Oxidation of Thioether Ligands in Pseudotetrahedral Cyclopentadienylruthenium Complexes: Toward a New Stereoselective Synthesis of Chiral Sulfoxides[1]

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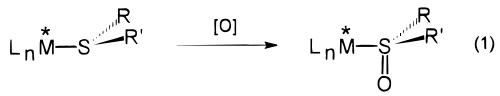
Received October 24, 1996[⊗]

Ionic ruthenium thioether complexes [Cp(LL′)Ru(SRR′)]PF_6 (LL′ = $Ph_2PCH_2PPh_2$ (**1**), $Ph_2PC_2H_4PPh_2$ (**2**), (Ph_3P, CO) (**3**), $Me_2PC_2H_4PPh_2$ (**4**), (*S*,*S*)-$Ph_2PCHMeCHMePPh_2$ (**5**), SRR′ = MeSPh (**a**), MeS-*i*-Pr (**b**), MeSBz (**c**), *i*-PrSBz (**d**), EtSBz (**e**), MeSCy (**f**), SC_4H_8 (**g**)) were synthesized from the corresponding chloro complexes [Cp(LL′)RuCl] and thioethers. **5a** crystallized in the orthorhombic system, space group $P2_12_12_1$ (No. 19), with a = 11.269(3) Å, b = 15.104(2) Å, c = 23.177(4) Å, and Z = 4. **5b** crystallized in the monoclinic system, space group $P2_1$ (No. 4), with a = 10.539(5) Å, b = 16.216(9) Å, c = 11.011(8) Å, β = 106.04(2)°, and Z = 2. A similar ligand exchange reaction yielded the analogous sulfoxide complexes [Cp(LL′)Ru(S(O)RR′)]PF_6 (**6**−**10**). **10a** crystallized in the orthorhombic system, space group $P2_12_12_1$ (No. 19), with a = 14.1664(13) Å, b = 15.792(2) Å, c = 17.641(2) Å, and Z = 4. **10b**·0.93CH_2Cl_2 crystallized in the orthorhombic system, space group $P2_12_12_1$ (No. 19), with a = 12.069(2) Å, b = 17.379(2) Å, c = 19.760(5) Å, and Z = 4. The thioether complexes can also be directly converted to sulfoxide complexes with the strong oxygen transfer reagent dimethyldioxirane (DMD). No crossover products are formed when mixtures of two thioether complexes (e.g., **1a**/**2c** or **1c**/**2a**) are treated with DMD, demonstrating that no Ru−S bond cleavage is involved. Moderate diastereoselectivities are observed for the oxygen transfer to chiral, racemic thioether complexes **3** (8−28%) and **4** (34−60%). Oxidation of the (*S*,*S*)-CHIRAPHOS complexes **5**, however, is highly stereoselective (de = 46−98%). Treatment of the sulfoxide complexes **10** with sodium iodide removes the chiral, nonracemic sulfoxides from the metal with retention of the configuration at sulfur.

Introduction

Homochiral sulfoxides have a prominent role as intermediates in enantioselective syntheses.[3] Their methods of preparation fall into roughly two categories: (i) nucleophilic substitution at enantiomerically pure esters or amides of sulfinic acids[4,5] and (ii) enantioselective oxidation of thioethers.[4,6−9] The latter method may involve either chiral oxidants such as camphor-derived oxaziridines[7] or achiral oxidants in the presence of chiral catalysts including enzymes[6,9] or the well-known Sharpless reagent in its original[8b] or modified[8a] form. All of these methods, however, suffer from certain drawbacks. The sulfinic ester/amide route gives high selectivities only for aryl or *tert*-butyl sulfoxides,[5] enzyme reactions are often unpredictable with respect to optical purity and yield of products,[6] and enantioselective oxidations including the Kagan method[8a] are reliable only for the synthesis of aryl alkyl sulfoxides. Thus, although an impressive range of methods is available for the enantioselective generation of sulfoxides,[10] there is still a need to develop novel strategies which might favorably supplement the existing methodologies.

Knowing that oxidations of α-chiral thioethers to sulfoxides often proceed with high diastereoselectivities,[10] we expected that oxygen transfer to a thioether which is coordinated to a chiral transition metal complex would also be highly stereoselective (eq 1). Addition of a transition metal to a thioether will of



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course dramatically reduce its reactivity; however, there is some

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⊗ Abstract published in *Advance ACS Abstracts,* April 15, 1997.

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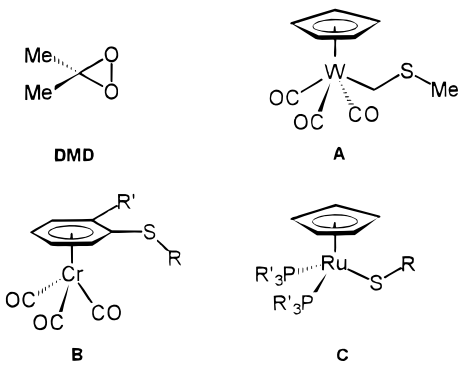
S0020-1669(96)01280-3 CCC: $14.00

precedent in the literature that electrophilic attack at coordinated thioethers is still possible.[11] Some isolated reports of oxidations of thioether complexes do in fact exist;[12] the conditions, however, were such that these reactions almost certainly proceeded via (i) dissociation of the thioether, (ii) oxidation, and (iii) readdition of the sulfoxide. A mechanistically clean oxidation of a *coordinated* thioether requires kinetically stable complexes as well as a powerful yet selective oxygen transfer reagent. We expected that dimethyldioxirane (DMD) would



fulfill these requirements.[13] DMD had, inter alia, been used previously for oxygen transfer to remote thioether functions such as in **A** or **B**[14,15] and to the sulfur of transition metal thiolate complexes of type **C**.[14] A preliminary account of the work described here has been published.[1]

Experimental Section

Analytical Measurements. C, H, and S analyses were carried out by the Analytical Laboratory of the Institute of Inorganic Chemistry, University of Würzburg. Melting points were determined in sealed capillaries in a copper block apparatus. Infrared spectra were run on a Bruker IFS 25 instrument. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded using a Bruker AMX 400 instrument. Chemical shifts are reported relative to TMS (^{1}H, ^{13}C) or 85% H_3PO_4 (^{31}P). Enantiomeric excesses of the sulfoxides were determined by HPLC (Knauer HPLC 64) using a Ciralcel OD column (DAICEL Chemical Industries Ltd.), hexane/2-propanol (9:1) as eluent, and combined UV (Hewlett-Packard 1040 A) and ChiraLyzer (IBM Messtechnik) detection.

Materials. $RuCl_3 \cdot 3H_2O$ was purchased from Degussa AG, Hanau, Germany; 2(*S*),3(*S*)-bis(diphenylphosphino)butane [(*S*,*S*)-CHIRAPHOS, henceforth abbreviated as "chir"] was obtained from Strem Chemicals and used without further purification. The phosphine ligands dppm, dppe, and (2-(dimethylphosphino)ethyl) diphenylphosphine (dpme) were prepared as described in the literature.[16] The ruthenium complexes [CpRu(LL′)Cl] (LL′ = $(PPh_3)_2$; dppm; dppe; CO, PPh_3; dpme; chir) were obtained by published methods or adaptations thereof.[17] Thioethers were obtained from Aldrich or prepared by alkylation of the corresponding thiols. Oxidation of the thioethers with 3-chloroperbenzoic acid gave the required sulfoxides. Dimethyldioxirane (DMD) was employed as a freshly prepared 0.08−0.12 M solution in acetone.[18]

In the following, only representative examples are given. A full description of experimental details is available as Supporting Information.

Ruthenium Thioether Complexes 1−5. General Procedure. [CpRu(LL′)Cl] (0.25 mmol), NH_4PF_6 (0.30 mmol), and the appropriate thioether (1.00 mmol) were suspended in methanol (15 mL) and the suspension was heated to 60 °C for 3 h (16 h for (LL′) = (CO, PPh_3)). All volatiles were then removed under vacuum, and the residue was extracted with several portions of dichloromethane. After filtration, the products were precipitated by partial evaporation and addition of diethyl ether.

(a) [CpRu(chir)(MeSPh)]PF_6, 5a: yield 95%; mp 148−155 °C. Anal. Calcd for $C_{40}H_{41}F_6P_3RuS$: C, 55.75; H, 4.80. Found: C, 56.32; H, 5.10. ^{1}H NMR (acetone-d_6): δ 1.90 (s, SMe), 4.82 (s, Cp). ^{13}C NMR (acetone-d_6): δ 31.9 (d, J(P,C) = 4 Hz, SMe), 86.0 (dd, J(P,C) = J(P′,C) = 2 Hz, Cp). ^{31}P NMR (acetone-d_6): δ 63.8 (d, J(P,P) = 41 Hz), 82.1 (d, J(P,P) = 41 Hz).

(b) [CpRu(chir)(MeS-*i*-Pr)]PF_6, 5b: yield 98%; mp 187−189 °C. Anal. Calcd for $C_{37}H_{43}F_6P_3RuS$: C, 53.69; H, 5.24. Found: C, 53.91; H, 5.19. ^{1}H NMR (acetone-d_6): δ 0.82 (d, J(H,H) = 6.8 Hz, Me), 1.07 (d, J(H,H) = 6.7 Hz, Me), 1.50 (s, SMe), 1.97 (m, SCH), 4.73 (s, Cp). ^{13}C NMR (acetone-d_6): δ 21.1 (s, Me), 21.6 (s, Me), 21.8 (s, SMe), 45.6 (d, J(P,C) = 5 Hz, SCH), 85.1 (dd, J(P,C) = J(P′,C) = 2 Hz, Cp). ^{31}P NMR (acetone-d_6): δ 64.4 (d, J(P,P) = 42 Hz), 81.4 (d, J(P,P) = 42 Hz).

(c) [CpRu(chir)(MeSBz)]PF_6, 5c: yield 96%; mp 212−217 °C dec. Anal. Calcd for $C_{41}H_{43}F_6P_3RuS$: C, 56.23; H, 4.95. Found: C, 56.23; H, 4.93. ^{1}H NMR (acetone-d_6): δ 1.41 (br, SMe), SCH_2 signal at room temperature too broad to be observed, 4.85 (s, Cp). ^{31}P NMR (acetone-d_6): δ 66.8 (d, J(P,P) = 40 Hz), 82.2 (d, J(P,P) = 40 Hz).

Ruthenium Sulfoxide Complexes 6−10. General Procedure. [CpRu(LL′)Cl] (0.25 mmol), NH_4PF_6 (0.30 mmol), and the appropriate sulfoxide (1.50 mmol) were suspended in methanol (15 mL), and the suspension was heated to 60 °C for 6 h (48 h for (LL′) = (CO, PPh_3)). Reactions were then worked up as described for thioether complexes **1**−**5**.

Oxidation of Thioether Complexes. General Procedure. To a solution of the thioether complex (0.12 mmol) in acetone (10 mL) was slowly added at 0 °C a 4-fold excess of a cooled (−30 °C) solution of dimethyldioxirane in acetone. After 45 min (2 h in case of **3a**−**c**), all volatiles were removed under vacuum. Diastereoisomer rations were determined from the NMR spectra of the crude reaction mixture. Further purification was effected by crystallization from dichloromethane/ether. Yields were nearly quantitative except those for **6d** (20%), **8b** (45%), **8c** (30%), **9d** (10%), **10e** (5%), **10f** (70%), and **10h** (7%).

(a) [CpRu(chir)(MeS(O)Ph)]PF_6, 10a,a′: yield 89%. Anal. Calcd for $C_{40}H_{41}F_6OP_3RuS$: C, 54.73; H, 4.71. Found: C, 54.72; H, 4.88. Major (93%) isomer **10a**: ^{1}H NMR (acetone-d_6) δ 2.64 (s, SMe), 5.09 (s, Cp); ^{13}C NMR (acetone-d_6) δ 57.9 (s, SMe), 88.0 (dd, J(P,C) = J(P′,C) = 2 Hz, Cp); ^{31}P NMR (acetone-d_6) δ 60.3 (d, J(P,P) = 36 Hz), 81.8 (d, J(P,P) = 36 Hz). Minor (7%) isomer **10a′**: ^{1}H NMR (acetone-d_6) δ 2.82 (s, SMe), 4.90 (s, Cp); ^{31}P NMR (acetone-d_6) δ 62.3 (d, J(P,P) = 36 Hz), 79.1 (d, J(P,P) = 36 Hz). Careful crystallization from dichloromethane/hexane gave a sample of pure (R_S)-**10a**, mp 124 °C dec.

(b) [CpRu(chir)(MeS(O)-*i*-Pr)]PF_6, 10b,b′: yield 86%. Anal. Calcd for $C_{37}H_{43}F_6OP_3RuS$: C, 52.67; H, 5.14. Found: C, 53.01; H, 5.28. Major (88%) isomer **10b**: ^{1}H NMR (acetone-d_6) δ 0.89 (d,

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Table 1. Crystallographic Data for **5a**, **5b**, **10a**, and **10b**

	5a	5b	10a	10b
empirical formula	$C_{40}H_{41}F_6P_3RuS$	$C_{37}H_{43}F_6P_3RuS$	$C_{40}H_{41}F_6OP_3RuS$	$C_{37}H_{43}F_6OP_3RuS{\cdot}0.93CH_2Cl_2$
fw	861.81	827.80	877.81	843.80 + 79.0
temp, K	293	193	293	293
space group	$P2_12_12_1$ (No. 19)	$P2_1$ (No. 4)	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)
a, Å	11.269(3)	10.539(5)	14.1664(13)	12.069(2)
b, Å	15.104(2)	16.216(9)	15.792(2)	17.379(2)
c, Å	23.177(4)	11.011(8)	17.641(2)	19.760(5)
β, deg	90	106.04(2)	90	90
V, Å^3	3944.8(13)	1809(2)	3946.5(7)	4144.7(14)
Z	4	2	4	4
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73
ρ_{calc}, g cm^{-3}	1.451	1.520	1.477	1.479
μ, cm^{-1}	2.6	6.8	2.65	3.72
R1 [$I > 2\sigma(I)$]	0.071	0.038	0.050	0.048
wR2 [$I > 2\sigma(I)$][a]	0.097	0.098	0.128	0.136

[a] wR2 = $\{[\sum w(F_c^2 - F_o^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$.

J(H,H) = 7.0 Hz, Me), 1.08 (d, *J*(H,H) = 6.9 Hz, Me), 2.16 (s, SMe), 2.48 (m, SCH), 4.93 (s, Cp); ^{13}C NMR (acetone-d_6) δ 15.4 (s, Me), 16.5 (s, Me), 45.3 (d, *J*(P,C) = 2 Hz, SMe), 62.7 (d, *J*(P,C) = 1 Hz, SCH), 86.7 (dd, *J*(P,C) = *J*(P′,C) = 2 Hz, Cp); ^{31}P NMR (acetone-d_6) δ 57.8 (d, *J*(P,P) = 37 Hz), 80.6 (d, *J*(P,P) = 37 Hz). Minor (12%) isomer **10b′**: ^{1}H NMR (acetone-d_6) δ 5.01 (s, Cp), other signals not detected; ^{31}P NMR (acetone-d_6) δ 60.4 (d, *J*(P,P) = 37 Hz), 78.6 (d, *J*(P,P) = 37 Hz). Careful crystallization from dichloromethane/hexane gave a sample of pure (R_S)-**10b**.

(c) [CpRu(chir)(MeS(O)Bz)]PF$_6$, 10c,c′: yield 87%. Anal. Calcd for $C_{41}H_{43}F_6OP_3RuS$: C, 55.22; H, 4.86. Found: C, 54.95; H, 4.88. 50% isomer **10c**: ^{1}H NMR (acetone-d_6) δ 2.25 (s, SMe), 3.28 (d, *J*(H,H) = 13.5 Hz, SCH_2), 3.92 (d, *J*(H,H) = 13.5 Hz, SCH_2), 5.15 (s, Cp); ^{13}C NMR (acetone-d_6) δ 49.4 (d, *J*(P,C) = 2 Hz, SMe), 69.8 (d, *J*(P,C) = 2 Hz, SCH_2), 87.1 (dd, *J*(P,C) = *J*(P′,C) = 2 Hz, Cp); ^{31}P NMR (acetone-d_6) δ 61.8 (d, *J*(P,P) = 36 Hz), 80.9 (d, *J*(P,P) = 36 Hz). 50% isomer **10c′**: ^{1}H NMR (acetone-d_6) δ 1.96 (s, SMe), 3.78, 3.82 (AB system, *J*(H,H) = 13.6 Hz, SCH_2), 5.01 (s, Cp); ^{13}C NMR (acetone-d_6) δ 48.4 (d, *J*(P,C) = 2 Hz, SMe), 70.5 (dd, *J*(P,C) = *J*(P′,C) = 1 Hz, SCH_2), 87.2 (dd, *J*(P,C) = *J*(P′,C) = 2 Hz, Cp); ^{31}P NMR (acetone-d_6) δ 61.2 (d, *J*(P,P) = 37 Hz), 80.8 (d, *J*(P,P) = 37 Hz).

Liberation of the Sulfoxides from 10a−c. The complex (0.10 mmol), sodium iodide (0.50 mmol), and acetone (5 mL) were heated under reflux (15 h). The mixture was then evaporated to dryness, and the residue was extracted with dichloromethane (2 mL) and chromatographed over a short (10 cm) silica column. First, the complex [CpRu(chir)I] (**11**) was eluted with dichloromethane as a yellow band, and then, using acetone as eluent, the sulfoxides were removed from the column. Upon evaporation of the solvent, **12a−c** remained as colorless oils in quantitative yield (by ^{1}H NMR). The ee's as determined by HPLC were identical with the de's of the corresponding complexes.

Anal. Calcd for **11** $C_{33}H_{33}IP_2Ru$: C, 55.08; H, 4.62. Found: C, 55.37; H, 4.52. ^{1}H NMR ($CDCl_3$): δ 1.05 (dd, *J*(H,H) = 7.1 Hz, *J*(P,H) = 11.7 Hz, Me), 1.15 (dd, *J*(H,H) = 6.9 Hz, *J*(P,H) = 10.9 Hz, Me), 2.12 (m, CH), 3.07 (m, CH), 4.45 (s, Cp). ^{13}C NMR ($CDCl_3$): δ 15.8 (dd, ^2J(P,C) = 14 Hz, ^3J(P,C) = 4 Hz, Me), 17.5 (dd, ^2J(P,C) = 16 Hz, ^{3}J(P,C) = 2 Hz, Me), 37.7 (dd, ^1J(P,C) = 27 Hz, ^2J(P,C) = 16 Hz, CH), 40.3 (dd, ^1J(P,C) = 31 Hz, ^2J(P,C) = 17 Hz, CH), 81.2 (s, Cp). ^{31}P NMR ($CDCl_3$): δ 73.6 (d, *J*(P,P) = 33 Hz), 81.9 (d, *J*(P,P) = 33 Hz).

Crystallographic Studies. (a) X-ray Measurements of 5a, 10a, and 10b. Crystals were grown from dichloromethane/hexane. The data sets were collected on an Enraf-Nonius CAD4 using Mo Kα radiation. Semiempirical absorption corrections were applied.[19a] The structures were solved by Patterson methods with SHELXS-86.[19b] **10b** crystallizes with one molecule of dichloromethane in the asymmetric unit. The disordered PF_6^- ion in **10a** was refined to a split occupancy of 0.53 and 0.47 with distance restraints.

Table 2. Bond Distances (Å) and Angles (deg) within the Cations of **5a**, **5b**, **10a**, and **10b**

	5a	5b	10a	10b
Ru−S	2.349(3)	2.380(4)	2.2791(14)	2.299(2)
Ru−P(1)	2.305(3)	2.307(2)	2.3334(14)	2.329(2)
Ru−P(2)	2.282(3)	2.301(2)	2.293(2)	2.284(2)
Ru−Cp[a]	1.877	1.894	1.891	1.903
S−C(Me)	1.795(10)	1.855(7)	1.799(6)	1.798(11)
S−C(R)	1.787(12)	1.817(8)	1.803(6)	1.858(11)
S−O			1.479(4)	1.476(7)
P(1)−Ru−P(2)	82.51(11)	83.50(5)	81.85(5)	82.45(8)
P(1)−Ru−S	95.25(11)	94.32(10)	97.07(5)	92.74(8)
P(2)−Ru−S	85.90(11)	82.89(11)	88.97(5)	89.52(8)
Ru−S−C(Me)	110.2(4)	106.1(3)	110.1(3)	110.7(4)
Ru−S−C(R)	115.3(5)	121.2(4)	116.1(2)	116.0(4)
Ru−S−O			119.7(2)	117.9(3)
C(R)−S−C(Me)	99.2(5)	101.3(4)	99.3(3)	103.6(5)
C(R)−S−O			104.7(3)	103.5(5)
C(Me)−S−O			104.3(3)	103.6(5)

[a] Cp Denotes the midpoint of the cyclopentadienyl ring.

(b) X-ray Measurements of 5b. Crystals were grown from dichloromethane/hexane. The data were collected on a Stoe-Huber-Siemens diffractometer fitted with a Siemens CCD-detector at a temperature of 153 K[20] using Mo Kα radiation. A semiempirical absorption correction was applied. The structure was solved by direct methods with SHELXS-90.[19b] The disordered S(Me)-*i*-Pr moiety was refined to a split occupancy of 0.66 and 0.34, while the disordered PF_6^- anion was refined to a split occupancy of 0.70 and 0.30, respectively, using distance and rigid-bond restraints with the anisotropic displacement parameters being similar. All structures were refined by full-matrix least-squares procedures on F^2, with a weighting scheme $w^{-1} = \sigma^2F_o^2 + (g_1P)^2 + g_2P$, where $P = (F_o^2 + 2F_c^2)/3$, using SHELXL93.[19c] All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the refinement of the hydrogen atom positions. Relevant crystallographic data can be found in Table 1, and selected bond lengths and angles are give in Table 2. Further details on the structure investigation are reported as Supporting Information or may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD 405919 (**5a**), CSD 406080 (**5b**), CSD 405920 (**10a**), and CSD 405921 (**10b**) and the full journal citation.

Results

Synthesis of Ruthenium Thioether and Sulfoxide Complexes. Substitution of Cl^- in a polar medium[21] is the method

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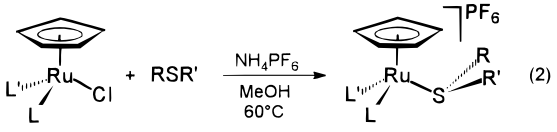
of choice for the preparation of the ionic thioether complexes **1**−**5** (eq 2; **2c** and **3c** had been obtained previously by



1 - 5

LL'	R	Me	Me	Me	*i*-Pr	Et	Me	C_4H_8S
	R'	Ph	*i*-Pr	Bz	Bz	Bz	Cy	
dppm		**1a**	**1b**	**1c**	**1d**			**1g**
dppe		**2a**	**2b**	**2c**	**2d**			**2g**
Ph_3P, CO		**3a**	**3b**	**3c**				
dpme		**4a**	**4b**	**4c**	**4d**			
chir		**5a**	**5b**	**5c**	**5d**	**5e**	**5f**	

dppm = $Ph_2PCH_2PPh_2$, dppe = $Ph_2PC_2H_4PPh_2$,
dpme = $Me_2PC_2H_4PPh_2$, chir = (*S*,*S*)-$Ph_2PCHMeCHMePPh_2$

methylation of the corresponding phenylmethanethiolate complexes).[22] The products are bright yellow, moderately air-stable compounds which are quite readily soluble in polar organic solvents.

At room temperature, thioether complexes undergo a rapid pyramidal inversion at sulfur.[23] Therefore, complexes **1** and **2** are achiral on the NMR time scale and accordingly give the expected simple ^{1}H, ^{13}C, and ^{31}P NMR spectra. For the same reason, chiral racemic complexes **3** and **4** do not form distinguishable diastereoisomers. In some cases, line-broadening can be observed even at room temperature, but we have not investigated this in much detail since this has been done previously for many similar cases,[23] including the closely related ruthenium complexes $[CpRu(dppe)(SRR')]^+$ (R, R′ = Et, Ph)[24] as well as a number of chiral rhenium cations $[CpRe(NO)(PPh_3)(SRR')]^+$.[25] A noteworthy feature of the ^{13}C NMR spectra of complexes **3** is the lack of observable coupling ^3J(P,C) of the SMe group. X-ray structure determinations of $[CpRu(CO)(PPh_3)(MeS(O)$-*t*-Bu)]SbF_6[26] and the above-mentioned rhenium complexes[25] indicate that the thioether ligand assumes a preferred rotational orientation with the dihedral angle Me−S−Ru−P close to 90°. For similar reasons, the two possible couplings, ^3J(P,C) in chiral, racemic complexes **4** as well as in chiral, enantiomerically pure complexes **5** are very different. For two examples of the latter case, we have recorded low-temperature NMR spectra. In **5c**, the two groups R and R′ are of similar sizes, and consequently two diastereoisomers are observed at −40 °C in a 60:40 ratio. [Major isomer: ^{1}H NMR δ 1.40 (s, SMe), 2.37, 3.54 (AB system, J(H,H) = 13.0 Hz, SCH_2), 4.95 (s, Cp); ^{31}P NMR δ 66.4, 82.4 (AX system, J(P,P) = 39 Hz). Minor isomer: ^{1}H NMR δ 1.20 (s, SMe), 2.89, 3.50 (AB system, J(H,H) = 13.2 Hz, SCH_2), 4.85 (s, Cp); ^{31}P-NMR δ 65.7, 82.1 (AX system, J(P,P) = 40 Hz)]. NOE measurements at this temperature indicate that, for each of the two diastereoisomers, the rotamer with both the methyl and the benzyl groups oriented toward the Cp ring is the preferred form (irradiation of the Cp resonances gives approximately equal enhancements of the methyl and one of the benzyl signals, and *vice versa*). This rotational preference is quite expected since

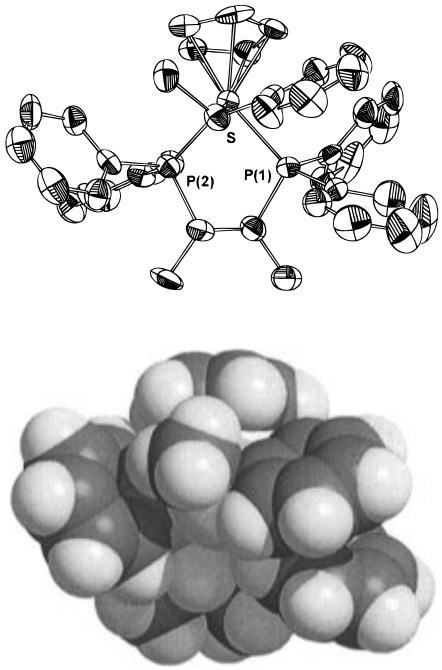


Figure 1. Ortep plot and space-filling model of the cation $[CpRu(chir)(MeSPh)]^+$ (**5a**$^+$).

the aryl groups at the chelate ligand occupy considerably more space than does the Cp ring,[27] and even for the less bulky ligand combinations PPh_3/CO and PPh_3/NO, this is the preferred orientation.[25,26] In **5b**, the organic groups at the sulfur atom (Me and *i*-Pr) are of very different sizes. Consequently, the diastereoisomer ratio at −60 °C is quite high [94:6. Major isomer: ^{1}H NMR δ 0.58 (d, J(H,H) = 7.0 Hz, *i*-Pr), 1.08 (d, J(H,H) = 6.6 Hz, *i*-Pr), 1.33 (s, SMe), 4.76 (s, Cp); ^{31}P NMR δ 62.7, 81.7 (AX system, J(P,P) = 41 Hz). Minor isomer: ^{1}H NMR δ 1.06 (d, J(H,H) = 7.3 Hz, *i*-Pr), 1.14 (d, J(H,H) = 6.7 Hz, *i*-Pr), 1.47 (s, SMe), 4.84 (s, Cp); ^{31}P NMR δ 63.4, 81.5 (AX system, J(P,P) = 42 Hz)]. Crystal structure determinations of **5a** and **5b** (Figures 1 and 2) unequivocally corroborate the spectroscopically determined conformations and indicate that in all likelihood this rotational orientation is the preferred one for all complexes of this kind. Bond distances and angles around the ruthenium atom (Table 2) are within the expected range.[21] The steric strain between the thioether and phosphine ligands is apparent from an increased Ru−S bond distance in **5b**. The orientation of the phenyl groups of the phosphine ligand deserves some comment. In square-planar complexes relevant to catalysis, it is often observed that chelating chiral phosphines adopt an "edge−face" conformation, which means that the coordinated substrate molecule is exposed to the edge of a phenyl group on one side and to the face of a phenyl group on the opposite side. Indeed, it is frequently emphasized that this "edge−face" arrangement is primarily responsible for diastereoselection.[28] While the structure of **5a** conforms to this expectation, it is easily seen that the thioether ligand in **5b** is on both sides framed by the faces of phenyl groups. Thus 2(*S*),3(*S*)-bis(diphenylphosphino)butane is, despite the fixed configuration at the two carbon atoms of the backbone, a remarkably flexible ligand.[29] The *R* configuration imposed on the thioether ligands is, therefore, mainly due to the puckering of the five-membered chelate ring, which pushes one phenyl

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(28) Halpern, J. *Science* **1982**, *217*, 401 and references cited therein.
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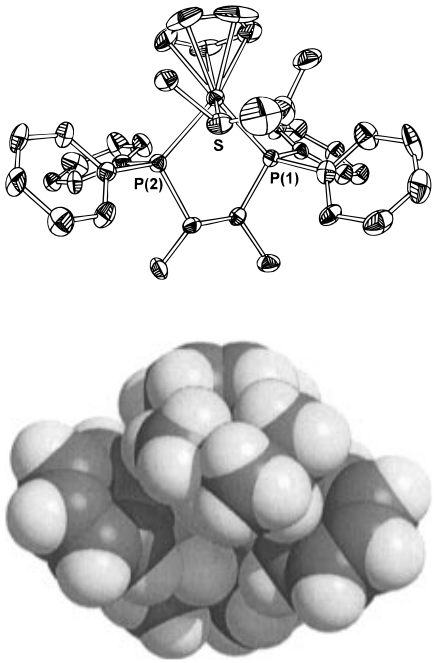
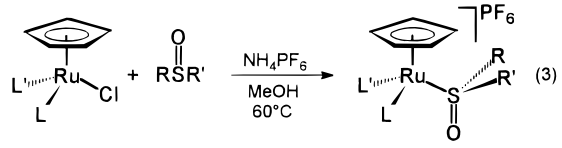


Figure 2. Ortep plot and space-filling model of the cation [CpRu(chir)(MeS-*i*-Pr)]$^+$ (**5b**$^+$).

group toward the thioether ligand. Thus, the coordination site occupied by the thioether ligand breaks down into three sectors of decreasing size which are taken up by the substituent R, the CH_3 group, and the remaining lone pair at sulfur. Since there exist no pronounced intermolecular contacts in the lattices of **5a** and **5b**, we can be sure that also in solution the *R* configuration at sulfur is thermodynamically favored.

For the synthesis of the sulfoxide complexes **6**−**10** considerably longer reaction times are required to compensate for the reduced nucleophilicity of sulfoxides (eq 3). The sulfoxide



6 - 10

LL'	R	Me	Me	Me	*i*-Pr
	R'	Ph	*i*-Pr	Bz	Bz
dppm		**6a**	**6b**	**6c**	**6d**
dppe		**7a**	**7b**	**7c**	**7d**
Ph_3P, CO		**8a,a'**	**8b,b'**	**8c,c'**	
dpme		**9a,a'**	**9b,b'**	**9c,c'**	**9d,d'**
chir		**10a,a'**	**10b,b'**	**10c,c'**	**10d,d'**

complexes are light yellow, moderately air-stable compounds which in their physical properties closely resemble the analogous thioether complexes **1**−**5**. The formation of **7d** and **10d**,**d′** could only be observed spectroscopically. Apparently, the combination of a bulky sulfoxide and a bulky metal complex makes the Ru−S bond quite labile.

Sulfoxides are configurationally stable. Consequently, complexes **6** and **7** are chiral which can be seen, *inter alia*, from the nonequivalence of the two phosphorus nuclei. Complexes **8** and **9** are formed as pairs of enantiomeric diastereoisomers. The dpme ligand imparts only negligible diastereo-discriminating ability to the complex. Quite high diastereomeric excesses, however, can be found for the ligand combination CO/PPh_3 (**8a**,**a′**, 4%; **8b**,**b′**, 72%; **8c**,**c′**, 72%). Similar observations have

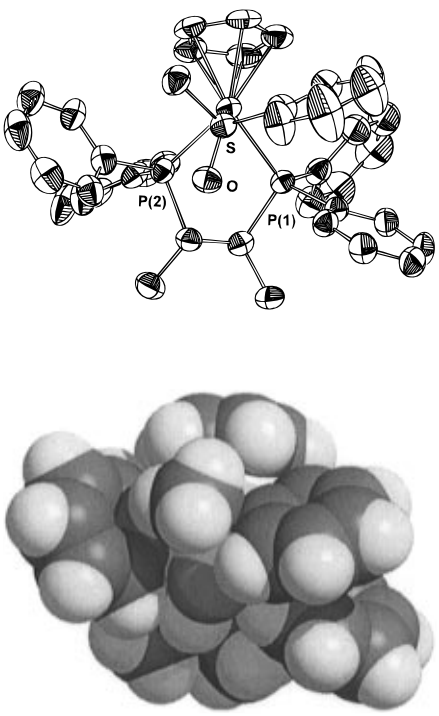


Figure 3. Ortep plot and space-filling model of the cation [CpRu(chir)(MeS(O)Ph)]$^+$ (**10a**$^+$).

been made with [CpRu(CO)(PPh_3)(MeS(O)-*t*-Bu)]$^+$ [26] and related rhenium sulfoxide complexes.[25] Complexes **10** finally are formed as mixtures of diastereoisomers; the observed de's (**10a**,**a′**, 86%; **10b**,**b′**, 76%; **10c**,**c′**, 0%) are the result of a preference of the chiral, enantiomerically pure metal fragment [Cp(chir)Ru]$^+$ for one enantiomer of the sulfoxide. NOE-difference spectra of **10a** and **10c**,**c′** were recorded; in all cases, strong signal enhancements were found between the Cp ligand and the methyl and benzyl protons of the groups at sulfur. This means that in the sulfoxide complexes, too, the organic substituents at sulfur are oriented toward the Cp ligand while oxygen, the smallest substituent, occupies the crowded space between the phenyl groups of the bidentate phosphine ligand, as expected. This is again corrobated by the crystal structure determination of the major diastereoisomers **10a** and **10b** with the *R* configuration at sulfur (Figures 3 and 4). Bond distances and angles (Table 2) are again within the expected ranges.[21,26] The Ru−S bonds are shorter than those in the corresponding thioether complexes due to contraction of the sulfur valence orbitals brought about by the electronegative oxygen atom.

Oxygen Transfer from Dimethyldioxirane to Thioether Complexes. To test the feasibility of the oxidation concept outlined in eq 1, complexes **1** and **2** were treated with an excess of DMD at temperatures between −40 and 0 °C (eq 4). No

1a - d, g
2a - c, g

6a - d, g
7a - c, g

R	Me	Me	Me	Bz	C_4H_8S
R'	Ph	*i*-Pr	Bz	*i*-Pr	
	a	**b**	**c**	**d**	**g**

reaction was observed between **2d** and DMD, and **1d** gave only

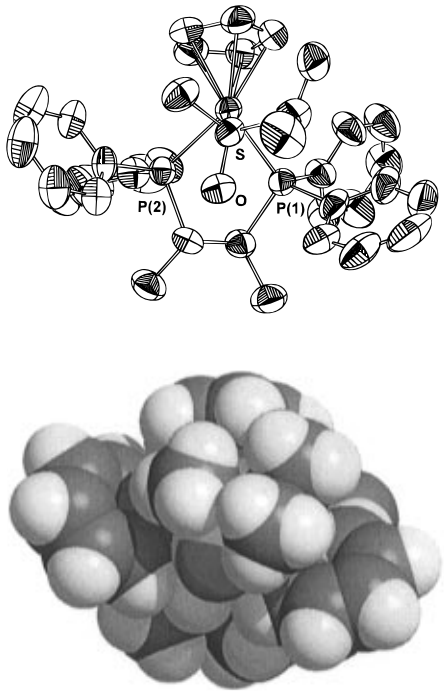


Figure 4. Ortep plot and space-filling model of the cation [CpRu(chir)(MeS(O)-*i*-Pr)]$^+$ (**10b**$^+$).

low yields of **6d**, while the other sulfoxide complexes were produced in good yields and without noticeable side reactions. When the DMD oxidations were carried out under an atmosphere of carbon monoxide, no CO incorporation was found. In a crossover experiment, an equimolar mixture of **1a** and **2c** was treated with DMD, giving only the sulfoxide complexes **6a** and **7c** and none of the crossover products **6c** and **7a**. Analogously, when a mixture of **1c** and **2a** was treated with DMD, only **6c** and **7a** and none of the crossover products **6a** and **7c** were obtained. To compare the reactivities of coordinated and free thioether, an equimolar mixture of **1a** and thioanisol was treated with a slight excess of DMD at 0 °C. The thioether was oxidized to sulfoxide and sulfone, while most of **1a** remained unreacted. Not unexpectedly, coordinated thioethers are much more difficult to oxidize than uncoordinated ones.

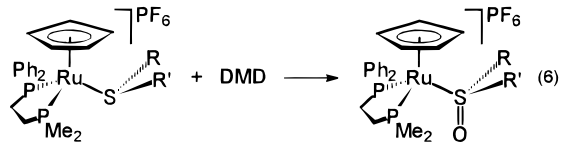
The following experiments were aimed at the development of a novel strategy for the enantioselective oxidation of thioethers. First, the chiral racemic carbonyl complexes **3a**−**c** were treated with DMD at 0 °C (eq 5). Monitoring the reaction

3a - c **8a - c**

(Only one of the two possible configurations at Ru and S is shown)

R	Ph	*i*-Pr	Bz
	a	**b**	**c**
de(%)	8	28	24

by NMR revealed that the oxidation is much slower in this case than in the case of complexes **1** and **2**. Even with a 10-fold excess of DMD, conversions were less than quantitative, and the diastereoselectivity was disappointing. Next, the more electron-rich complexes **4a**−**d** were chosen as substrates. Here, indeed, a quantitative oxidation to the sulfoxide complexes **9a**−**d** could be readily achieved. Diastereoselectivities were much better too (eq 6) but were still too low to be synthetically



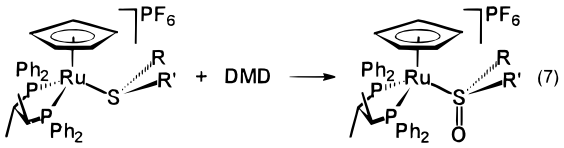
4a - d **9a - d**

(Only one of the two possible configurations at Ru and S is shown)

R	Me	Me	Me	Bz
R'	Ph	*i*-Pr	Bz	*i*-Pr
	a	**b**	**c**	**d**
de(%)	60	60	50	34

useful. Since, additionally, the diastereomer separation of the related starting material [NmcpRu(dpme)Cl] (Nmcp = neomenthylcyclopentadienyl) was more tedious than expected,[30] we finally abandoned the concept of chirality-at-the-metal.

Much better results, in terms of yield and diastereoselectivity, were obtained with oxidation of the 2(*S*),3(*S*)-bis(diphenylphosphino)butane complexes **5** (eq 7). In the case of the methyl



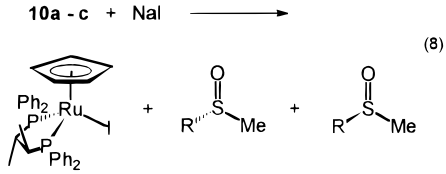
5a - f **10a - f**

R	Me	Me	Me	Et	Me
R'	Ph	*i*-Pr	Bz	Bz	Cy
	a	**b**	**c**	**e**	**f**
de(%)	46	86	>98	90[a]	84

[a] Low conversion

thioether complexes, a 4-fold excess of DMD at 0 °C in acetone was sufficient to give nearly quantitative conversions to the sulfoxide complexes **10**. Conversions drop sharply when both substituents at sulfur are sterically more demanding (**5e**). Using a larger excess of DMD in this case leads to increased decomposition. Diastereoselectivities are, with the conspicuous exception of the thioanisole complex **10a**, excellent. A distinct advantage of DMD as an oxidant is the fact that any excess can be readily removed under vacuum. This greatly simplifies the isolation of the sulfoxide complexes.

Liberation of the Sulfoxides. To liberate the sulfoxides from the metal, complexes **10a**−**c** were refluxed with sodium iodide in acetone (eq 8). The iodo complex **11** was isolated from the



11 **(*R*) - 12** **(*S*) - 12**

R		*R*(%)	*S*(%)
Ph	**a**	27	73
i-Pr	**b**	7	93
Bz	**c**	<1	>99

crude reaction mixture by chromatography in almost quantitative yield. With $AgPF_6$ as the halide abstraction reagent, **11** was employed again to prepare the thioether complexes **5**. The enantiomeric purity of sulfoxides **12** was checked by HPLC

(30) (a) Bezler, J. Dissertation, University of Würzburg, 1995. (b) Schenk, W. A.; Bezler, J. Unpublished results.

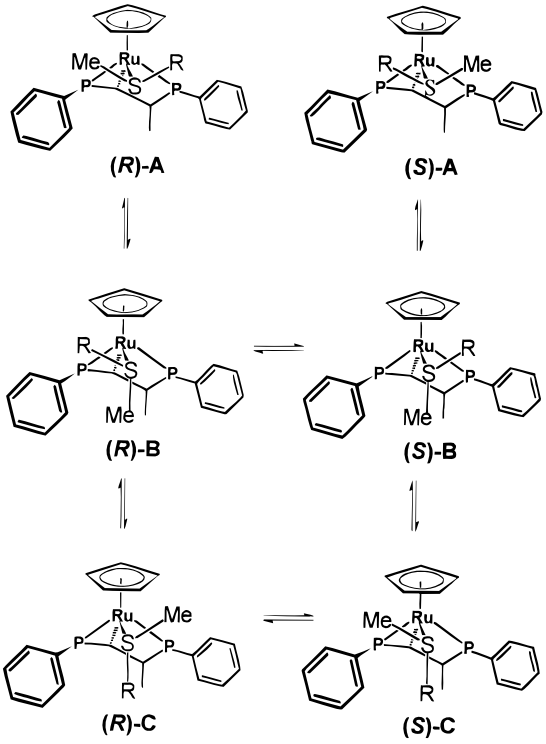
using a Chiralcel OD column in combination with UV and optical rotation detectors. The reaction according to eq 8 was repeated by employing diastereomerically pure samples of **10a** and **10b**. In all cases, the ee's of the sulfoxides were identical to the de's of the complexes. The absolute configurations follow from the structures of **10a** and **10b** and the known specific rotations of **12a** and **12c**.[3a,6a] In our previous publication,[1] we erroneously assigned the *R* configuration to the major enantiomer of **12b** by analogy to the reported[3a] absolute configurations of (*R*)-(+)-*i*-BuS(O)Me and (*S*)-(−)-*n*-PrS(O)Me.

Discussion

A kinetically stable metal−sulfur bond is a necessary prerequisite for chirality transfer from a metal complex to sulfur as outlined as eq 1. A low-spin, d^6-cationic complex of a second-row late transition element offers the best probability to fulfill this requirement. We[22] and others[24,26] found previously that neither thioethers nor sulfoxides dissociate readily from 18-electron complexes of the type described here. Nevertheless, the presence of a strong oxidant in the reaction mixture could lead to the formation of 17-electron intermediates which might then undergo rapid ligand exchange, possibly even in a catalytic cycle.[31] Good evidence that this does not occur comes from the observation that no carbonyl complexes are formed when the oxidations are carried out in the presence of carbon monoxide. The crossover experiments described in the preceding section finally prove that the oxygen transfer takes place at the complex, while the metal−sulfur bond remains intact. Furthermore, diastereoselectivities of the formation of sulfoxide complexes **8**−**10** by oxidation (eqs 5−7) are very different from those obtained by ligand exchange. Striking examples are **10c**,**c′**, which are formed by ligand exchange with 0% de and by oxidation with >98% de, and **8b**,**b′**, for which opposite diastereoisomers are favored by the two different routes. Not only is this additional proof that oxidation does not involve ligand dissociation and readdition, but it also demonstrates that the observed selectivities are a result of kinetic control. A mechanism which involves the formation of a Ru=O intermediate followed by an O atom shift to sulfur can be ruled out on the basis of the observation that the de of the oxidation depends markedly on the nature of the oxidant.[32]

A detailed interpretation of the oxygen transfer reaction has to take into account all possible rotamers/diastereomers of the thioether complexes **5** (Scheme 1). Of these, only (*R*)-**A** and (*S*)-**A** may be observed by NMR at low temperature. The fact that there is no correlation between (*R*)/(*S*) equilibria and the diastereoselectivity of the oxidation strongly suggests that rotamers **A** are not the reactive species. Of the remaining conformers, (*R*)-**B** and (*S*)-**B** should be present in higher proportions than (*R*)-**C** and (*S*)-**C**, in which the largest substituent on sulfur occupies the narrowest space of the [CpRu(chir)] complex. The final outcome of the reaction will, therefore, be determined by the ratio (*R*)-**B**/(*S*)-**B** (which is in favor of (*S*)-**B** since there the largest substituent R occupies the largest sector around ruthenium) and the relative reactivity of these two conformers. The predominant formation of (*S*)-sulfoxides indicates that oxygen transfer is fastest for the

Scheme 1



conformer (*R*)-**B**, in which the oxidant can approach the sulfur atom from the sterically least encumbered direction. (Note that if all steps in the sequence [Ru]−SMeR → [Ru]−S(O)MeR → RS(O)Me proceed with retention of configuration at sulfur, the stereochemical descriptor changes as (*R*) → (*R*) → (*S*)). This interpretation also explains why the oxygen transfer is largely limited to methyl thioethers: for substituents larger than CH_3 even conformers **B** become unaccessible.[33]

The limitation to methyl sulfoxides can probably be overcome in two ways: first, oxidants which are more reactive or thermally more stable than DMD should be able to attack rotamers **B** even if present in only very small concentrations; second, other chiral diphosphines might favor rotamers analogous to **B** while at the same time give high diastereomeric excesses. Work in both directions is in progress in our laboratory.

Acknowledgment. This work was generously supported by the Deutsche Forschungsgemeinschaft (SFB 347). We are indebted to Dr. U. Hoch, Institute of Pharmacy and Food Chemistry, University of Würzburg, for carrying out the HPLC separations of the sulfoxides.

Supporting Information Available: Analytical and spectroscopic textual data for the thioether and sulfoxide complexes **1**−**10** (14 pages). X-ray crystallographic files, in CIF format, for compounds **5a**, **5b**, **10a**, and **10b** are available on the Internet only. Ordering and access information is given on any current masthead page.

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(31) (a) Astruc, D. *Angew. Chem.* **1988**, *100*, 662; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 643. (b) Baird, M. C. *Chem. Rev.* **1988**, *88*, 1217.
(32) Schenk, W. A.; Dürr, M. To be published.
(33) A reviewer suggested that in a mechanism such as described by Scheme 1 the ee's might be temperature dependent. We have found no pronounced changes in the −20 to 0 °C range (at higher temperatures DMD decomposes too rapidly), but are addressing this question using other oxidants.