scheme 3, in which adventitious electrophiles assist the formal dissociation of a $^-S(O)CH_3$ or $^-OSCH_3$ moiety.[13] This would generate the methylidene complex [(η^5-C_5H_5)Re(NO)(PPh_3)(=CH_2)]$^+X^-$ (4^+X^-), which has been previously isolated[14] and shown to readily alkylate phosphorus, nitrogen, and sulfur nucleophiles.[14-16] Accordingly, when a $CDCl_3$

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[9] (a) The configuration at rhenium is specified before that at sulfur, utilizing the priority sequence η^5-C_5H_5 > PPh_3 > NO > $CH_2S(O)CH_3$. See: Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 6598. Sloan, T. E. *Top. Stereochem.* **1981**, *12*, 1. Lecomte, C.; Dusausoy, Y.; Protas, J.; Tirouflet, J.; Dormand, J. *J. Organomet. Chem.* **1974**, *73*, 67. Isomer ratios are normalized to 100, and error limits on each integer are ±2; e.g., 4:96 ≡ (4 ± 2):(96 ± 2).

[10] Additional data: 1 day, 38:62; 3 days, 15:85; 4 days, 8:92.

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Table 1. Summary of Crystallographic Data for (*SS,RR*)-(η^5-C_5H_5)Re(NO)(PPh_3)($CH_2S(O)CH_3$) ((*SS,RR*)-2)

mol formula	$C_{25}H_{25}NOPReS$
mol wt	620.722
cryst syst	orthorhombic
space group	$Pna2_1$ (No. 33)
cell dimens (16 °C)	
a, Å	9.568(1)
b, Å	19.916(3)
c, Å	12.976(2)
V, Å^3	2472.60
Z	4
d_{calc}, g/cm^3	1.667
d_{obs}, g/cm^3 (Et_2O/CH_2I_2)	1.68
cryst dimens, mm	0.43 × 0.25 × 0.25
diffractometer	Syntex $P\bar{1}$
radiation, Å	λ(Mo Kα), 0.710 73
data collcn method	$\theta-2\theta$
scan speed, deg/min	3.0
no. of reflns measured	2567
range/indices (hkl)	0−11, 0−23, −14 to 0
scan range	$K_{\alpha1} - 1.25$ to $K_{\alpha2} + 1.25$
2θ limit, deg	3.00−50.00
std reflns check	1 X-ray h
total unique data	2513
no. of obsd data, $I > 3\sigma(I)$	1645
abs coeff, cm^{-1}	51.458
min transm, %	92.40
max transm, %	99.99
no. of variables	279
goodness of fit	1.6276
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.0366
$R_w = \sum\|\|F_o\| - \|F_c\|\|w^{1/2}/\sum\|F_o\|w^{1/2}$	0.0585
Δ/σ (max)	0.010
$\Delta\varrho$ (max), e/Å^3	1.293 (ca. 0.850 Å from Re)

solution of **2** (99:1 *SR,RS/SS,RR*) was treated with the phosphine P(p-tol)$_3$ (4 equiv), the phosphonium salt [(η^5-C_5H_5)Re(NO)(PPh_3)($CH_2P(p\text{-tol})_3$)]$^+X^-$ ($\mathbf{5}^+X^-$) slowly formed. After 1 day, a 57:43 mixture of **2** (26:74 *SR,RS/SS,RR*) and $\mathbf{5}^+X^-$ was present. After 7 days, conversion was >99% complete. The hexafluorophosphate salt $\mathbf{5}^+PF_6^-$ has been previously characterized.[16] Thus, the ammonium salt $NH_4^+PF_6^-$ was added to a preparative reaction. Workup gave $\mathbf{5}^+PF_6^-$ in 43% yield. The ^{1}H and ^{31}P NMR spectra matched those reported earlier.

In order to confirm the configurations given for **2** above, a crystal structure was sought. Thus, heptane vapor was allowed to slowly diffuse into a CH_2Cl_2 solution of the kinetic product (*SR,RS*)-**2**. Orange prisms formed, and X-ray data were collected as outlined in Table 1 and the Experimental Section. Refinement yielded the structures in Figure 1. A sulfur lone pair (LP) position was calculated. Atomic coordinates and selected bond lengths, bond angles, and torsion angles are summarized in Tables 2 and 3. Interestingly, these data showed that a crystal of the thermodynamic product (*SS,RR*)-**2** had been isolated. As a check, the crystal utilized was dissolved in CD_2Cl_2. A ^{31}P NMR spectrum confirmed the assignment (21.8 ppm).[17]

Some extensions of Scheme 2 were briefly explored. Complex **2** rapidly reacted with Br_2 and NBS. However, in no case was any bromodimethyl sulfoxide[18] detected by IR or ^{1}H NMR. Reactions of other symmetrical sulfoxide complexes of **I** and t-BuO$^-$K$^+$ were examined.

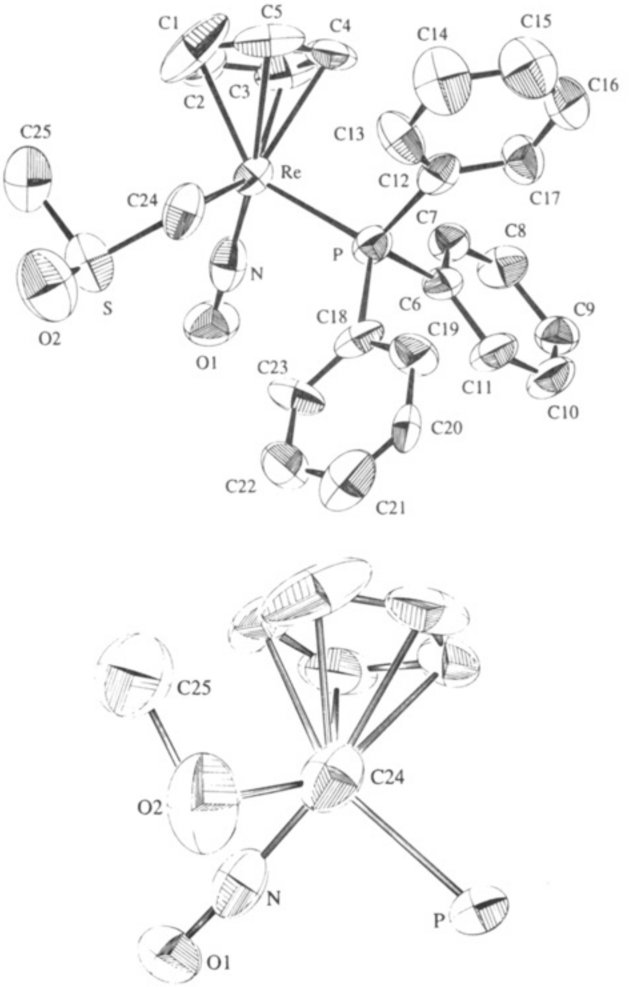

Figure 1. Structure of (*SS,RR*)-(η^5-C_5H_5)Re(NO)(PPh_3)($CH_2S(O)CH_3$) ((*SS,RR*)-**2**)): (top) numbering diagram; (bottom) Newman-type projection with phenyl rings omitted and sulfur obscured by O2.

These appeared to give analogous rearrangement products but were not further studied since the ligating carbons were now also stereocenters, complicating analyses of the epimerizations. The dimethyl sulfide complex of **I**,[5] which is likely less acidic than $\mathbf{1}^+BF_4^-$, did not give comparable chemistry. Finally, when $\mathbf{1}^+BF_4^-$ and t-BuO$^-$K$^+$ were combined as in Scheme 2 but in the presence of CH_3I, only **2** (and unreacted $\mathbf{1}^+BF_4^-$) were detected.

Discussion

The preceding data establish a new base-promoted reaction of coordinated sulfoxides. With neutral metal complexes, there is abundant precedent for the generation of carbanions on coordinated ligands. However, analogous deprotonations of cationic metal complexes appear to have received much less attention.[19] In many cases, the latter will give ylides or zwitterions—species that in our opinion have considerable potential for unusual rearrangements or synthetic applications. For

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(17) This spectrum required several hours to acquire. A spectrum of a known *SR,RS/SS,RR* mixture was subsequently recorded under identical conditions (23.4/21.8 ppm). The bulk sample of crystals was a 80:20 *SR,RS/SS,RR* mixture. Thus, X-ray data were collected on the minor diastereomer present.

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(20) See, for example: Wiegand, B. C.; Friend, C. M. *Chem. Rev.* **1992**, *92*, 491 and references therein.

Table 2. Atomic Coordinates and Equivalent Isotropic Thermal Parameters of Located Atoms of (*SS,RR*)-2[a]

atom	*x*	*y*	*z*	*B* (Å^2)
Re	0.99559(4)	0.96274(2)	0.993	3.370(9)
S	1.0028(4)	1.1190(2)	0.9032(4)	5.7(1)
P	1.1900(3)	0.9070(2)	0.9158(3)	3.44(6)
O1	1.177(1)	1.0363(5)	1.1346(8)	5.6(3)
O2	1.008(1)	1.1642(8)	0.810(2)	8.6(5)
N	1.105(1)	1.0075(5)	1.0697(9)	4.3(3)
C1	0.761(1)	0.960(1)	0.974(2)	8.6(5)
C2	0.787(1)	0.9532(8)	1.075(1)	5.1(4)
C3	0.860(1)	0.8942(8)	1.085(2)	6.0(4)
C4	0.874(1)	0.8629(6)	0.981(2)	4.6(3)
C5	0.808(1)	0.9069(9)	0.918(1)	5.9(3)
C6	1.296(1)	0.8638(6)	1.010(1)	3.6(3)
C7	1.238(1)	0.8380(6)	1.098(1)	3.4(3)
C8	1.311(1)	0.8037(7)	1.169(1)	4.2(3)
C9	1.453(1)	0.7905(7)	1.152(1)	3.8(3)
C10	1.514(1)	0.8161(9)	1.067(2)	4.8(4)
C11	1.437(1)	0.8530(6)	0.993(2)	4.3(3)
C12	1.138(1)	0.8396(7)	0.824(1)	3.7(3)
C13	1.059(2)	0.8592(7)	0.742(1)	4.7(3)
C14	1.008(2)	0.814(1)	0.669(2)	6.9(5)
C15	1.052(2)	0.747(1)	0.682(1)	6.7(4)
C16	1.132(2)	0.7260(7)	0.762(1)	6.0(4)
C17	1.179(2)	0.7736(7)	0.832(1)	4.6(3)
C18	1.322(1)	0.9557(7)	0.844(1)	4.2(3)
C19	1.389(1)	0.9280(7)	0.757(1)	4.8(3)
C20	1.494(1)	0.9634(6)	0.709(2)	4.7(4)
C21	1.526(2)	1.022(1)	0.739(2)	6.9(5)
C22	1.454(2)	1.0559(8)	0.825(2)	6.6(2)
C23	1.358(1)	1.0194(7)	0.874(1)	5.2(3)
C24	1.000(1)	1.0355(7)	0.858(2)	4.9(4)
C25	0.831(2)	1.130(1)	0.944(2)	9.5(7)

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

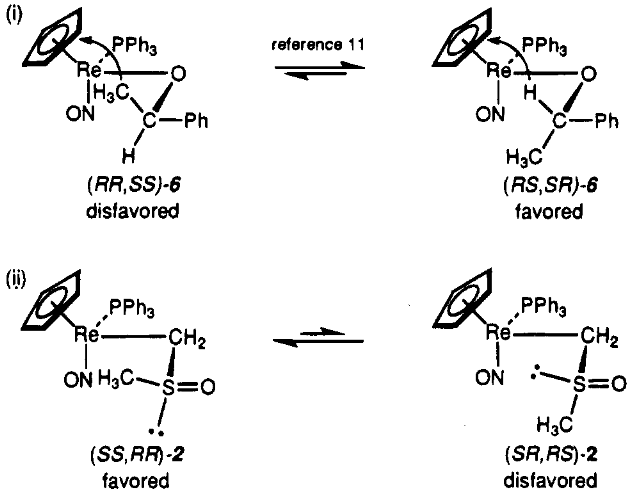
Table 3. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) in (*SS,RR*)-2

Re−P	2.386(4)	Re−C5	2.32(2)
Re−N	1.70(2)	Re−C24	2.28(2)
Re−C1	2.26(2)	S−O2	1.51(3)
Re−C2	2.27(1)	S−C24	1.77(2)
Re−C3	2.23(2)	S−C25	1.74(3)
Re−C4	2.31(1)	N−O1	1.23(1)
P−Re−N	90.5(4)	C1−C2−C3	106(2)
P−Re−C24	87.5(4)	C2−C3−C4	108(2)
N−Re−C24	96.1(6)	C3−C4−C5	104(2)
Re−C24−S	110(1)	C4−C5−C1	109(2)
C24−S−O2	107(1)	C5−C1−C2	113(2)
C24−S−C25	102(9)	Re−N−O1	173(1)
O2−S−C25	101(1)		
N−Re−C24−S	−38.0 (0.7)	P−Re−C24−S	−128.3 (0.5)
Re−C24−S−O2	179.2 (0.6)	Re−C24−S−C25	−75.0 (1.0)
Re−C24−S−LP	53.0 (0.7)		

example, new methods for activating sulfur donor ligands can potentially impact upon catalytic hydrosulfurization technology.[20]

There are several interesting stereochemical aspects of the above transformations. First, the highly diastereoselective formation of (*SR,RS*)-**2** suggests that only one of the two diastereotopic methyl groups in DMSO complex $1^+BF_4^-$ is deprotonated. If it were possible to label one methyl group selectively, this could be tested. However, since $1^+BF_4^-$ is prepared from free DMSO,[5] an enantiomerically pure $*CH_3S(O)CH_3$ species would be required. Regardless, the formation of (*SR,RS*)-**2** is consistent with the transition state model **II** in Scheme 2. This model employs, as an arbitrary starting point, the Re−S conformation in crystalline $1^+BF_4^-$.[5] However, this in turn has the intuitively satisfying consequence that deprotonation must occur on the methyl group in the least hindered interstice—that between the small nitrosyl and medium-sized cyclopentadienyl ligands.[16,21]

Scheme 4. Models for Diastereomeric Equilibria in (i) $OCH(CH_3)Ph$ and (ii) $CH_2S(O)CH_3$ Complexes of I[24]



(*RR,SS*)-**6** disfavored

(*RS,SR*)-**6** favored

(*SS,RR*)-**2** favored

(*SR,RS*)-**2** disfavored

As noted above, attempts to trap the ylide **3** prior to rearrangement have to date been unsuccessful. However, we have previously generated a conceptually related species by deprotonation of the methylene group of phosphonium salt $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2PPh_3)]^+ PF_6^-$.[16] The resulting ylide could be observed by ^{31}P NMR, and reaction with CH_3OTf gave a phosphonium salt with a new C_α stereocenter. Only one product diastereomer could be detected. If species such as **3** could be similarly intercepted, there would be attractive possibilities for enantioselective syntheses of free sulfoxides.

The 4:96 (*SR,RS*)-**2**/(*SS,RR*)-**2** equilibrium ratio ($CHCl_3$, 298 K) corresponds to a ΔG value of 1.9 kcal/mol. At present, we find it difficult to formulate a simple explanation for this stability difference. We have previously obtained equilibrium data for related adducts of **I** in which (1) the ligating atom bears only lone pairs or hydrogen atoms and (2) the atom β to rhenium bears three sterically distinct substituents (L, M, S).[11,12,22] For example, the diastereomeric alkoxide complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OCH(CH_3)Ph)$ (**6**), illustrated in Scheme 4, equilibrate to (82−83):(18−17) *RS,SR*/*RR,SS* mixtures in C_6D_6 at 65 °C.[12,23,24] The direction of this equilibrium can be rationalized by a model in which antiperiplanar conformations or 180° torsion angles are maintained along the $Ph_3P{-}Re{-}O{-}C{-}R_L$ backbone—a linkage that contains the bulkiest rhenium (PPh_3) and carbon (R_L) substituents. This predicts that (*RR,SS*)-**6** should experience a destabilizing interaction between

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[24] For ease of comparison, eq i of Scheme 4 is illustrated as a carbon as opposed to rhenium epimerization.

the cyclopentadienyl ligand and the methyl alkoxide substituent (Scheme 4). However, the crystal structure of (*RS,SR*)-**6** shows that the conformation utilized in the model is approximate (P−Re−O−C and Re−O−C−C_{Ph} torsion angles = 158 and 149°).[23]

There are several ambiguities in applying this model to (*SR,RS*)-**2** and (*SS,RR*)-**2**. First, there is not a large size difference between the three sulfur substituents (methyl, oxygen, lone pair). Second, there is a striking antiperiplanar relationship of the O=S and C−Re bonds in crystalline (*SS,RR*)-**2**, as reflected by the O=S−C−Re torsion angle (179.2(6)°) and the bottom view in Figure 1. This suggests a possible electronic control element. However, crystal structures of two other complexes with M−$CH_2S(O)R$ linkages have been determined, and one shows a O=S−C−M angle of only 71°.[25] Third, the P−Re−C−S torsion angle (128.3(5)°) is the lowest observed to date in a compound fulfilling criterion (1) above. This places the *S*-methyl group in (*SS,RR*)-**2** further from the cyclopentadienyl ligand than the *C*-methyl group in (*RR,SS*)-**6**. Hence, we hesitate based upon the limited data available to ascribe the appreciable stability difference to a single feature.

Finally, there is abundant precedent for the epimerization mechanism in Scheme 3. First, the sulfonium salt $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2S(CH_3)_2)]^+PF_6^-$ has previously been shown to be in facile equilibrium with methylidene complex **4**$^+PF_6^-$ and free dimethyl sulfide.[15] Second, organic sulfoxides can undergo heterolytic sulfur−carbon bond cleavage reactions in the presence of electrophiles.[26] These entail initial electrophile attack at the sulfoxide oxygen and are particularly facile when a stabilized carbocation is generated. Third, although species such as $^-OSCH_3$ and $HOSCH_3$ are usually encountered only as reactive intermediates, they have been shown to serve as leaving groups and/or nucleophiles in a variety of transformations.[13]

The chemistry of ylides derived by the deprotonation of other adducts of **I** and neutral donor ligands is under active investigation. Additional reactions will be described in future reports from this laboratory.[7b]

Experimental Section

General procedures and CH_2Cl_2 and toluene purifications were identical with those given in a recent paper.[27] The following were used as received: $CDCl_3$, $CHCl_3$, *t*-BuO$^-$K$^+$ (1.0 M in THF), HOTf, P(*p*-tol)$_3$, $NH_4^+PF_6^-$.

$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2S(O)CH_3)$ (2). A. A Schlenk flask was charged with $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(S(O)(CH_3)_2)]^+BF_4^-$ ($1^+BF_4^-$;[5] 0.557 g, 0.786 mmol), CH_2Cl_2 (20 mL), and a stir bar, and cooled to −80 °C (CO_2/acetone). Then *t*-BuO$^-$K$^+$ (0.786 mL, 0.786 mmol, 1.0 M in THF) was added with stirring. The red solution turned orange. After 30 min, the solvent was removed via rotary evaporation, and the orange-red residue was dissolved in toluene (20 mL). The solution was filtered through a Celite pad (1 cm), which was washed with toluene (60 mL) until the eluate was colorless. The solvent was removed via rotary evaporation to give **2** as an orange solid, which was dried under oil pump vacuum (0.467 g, 0.752 mmol, 96%; 99:1 *SR,RS*/*SS,RR*),[9] mp 183 °C dec. Calcd for $C_{25}H_{25}NO_2PReS$: C, 48.37; H, 4.07. Found: C, 48.16; H, 4.13. IR (cm^{-1}, KBr): 1638 (vs) (ν_{NO}), 1434 (m), 1093 (m), 1015 (m), 998 (m sh). UV/vis (nm (ϵ, M^{-1} cm^{-1}), 1.1×10^{-4} M in CH_2Cl_2): 306 (2200).

B. A 5 mm NMR tube was charged with **2** (0.0149 g, 0.0240 mmol; 99:1 *SR,RS*/*SS,RR*) and $CDCl_3$ (0.5 mL) and capped with a septum. The isomerization to (*SS,RR*)-**2** was monitored by ^{31}P NMR. Data: see text.

C. A 5 mm NMR tube was similarly charged with **2** (0.0129 g, 0.0208 mmol; 99:1 *SR,RS*/*SS,RR*), $CDCl_3$ (0.6 mL), and pyridine (0.0025 g, 0.0026 mL, 0.0320 mmol) and capped with a septum. Data: see text.

NMR for (*SR,RS*)-**2**: ^1H (δ, $CDCl_3$) 7.44−7.20 (m, $3C_6H_5$), 5.10 (s, C_5H_5), 3.70 (dd, J_{HH} = 11.5 Hz, J_{HP} = 9.6 Hz, ReCH), 3.25 (dd, J_{HH} = 11.5 Hz, J_{HP} = 2.4 Hz, ReCH′), 2.59 (s, CH_3); $^{13}C\{^1H\}$ (ppm, $CDCl_3$) 134.6 (d, J_{CP} = 53.1 Hz, *i*-Ph), 133.3 (d, J_{CP} = 10.5 Hz, *o*-Ph), 130.4 (d, J_{CP} = 2.2 Hz, *p*-Ph), 128.5 (d, J_{CP} = 10.4 Hz, *m*-Ph), 89.6 (s, C_5H_5), 41.2 (s, SCH_3), 15.3 (d, J_{CP} = 3.9 Hz, ReCHH′); $^{31}P\{^1H\}$ (ppm, $CDCl_3$/CD_2Cl_2) 23.6/23.4 (s). NMR for (*SS,RR*)-**2**: ^1H (δ, $CDCl_3$) 7.44−7.20 (m, $3C_6H_5$), 5.08 (s, C_5H_5), 3.48 (dd, J_{HH} = 12.3 Hz, J_{HP} = 8.1 Hz, ReCH), 3.27 (br d, J_{HH} = 11.1 Hz, ReCH′), 2.55 (s, CH_3); $^{13}C\{^1H\}$ (ppm, $CDCl_3$) 135.1 (d, J_{CP} = 53.4 Hz, *i*-Ph), 133.3 (d, J_{CP} = 10.3 Hz, *o*-Ph), 130.4 (d, J_{CP} = 2.2 Hz, *p*-Ph), 128.7 (d, J_{CP} = 10.5 Hz, *m*-Ph), 90.1 (s, C_5H_5), 39.3 (s, SCH_3), 21.2 (d, J_{CP} = 3.9 Hz, ReCHH′); $^{31}P\{^1H\}$ (ppm, $CDCl_3$/CD_2Cl_2) 22.0/21.8 (s).

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2P(p\text{-}tol)_3)]^+X^-$ (5^+X^-). A. A 5 mm NMR tube was charged with **2** (0.0149 g, 0.0240 mmol; 99:1 *SR,RS*/*SS,RR*), $CDCl_3$ (0.5 mL), and P(*p*-tol)$_3$ (0.0299 g, 0.0982 mmol) and capped with a septum. After ca. 0.5 h, a ^{31}P NMR spectrum showed **2** (93:7 *SR,RS*/*SS,RR*; 23.6, 22.0 ppm) and P(*p*-tol)$_3$ (−7.0 ppm). After 7 days, the formation of $\mathbf{5}^+X^-$ (41.6, d, J_{PP} = 17.6 Hz; 22.0, d, J_{PP} = 17.7 Hz) was complete.

B. A Schlenk flask was charged with **2** (0.107 g, 0.172 mmol; 99:1 *SR,RS*/*SS,RR*), $CHCl_3$ (30 mL), P(*p*-tol)$_3$ (0.263 g, 0.865 mmol), HOTf (5 μL), and a stir bar. The mixture was stirred for 14 days. The solvent was removed via rotary evaporation and the dark brown residue dissolved in acetone (50 mL). Then $NH_4^+PF_6^-$ (2.910 g, 17.8 mmol) was added with stirring. After 1 h, the solvent was removed and the residue dissolved in CH_2Cl_2 (20 mL). The dark brown solution was filtered through silica gel (10 cm), which was washed with CH_2Cl_2 (100 mL). The solvent was removed by rotary evaporation. The residue was washed with ether (20 mL) and pentane (60 mL) to give $\mathbf{5}^+PF_6^-$ (0.076 g, 0.074 mmol, 43%)[16] as a dark orange solid.

NMR: ^1H (δ, $CDCl_3$/CD_2Cl_2) 7.26−7.55/7.30−7.50 (m, $3C_6H_5$), 4.68/4.71 (s, C_5H_5), 3.04/3.18 (ddd, J_{HH} = 14.1/14.1 Hz, J_{HP} = 10.5/10.8 Hz, J_{HP} = 8.1/7.9 Hz, ReCH), 2.87/2.53 (dd, J_{HH} = 15.1/14.4 Hz, J_{HP} = 15.1/13.2 Hz, ReCH′), 2.41/2.45 (s, CH_3); $^{31}P\{^1H\}$ (ppm, $CDCl_3$, CD_2Cl_2) 40.9/40.3 (d, J_{PP} = 18.3/18.3 Hz, P(*p*-tol)$_3$), 21.6/20.8 (d, J_{PP} = 18.2/18.2 Hz, PPh_3).

Crystallography. An orange prism of (*SS,RR*)-**2** was grown over the course of 2 days by diffusion of heptane vapor into a CH_2Cl_2 solution of the opposite diastereomer, (*SR,RS*)-**2** (NMR data: see text). Data were collected as outlined in Table

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1. Cell constants were obtained from 30 reflections with 10° $< 2\theta < 15°$. The space group was determined from systematic absences ($0kl$ $k + l = 2n + 1$, $h0l$ $h = 2n + 1$) 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.[28] Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were calculated and added to the structure factor calculations but were not refined. Scattering factors, and $\Delta f'$ and $\Delta f''$ values, were taken from the literature.[29]

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Supplementary Material Available: Anisotropic thermal parameters for (*SS*,*RR*)-**2** (1 page). Ordering information is given on any current masthead page.

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