

Synthesis and Structural Characterization of Molybdenum(VI) and Iron(II) Coordination Compounds with *S*-Alkyl-*N*-methyl-*S*-(2-pyridyl)sulfoximines and Catalytic Epoxidation Activity of the Molybdenum Complexes

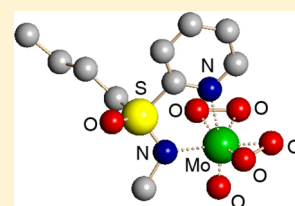
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S Supporting Information

ABSTRACT: Coordination compounds oxido(diperoxido)(*S*-butyl-*N*-methyl-*S*-(2-pyridyl)sulfoximine)molybdenum(VI), $[\text{MoO}(\text{O}_2)_2\{\text{SO}(\text{NMe})^n\text{Bu}(\text{NC}_5\text{H}_4)\}]$ (**5c**), and bis- $\{(\text{dichlorido})(\text{N},\text{S}\text{-dimethyl-2-pyridylsulfoximine})\text{iron(II)}\}$, tetrahydrofuran solvate (1:1) (**6**), $[\text{FeCl}_2\{\text{SO}(\text{NMe})\text{Me}(\text{NC}_5\text{H}_4)\}]_2\cdot\text{THF}$ are prepared from the free ligand **4** and molybdenum(VI) oxidediperoxide(dihydrate) and iron dichloride, respectively. The crystal structures reveal a trigonal bipyramid with the pyridine ring and the single oxygen on molybdenum in a trans arrangement for **5c** and a planar $\mu^2\text{-Cl}_2\text{Fe}_2$ ring with trans-oriented exocyclic Cl atoms for **6** whereas the structures of the N,N-dicoordinated ligands are only little effected by the metals. Coordination compounds (**5**) efficiently catalyze the epoxidation of cyclooctene or of monosubstituted alkenes by *tert*-butyl hydroperoxide.



INTRODUCTION

Sulfoximines are tetracoordinate sulfur compounds that formally result from the exchange of one oxygen for a nitrogen atom in a sulfone. However, in contrast to the well-known sulfones,^{1,2} sulfoximines have emerged only recently as synthetically useful compounds³ and as promising pharmacophores in medicinal chemistry.⁴ In particular, if different organyl substituents on sulfur are present, then sulfoximines are chiral at the sulfur atom and therefore play an important role in asymmetric synthesis as auxiliaries^{5,6} or as catalysts in the thriving field of enantioselective homogeneous catalysis using transition metal coordination compounds.^{7–9} The work of the Bolm group has especially shown that chiral complexes based on sulfoximines can be successfully applied as catalysts to give highly enantioselective addition and cycloaddition reactions mainly to carbonyl groups.^{10–12} With few exceptions,^{13,14} chelate complexes were used in this work. This implies the use of N,N-bidentate ligands in copper(II),^{11,15–18} palladium(0),¹⁰ palladium(II),^{19,20} or rhodium(I)¹² coordination compounds where the binding sites are offered by the nitrogen atoms of the two linked sulfoximine units in C₂ symmetric bis-sulfoximines^{12,15,16,20} or where besides the C₁ symmetric sulfoximine the nitrogen of a quinoline,²¹ of an aniline,^{11,17,22,23} or of an oxazoline¹⁸ offers a convenient binding site. Also, bidentate N,O complexation of nickel(II) in (2-hydroxyalkyl)sulfoximines and N,P complexation of iridium(0) by 2-(diphenylphosphino)aryl sulfoximines has been shown to allow efficient catalysis of conjugate addition to enones^{24,25} and asymmetric hydrogenation of imines,²⁶ respectively. N,P complexation has also been shown to be useful in palladium-catalyzed allylic alkylation.^{28,29} In these studies, the metal

complexes were usually generated in situ from an appropriate metal(II) salt,^{11,16–24,28,29} or a metal(0) precursor^{10,26} and the sulfoximine. With the exception of a copper,¹⁵ a palladium,¹⁹ and a rhodium complex,¹² the isolated N,N-bidentate sulfoximine complexes adopt a noncrystalline state^{10,26} and could only be characterized spectroscopically including the adduct with a potential cycloaddition partner.²⁷ For a full assessment of the catalyst structure, our goal was to synthesize crystalline transition metal–sulfoximine coordination compounds again with a chelate structure, where the role of the second coordination site is adopted by the nitrogen of a pyridine ring as substituent on sulfur. As for the central atom, we were aiming at metals that so far were not probed in sulfoximine chemistry with the idea to further improve catalytic efficiency and for a broader scope of reactions, which allow catalysis. Thus, we chose molybdenum(VI), the complexes of which are known to efficiently catalyze so divergent reactions as alkyne metathesis³⁰ for the type $(\text{Ar}_3\text{SiO})_3\text{Mo}\equiv\text{X}$ (X = N, CR) or alkene oxidation to epoxides for the type $\text{MoO}(\text{O}_2)_2(\text{L}-\text{L})$.^{31–34} Our second example involves an iron sulfoximine complex where iron has the virtue to be environmentally benign beyond any doubt and is known to catalyze carbon–carbon single bond formation especially well in cross-coupling reactions.^{35–37}

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■ EXPERIMENTAL SECTION

For the preparation of sulfides **1a**, **c**, **d**³⁸ and **1b**,³⁹ literature procedures were adopted. Compounds **4a–d** were prepared following the method of Franek and Claus.⁴⁰

Methyl 2-Pyridyl Sulfide (1a). A mixture of pyridine-2-thiol⁴¹ (1 with R = H; 19.40 g, 0.175 mol), MeCN (50 mL), and NEt₃ (23 mL) was cooled to 0 °C. MeI (24.84 g, 0.175 mol) was added dropwise. The reaction mixture was stirred at 0 °C for 1 h and then overnight at ambient temperature. The solvent was evaporated in vacuo, and the residue was diluted by addition of EtOAc (50 mL). After several hours in a refrigerator, the precipitated HNEt₃I was filtered by suction. The residue was concentrated in vacuo, and the product (**1a**) was isolated by column chromatography (silica, eluent petroleum ether/EtOAc 4:1 v/v). For final purification, the material was distilled (bp 77 °C/14 mbar). Yield 17.71 g (81%; lit.³⁸ 67%) of **1a** as a colorless oil. ¹H NMR (200 MHz, CDCl₃, room temperature): δ 2.56 (s, 3H), 6.97 (dd, 1H, *J* = 4.8, 7.6 Hz), 7.18 (d, 1H, *J* = 8.2 Hz), 7.48 (dd, 1H, *J* = 7.6, 8.2 Hz), 8.44 (d, 1H, *J* = 4.8 Hz). ¹³C NMR (50 MHz, CDCl₃, room temperature): δ 13.2, 119.1, 121.4, 135.8, 149.4, 159.9. IR (NaCl plate, cm⁻¹): ν 3068, 3045, 2995, 2925, 2854, 1581, 1556, 1455, 1436, 1415, 1315, 1279, 1243, 1167, 1146, 1127, 1090, 1043, 985, 964, 757, 712, 619.

Isopropyl 2-Pyridyl Sulfide (1b). At 0 °C, 2-propanethiol (11.75 mL, 9.7 g, 0.127 mol) was added to a suspension of NaOH (5 g, 0.125 mol) in DMF (100 mL). After 2 h at 20 °C, the NaOH had almost completely dissolved and 2-chloropyridine (11.25 mL, 13.63 g, 0.120 mol) was added. The mixture was gradually heated to 140 °C and stirred at this temperature for 6 h. The mixture was allowed to cool overnight and poured onto ice (100 g). Organic material was extracted with CH₂Cl₂ (4 × 50 mL). The combined organic phases were combined and dried (MgSO₄). The solvent was evaporated, and the residue was distilled to give 13.0 g (70%; lit.³⁸ 71%) of product, colorless liquid, bp 58 °C/2 mbar. ¹H NMR (200 MHz, CDCl₃, room temperature): δ 1.41 (d, 6H, *J* = 6.8 Hz), 3.99 (m, 1H), 6.96 (dd, 1H, *J* = 4.8, 7.6 Hz), 7.16 (d, 1H, *J* = 8.2 Hz), 7.47 (dd, 1H, *J* = 7.6, 8.2 Hz), 8.44 (d, 1H, *J* = 4.8 Hz). ¹³C NMR (50 MHz, CDCl₃, room temperature): δ 23.1, 35.0, 119.3, 122.8, 135.8, 149.5, 159.5. IR (NaCl plate, cm⁻¹): ν 3069, 3045, 2963, 2927, 2866, 1578, 1556, 1453, 1415, 1383, 1364, 1280, 1143, 1125, 1088, 1054, 985, 757, 725.

Butyl 2-Pyridyl Sulfide (1c). This compound was obtained analogously to **1a** from pyridine-2-thiol⁴¹ (8.89 g, 0.080 mol) and 1-iodobutane (14.72 g, 0.080 mol). Yield 12.77 g (95%) of a colorless oil. This compound was obtained previously by another route.⁴²

Decyl 2-Pyridyl Sulfide (1d). This compound was obtained analogously to **1a** from pyridine-2-thiol⁴¹ (5.0 g, 0.045 mol) and 1-iododecane (9.65 mL, 12.06 g, 0.045 mol) but was isolated by column chromatography on silica (eluent petroleum ether/EtOAc 4:1 v/v). Yield 10.89 g (93%) of a colorless oil.

Methyl Methylamino 2-Pyridyl Sulfonium 2,4,6-Trimethylphenylsulfonate (3a). To a solution of **1a** (3.74 g, 30.0 mmol) in CH₂Cl₂ (20 mL) was added freshly prepared *O*-mesitylsulfonyl-*N*-methylhydroxylamine⁴³ (**2**, 6.65 g, 29.0 mmol), and the mixture was stirred at ambient temperature overnight. Et₂O (150 mL) was carefully added. After 48 h at 3 °C, the colorless precipitate was removed by filtration and the residue was washed with Et₂O. Yield 7.51 g (73%) of salt **3a**. ¹H NMR (200 MHz, CDCl₃, room temperature): δ 2.23 (s, 3H), 2.69 (s, 6H), 2.74 (d, 3H, *J* = 4.8 Hz), 3.40 (s, 3H), 6.83 (s, 2H), 7.59 (dd, 1H, *J* = 4.8, 7.8 Hz), 8.04 (d, 1H, *J* = 8.0 Hz), 8.41 (broad s and dd, 2H, *J* = 7.8, 8.0 Hz), 8.70 (d, 1H, *J* = 4.8 Hz). ¹³C NMR (50 MHz, CDCl₃, room temperature): δ 20.4, 23.1, 32.2, 34.4, 126.7, 127.8, 131.0, 136.6, 138.7, 138.9, 141.2, 149.5, 150.2.

Isopropyl Methylamino 2-Pyridyl Sulfonium 2,4,6-Trimethylphenylsulfonate (3b) was prepared analogously from **2** (5.73 g, 25.0 mmol) and **1b** (4.02 g, 27.0 mmol) in CH₂Cl₂ (20 mL), and the crude product (ca. 70% conversion) was used as such in the preparation of **4b**.

Butyl Methylamino 2-Pyridyl Sulfonium 2,4,6-Trimethylphenylsulfonate (3c). This salt was prepared analogously to **3a** to give a yellow oil still containing about 25% of unreacted starting materials. This mixture was used as such in the next step.

Decyl Methylamino 2-Pyridyl Sulfonium 2,4,6-Trimethylphenylsulfonate (3d). Analogously to **3a**, freshly prepared **2** (4.59 g, 20.0 mmol) and **1d** (5.23 g, 20.8 mmol) were reacted to give salt **3d**. Yield 7.93 g (82%).

***N*,5-Dimethyl-2-pyridylsulfoximine (4a).** The salt **2a**, as obtained in the previous step, was dissolved in CH₂Cl₂, and the solution was cooled to -78 °C. At this temperature, a moderate stream of NH₃ was introduced for 5 min. After stirring for 10 min, the treatment with NH₃ was repeated. The mixture was allowed to slowly warm to 0 °C, and 3-chloroperbenzoic acid (5.2 g, 30.1 mmol) in CH₂Cl₂ (30 mL) was added dropwise at a pH value between 7 and 9. If the mixture became more acidic, again a stream of NH₃ was introduced. Then, the reaction mixture was stirred at 0 °C for 30 min, and the colorless precipitate was removed by filtration. The filtrate was concentrated in vacuo using a bath temperature not exceeding 30 °C. The product was isolated by column chromatography (silica, eluent CHCl₃) and finally purified by recrystallization from Et₂O/hexane. Yield 1.72 g (48%) of **4a** as colorless crystals, mp 52–53 °C. ¹H NMR (200 MHz, CDCl₃, room temperature): δ 2.68 (s, 3H), 3.25 (s, 3H), 7.52 (dd, 1H, *J* = 4.6, 7.6 Hz), 7.97 (d, 1H, *J* = 7.8 Hz), 8.13 (dd, 1H, *J* = 7.6, 7.8 Hz), 8.78 (d, 1H, *J* = 4.6 Hz). ¹³C NMR (50 MHz, CDCl₃, room temperature): δ 29.4, 40.9, 123.3, 126.4, 137.7, 150.3, 157.1. IR (KBr, cm⁻¹): ν 3100, 3035, 3006, 2959, 2928, 2877, 2805, 1577, 1453, 1426, 1413, 1322, 1290, 1237, 1156, 1124, 1105, 1076, 1041, 992, 953, 906, 854, 790, 771, 737, 704, 615. Elemental analysis is consistent with the gross formula C₇H₁₀N₂OS, *M*_w = 170.23. Anal. Calcd: C, 49.39; H, 5.92; N, 16.46; S, 11.38. Found: C, 49.37; H, 6.07; N, 16.43; S, 11.04.

***S*-Isopropyl-*N*-methyl-2-pyridylsulfoximine (4b).** The compound **4b** was obtained from the crude salt **3b** as obtained from **1b** and, after deprotonation with NH₃, the intermediate oxidized with 3-chloroperbenzoic acid (6.16 g, 35.7 mmol) in CH₂Cl₂ (30 mL). The product was isolated by column chromatography (silica, eluent CHCl₃) to give **4b** as a yellow oil. Yield 1.44 g (31%, based on the amount of **1b** used). ¹H NMR (200 MHz, CDCl₃, room temperature): δ 1.21 and 1.46 (each d, 3H, *J* = 6.9 Hz), 2.69 (s, 3H), 3.70 (m, 1H), 7.50 (dd, 1H, *J* = 4.6, 7.6 Hz), 7.95 (d, 1H, *J* = 8.0 Hz), 8.11 (dd, 1H, *J* = 7.6, 8.0 Hz), 8.80 (d, 1H, *J* = 4.6 Hz). ¹³C NMR (50 MHz, CDCl₃, room temperature): δ 14.8, 16.0, 29.5, 52.7, 125.5, 126.2, 137.5, 150.5, 155.9. IR (NaCl plate, cm⁻¹): ν 3076, 3043, 2962, 2932, 2806, 1558, 1466, 1446, 1365, 1265, 1238, 1144, 1116, 1079, 1050, 1036, 989, 939, 883, 857, 795, 749, 730, 678, 616. Elemental analysis is consistent with the gross formula C₉H₁₄N₂OS, *M*_w = 198.28. Anal. Calcd: C, 54.52; H, 7.12; N, 14.13; S, 16.17. Found: C, 54.42; H, 7.26; N, 13.99; S, 16.21.

***S*-Butyl-*N*-methyl-2-pyridylsulfoximine (4c).** The crude salt **3b** as obtained in the previous step from **1c** (2.01 g, 12.0 mmol), and freshly prepared **2** (2.48 g, 10.8 mmol) was treated with NH₃ as reported above for **4a** and oxidized with 3-chloroperbenzoic acid (2.5 g, 14.5 mmol) in CH₂Cl₂ (20 mL). The product was isolated by column chromatography (silica, eluent CHCl₃) to give **3c** as a yellow oil. Yield 813 mg (38%, based on the amount of **1c** used).

***S*-Decyl-*N*-methyl-2-pyridylsulfoximine (4d)** was prepared analogously to **4a** from salt **3d** (7.93 g, 15.5 mmol). Yield 1.94 g (39%). Yellowish oil.

Oxido(diperoxido)(*S*-butyl-*N*-methyl-*S*-(2-pyridyl)-sulfoximine)molybdenum(VI) (5c). MoO(O₂)₂(H₂O)₂ (24 mL of a 0.1 M aqueous solution, 24 mmol)⁴⁴ was added to **4a** (402 mg, 2.36 mmol) in MeOH (2 mL), and the reaction mixture was stirred at ambient temperature for 2 h. The resulting citrus yellow precipitate was removed by filtration and washed with H₂O, a little MeOH, and finally Et₂O to remove organic impurities. After it was dried in vacuo, **5c** (550 mg, 73%) was isolated as a microcrystalline yellow solid, mp 122 °C (dec). Yellow crystals were obtained by carefully placing hexane on top of a saturated solution in CH₂Cl₂. ¹H NMR (200 MHz, CDCl₃, room temperature): δ 1.01 (t, 3H, *J* = 7.2 Hz), 1.55 and 1.94 (each m, 2H), 3.73 (s, 3H), 3.82 (m, 2H), 7.69 (dd, 1H, *J* = 5.0, 7.8 Hz), 7.96 (d, 1H, *J* = 8.0 Hz), 8.15 (dd, 1H, *J* = 7.8, 8.0 Hz), 8.46 (d, 1H, *J* = 5.0 Hz, H-6). ¹³C NMR (50 MHz, CDCl₃, room temperature): δ 13.4, 21.6, 24.3, 37.2, 58.9, 122.8, 130.2, 140.6, 148.3, 149.5. IR (KBr, cm⁻¹): ν 3096, 3065, 2933, 2905, 2875, 1593, 1561, 1456, 1433, 1392, 1303, 1279, 1244, 1199, 1168, 1138, 1098, 1082, 1060, 1046, 1017,

Table 1. Selected Crystallographic Data of $[\text{MoO}(\text{O}_2)_2\{\text{SO}(\text{NMe})^n\text{Bu}(\text{NC}_5\text{H}_4)\}]$ (**5c**) and $[\text{FeCl}_2\{\text{SO}(\text{NMe})\text{Me}(\text{NC}_5\text{H}_4)\}]_2 \cdot \text{THF}$ (**6**)

parameter	5c	6
empirical formula	$\text{C}_{10}\text{H}_{16}\text{MoN}_2\text{O}_6\text{S}$	$\text{C}_{18}\text{H}_{28}\text{Cl}_4\text{Fe}_2\text{N}_4\text{O}_3\text{S}_2$
fw, g mol ⁻¹	388.25	666.08
cryst system	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
unit cell dimens		
<i>a</i> , Å	8.5057(1)	8.7334(1)
<i>b</i> , Å	18.5753(2)	8.9939(2)
<i>c</i> , Å	9.4720(1)	9.3967(2)
α, deg		96.880(1)
β, deg	100.701(1)	103.671(1)
γ, deg		104.004(1)
cell vol, Å ³	1470.51(3)	683.49(2)
<i>Z</i>	4	1
calcd density, g cm ⁻³	1.754	1.618
abs coeff, mm ⁻¹	1.058	1.632
cryst size, mm	0.50/0.50/0.40	0.60/0.40/0.05
λ, Å	0.71073	0.71073
temperature, K	173	173
θ range for data collection, deg	2.19–27.50	2.27–27.50
index ranges	−8 < <i>h</i> < 11, −24 < <i>k</i> < 23, −12 < <i>l</i> < 8	−11 < <i>h</i> < 10, −11 < <i>k</i> < 11, −12 < <i>l</i> < 12
reflins collected	9860	4732
independent reflns	3357	3088
obs reflns [<i>I</i> > 2σ(<i>I</i> _o)]	3031	2516
no. of parameters	187	178
goodness-of-fit on <i>F</i> ²	1.000	1.000
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i> _o)], all data	0.0222, 0.0259	0.0476, 0.0563
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i> _o)], all data	0.0577, 0.0593	0.1169, 0.1204
largest diff peak and hole, e·Å ⁻³	+0.608, −0.637	+0.968, −1.250
CCDC no. ⁵¹	904588	907772

955, 892, 865, 781, 760, 657, 585, 537. Elemental analysis is consistent with the gross formula $\text{C}_{10}\text{H}_{14}\text{MoN}_2\text{O}_6\text{S}$, $M_w = 388.25$. Anal. Calcd: C, 30.94; H, 4.15; N, 7.22; S, 8.26. Found: C, 30.68; H, 4.10; N, 7.06; S, 8.31.

Analogously, the following were prepared:

Oxido(diperoxido)(*S*-butyl-*N*-methyl-*S*-(2-pyridyl)sulfoximine)-molybdenum(VI) (5a) from sulfoximine **4a** (402 mg, 2.36 mmol) and the molybdenum peroxide solution (24 mL). Yield 647 mg (80%) of a microcrystalline yellow solid, mp 128–129 °C (dec). IR (KBr, cm⁻¹): ν 3099, 3013, 2997, 2913, 1593, 1561, 1457, 1432, 1395, 1321, 1304, 1237, 1169, 1143, 1094, 1042, 1018, 957, 899, 863, 758, 713, 654, 637. Elemental analysis is consistent with the gross formula $\text{C}_7\text{H}_{10}\text{MoN}_2\text{O}_6\text{S}$, $M_w = 346.17$. Anal. Calcd: C, 24.29; H, 2.91; N, 8.09; S, 9.26. Found: C, 24.09; H, 2.88; N, 7.90; S, 9.27.

Oxido(diperoxido)(*S*-isopropyl-*N*-methyl-*S*-(2-pyridyl)sulfoximine)molybdenum(VI) (5b) from sulfoximine **4b** (208 mg, 1.05 mmol) and the molybdenum peroxide solution (11 mL). Yield 270 mg (67%) of a microcrystalline yellow solid, mp 136 °C (dec).

Oxido(diperoxido)(*S*-decyl-*N*-methyl-*S*-(2-pyridyl)sulfoximine)-molybdenum(VI) (5d) from sulfoximine **4d** (203 mg, 0.68 mmol) and the molybdenum peroxide solution (9 mL). Yield 150 mg (47%) of a microcrystalline yellow solid, mp 84 °C (dec).

Bis{(dichlorido)(*N*,*S*-dimethyl-2-pyridylsulfoximine)iron(II)}, Tetrahydrofuran Solvate (1:1) (6). Dry FeCl_2 (80 mg, 0.63 mmol) in dry THF (50 mL) was stirred at ambient temperature till a clear solution was obtained (if traces of H_2O were excluded, this solution was almost colorless; otherwise a yellow or brown color developed and the subsequent reaction with the ligand did not proceed well). Ligand **4a** (112 mg, 0.65 mmol) was added, which led to an immediate orange-red color of the solution. The mixture was stirred overnight and concentrated to one-third of its volume. After 24 h at −5 °C, the Fe complex separated as a microcrystalline orange-red solid, which was removed by filtration and dried in vacuo. To the solution was added

Et_2O carefully, and the mixture was cooled to 0 °C. This led to the precipitation of more orange-red solid. Overall yield 173 mg (93%), mp 186 °C (dec). The solid was dissolved in dry THF, the insoluble material was removed by filtration, and the solution was carefully covered with a layer of Et_2O . After 15 days, yellow to orange-red crystals of **6** separated. IR (KBr, cm⁻¹): ν 3085, 3074, 3008, 2977, 2902, 2817, 1590, 1562, 1457, 1435, 1239, 1096, 1080, 1061, 1011, 959, 874, 784, 755, 704. Elemental analysis is consistent with the gross formula $\text{C}_{18}\text{H}_{28}\text{Cl}_4\text{Fe}_2\text{N}_4\text{O}_3\text{S}_2$, $M_w = 666.08$. Anal. Calcd: C, 32.46; H, 4.24; N, 8.41; S, 9.62; Cl, 21.29. Found: C, 32.22; H, 4.31; N, 8.16; S, 9.61; Cl, 21.35.

(*R*)-(+)-Methyl 2-Pyridylsulfoxide (7). Diethyl (2*R*,3*R*)-tartrate (3.26 g, 15.8 mmol), $\text{Ti}(\text{O}^i\text{Pr})_4$ (2.33 mL, 2.245 g, 7.9 mmol), CH_2Cl_2 (60 mL), and water (142 μL, 7.9 mmol) were stirred at room temperature till a homogeneous mixture was obtained. Sulfide **1a** (993 mg, 7.9 mmol) was added, and then at −21 °C tBuOOH (2.22 mL of a 3.7 M solution in PhMe, 8.2 mmol) was added. After stirring at this temperature for 18 h, the mixture was diluted with water (1.4 mL, 10 equiv) and the temperature was maintained for another 30 min. Then, the mixture was allowed to warm to room temperature and was stirred for 1 h for complete hydrolysis. The precipitate was removed by filtration through Celite, and the solution was concentrated in vacuo. The crude product was purified by column chromatography (silica, eluent petroleum ether/ EtOAc 1:2). Yield 705 mg (63%) of a colorless oil, $[\alpha]_D^{23.5} +62.5$ ($c = 0.980$ in CHCl_3), 64% ee as determined by GLC on Lipodex E. During chromatography, the first fractions contained almost enantiopure material (99% ee),^{45,46} but the optical purity then went continuously down to finally 46% ee.

(*R*)-(-)-*N*,*S*-Dimethyl-2-pyridylsulfoximine (4a). (*R*)-(+)-Sulfoxide **7** (357 mg, 2.5 mmol, 99% ee) and freshly prepared **2** (580 mg, 2.5 mmol) in CH_2Cl_2 (10 mL) were stirred at 28–30 °C for 24 h. Then, the solvent was widely removed in vacuo, and the mixture was

allowed to stand at ambient temperature for 5 days. According to the ^1H NMR spectroscopic evidence, 15–20% of **7** had reacted. The crude product was dissolved in CH_2Cl_2 (20 mL), and the mixture was cooled to 0°C . $\text{EtN}(\text{iPr})_2$ (0.2 mL, 1.15 mmol) was added, and the mixture was stirred first at 0°C for 1 h and then at ambient temperature for 2 h. The solvent was evaporated, and the residue was purified by column chromatography (silica, eluent CHCl_3), removing 264 mg of unreacted **7**. Yield 52 mg (12% based on the total amount of **7** used, 46% based on conversion), colorless oil, $[\alpha]_{\text{D}}^{23.5} -171.9$ ($c = 0.5$ in CHCl_3).

General Procedure for Epoxidation Reactions. Alkene **8**, **10**, or **12** (10 mmol) and catalyst **5** (0.05 mmol) were dissolved in toluene (20 mL) or CHCl_3 (25 mL). $^t\text{BuOOH}$ (2.7 mL, 3.7 M in PhMe, 10 mmol) was added, and the mixture was stirred at 100°C for 5 h or for 1 h at 55°C with toluene or CHCl_3 as solvent, respectively. Alcohol **12** was epoxidized in CHCl_3 at 50°C for 2 days. Yields were determined by capillary GLC on Lipodex E.

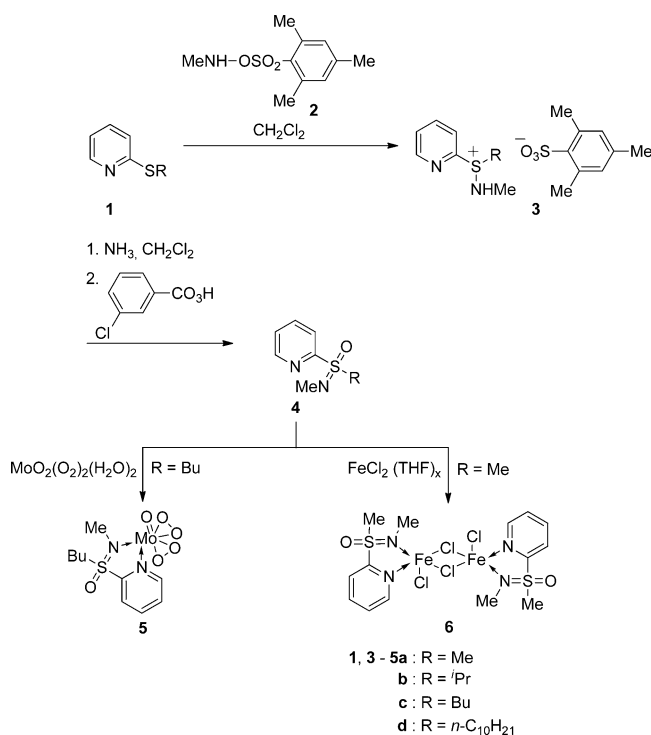
X-ray Data Collection, Structure Determination, and Refinement. The data sets for the complexes were collected on a Siemens axs SMART CCD system (Mo $K\alpha$ radiation, graphite monochromator, ω -scans). A full hemisphere of the reciprocal space was scanned with 1271 frames in three sets; each frame covered 0.3° in ω . An empirical absorption correction was carried out with the program SADABS⁴⁷ (**5c**: T_{min} 0.703, T_{max} 1.000. **6**: T_{min} 0.561, T_{max} 1.000). Both structures were solved with direct methods (SHELXS-97)⁴⁸ and refined with full-matrix least-squares against F_o^2 using the program SHELXL-97.⁴⁹ All non-hydrogen atoms were refined with anisotropic temperature factors. Hydrogen atoms were calculated in idealized positions using a riding model with isotropic temperature factors combined in different logical groups. For molecular graphics and publication materials, the program package SHELXTL-PLUS was used.⁵⁰ Special refinement procedures are given in the Supporting Information. Crystallographic details are provided in Table 1.

RESULTS AND DISCUSSION

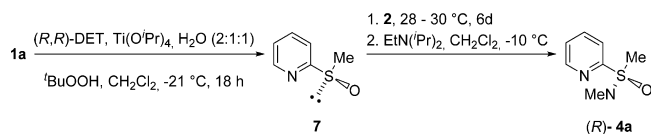
Synthesis. Ligands (**4**) are synthesized starting from 2-pyridyl sulfides (**1**), which can be *N*-methylated using *N*-methyl-*O*-mesitylsulfonyl-hydroxylamine (**2**) adopting a literature method.⁴⁰ The resulting salts (**3**) are deprotonated with gaseous ammonia and in situ oxidized with 3-chloroperbenzoic acid to give racemic sulfoximines (**4**) (Scheme 1). To obtain an optically active sulfoxime, a different route had to be taken (Scheme 2). The crucial intermediate is sulfoxide **7**, which could be obtained in optically pure form using a modified Sharpless procedure as suggested by Kagan,⁵² where a (2*R*,3*R*)-tartarate provides the sulfoxide in the shown (*R*) configuration.⁵² The subsequent imination is known to proceed without loss of optical purity.⁵³ However, for the methylimination of optically active sulfoxide **7** using hydroxylamine derivative (**2**), rather mild temperatures had to be applied to get a pure product (Scheme 2). Under these conditions, the reaction turned out to be rather inefficient, but unreacted starting material (**7**) could be recovered and used again. The final deprotonation step was best carried out using Hünig base, preferably at temperatures not much above ambient temperature (Scheme 2).

Molybdenum Complexes (5). Sulfoximines (**4**) undergo a smooth reaction with molybdenum(VI) oxidodiperoxide-(dihydrate) as generated from molybdenum trioxide and 30% hydrogen peroxide.⁴⁴ For **5c**, crystals of sufficient quality for an X-ray structure analysis can be precipitated by addition of hexane to a solution of the complex in dichloromethane. Complex **5c** is mononuclear and crystallizes in the monoclinic space group $P2_1/c$. If the peroxo groups are each considered as one ligand, the central metal ion Mo^{6+} is coordinated in a distorted trigonal-bipyramidal fashion, interestingly with the single oxygen on the metal and the pyridine nitrogen in the axial position; this configuration is considered the trans

Scheme 1. Synthesis Pathways to Coordination Compounds 5 and 6



Scheme 2. Enantioselective Synthesis of Sulfoxide (*R*)-(+)-7** and of Sulfoximine (*R*)-(-)-**4a****



arrangement (Figure 1); four independently studied crystals gave the same lattice parameters from which the consistent occurrence of the trans configuration in the crystalline state can be derived.⁵⁴ Also, the NMR spectroscopic evidence shows that only one diastereomer is formed to which then mutatis mutandis the trans configuration should be assigned. In contrast, the synthesis of similar molybdenum coordination compounds with *N,N*-dicoordination gave cis/trans mixtures.^{54,55} However, at room temperature in CDCl_3 solution, a slow partial isomerization of the trans to the cis isomer in **5c** is shown by the appearance of a new triplet at δ 0.89 for the *C*-methyl group of the butyl residue in the ^1H NMR spectrum. Similarly, a new H-6 signal shows up at δ 8.85. A striking feature of the structure is the long axial N(1)–Mo bond of 2.404(2) Å as compared to 2.175(2) Å for the equatorial N(2)–Mo bond. This may reflect the trans influence of the oxygen O(1) and may contribute to the strong preference of the trans arrangement (i.e., with the more weakly donating pyridine nitrogen in this position). The effect is more pronounced than in previously studied molybdenum complexes with 2,2'-bipyridines^{56,57} or 3-(2-pyridyl)pyrazoles.^{54,58} Similarly, only the N(2)–Mo value is close to the median of 2.24 Å for the Mo–N bond in Mo-(*N,N*) chelates as derived from 529 entries in the CSD.⁵⁹ However, it should be noted that the inherently longer S–C bond in the N–S–C–N unit of the ligand in **5c** as compared to the N–C–C–N unit in previously

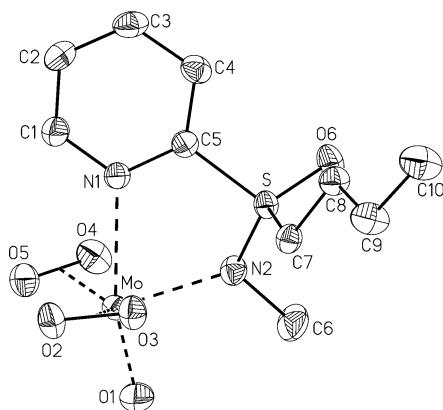


Figure 1. Structure of $[\text{MoO}_2(\text{O}_2)_2\{\text{SO}(\text{NMe})^t\text{Bu}(\text{NC}_5\text{H}_4)\}]$ (**5c**) without hydrogen atoms. (Displacement ellipsoids are shown at the 50% probability level.) Bond lengths (Å): Mo–O1 1.6869(13), Mo–O2 1.9353(13), Mo–O3 1.9645(13), Mo–O4 1.9554(13), Mo–O5 1.9255(13), Mo–N1 2.4038(14), Mo–N2 2.1750(14), S–O6 1.4498(12), S–N2 1.5746(15), S–C5 1.7854(17), S–C7 1.7917(17), N1–C1 1.335(2), N1–C5 1.344(2), N2–C6 1.497(2), O2–O3 1.4782(18), O4–O5 1.4804(19). Angles on S (deg): C5–S–C7 106.14(8), C5–S–O6 110.37(8), C7–S–O6 108.84(8), C5–S–N2 102.18(8), C7–S–N2 111.52(8), O6–S–N2 117.11(8).

studied coordination compounds (ca. 4.10 Å)^{46–50} gives a longer distance between the N atoms (4.703 Å), which allows some more flexibility, and obviously favors the observed trans arrangement of the sulfoximine ligand. The bond angles around sulfur correspond closely to those in the free ligand⁵ with the O–S–N angle being widest.

Iron Complex 6. Similar to **5**, coordination compound **6** is prepared from a solution of iron(II) dichloride in THF and ligand **4a**, with careful exclusion of water. From the orange-red solution in THF, well-developed crystals of **6** slowly deposit. Complex **6** is sensitive against air and moisture but could be subjected to a single-crystal X-ray investigation. Coordination compound **6** crystallizes as a dimeric, binuclear complex in the triclinic space group $P\bar{1}$ and was found to contain a dinuclear structure with one molecule of THF positioned close to the inversion center (Figure 2). In contrast to **5c**, ligands around the iron(2+) atom are arranged to give a distorted square-pyramidal environment, where the metal atom is 0.635(1) Å above the best plane through N1, N2, Cl2, and Cl2A. The central unit of the structure of **6** is a planar $\mu\text{-Cl}_2\text{Fe}_2$ four-membered ring with the inversion center of the molecule as central point. The bond lengths of the iron to the chelate nitrogens differ much less than in **5c** with Fe–N(1) = 2.204(3) Å and Fe–N(2) = 2.107(2) Å. In contrast to the trans-oriented external chlorine atoms in **6**, an otherwise closely related $\mu\text{-Cl}_2\text{Fe}_2$ complex with a bithiazole ligand shows the cis orientation of the terminal chlorine atoms.⁶⁰ But a $\mu\text{-Cl}_2\text{Fe}_2$ complex with a dithiolato chelate was also found to have trans orientation of the chlorine atoms and reveals very similar bond lengths to **6**.⁶¹

Sulfoximino Ligands. In both complexes **5c** and **6**, the sulfoximine ligands are coordinated to the metal ions via the two nitrogen atoms (N1, N2). In view of the oxophilic nature of the metals, this may be surprising but appears to be the uniform coordination mode in uncharged sulfoximine complexes.^{12,15,19,62} Not unexpectedly, the main effect of metal coordination is on the S=N bond, which is significantly longer than in free sulfoximines with an average value of 1.537 Å

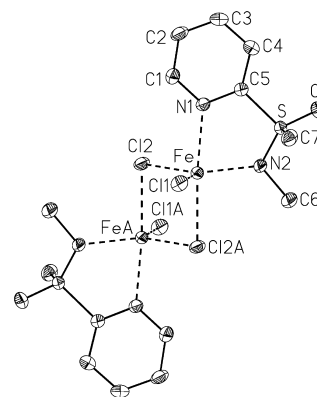
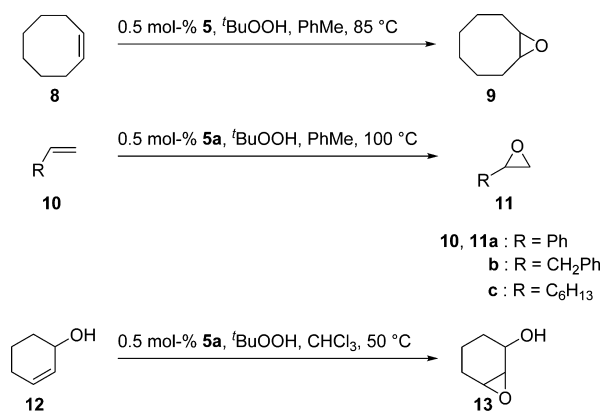


Figure 2. Structure of $[\text{FeCl}_2\{\text{SO}(\text{NMe})\text{Me}(\text{NC}_5\text{H}_4)\}]_2 \cdot \text{THF}$ (**6**) without hydrogen atoms and THF solvent molecule (displacement ellipsoids are shown at the 50% probability level). Bond lengths (Å): Fe–Cl1 2.3033(9), Fe–Cl2 2.3915(8), Fe–Cl2A 2.4796(8), Fe–N1 2.204(3), Fe–N2 2.107(2), S–O 1.449(2), S–N2 1.551(3), S–C5 1.777(3), S–C7 1.770(3), N1–C1 1.338(4), N1–C5 1.341(4), N2–C6 1.491(4). Symmetry operation: A –x + 1, –y + 1, –z. Angles on S (deg): C5–S–C7 104.52(15), C7–S–O 107.66(16), C5–S–O 109.74(14), C5–S–N2 102.88(14), C7–S–N2 111.56(15), O–S–N2 119.43(15).

reflecting the electron transfer from nitrogen to the metal.^{5,12} So the difference in the S=N(2) bond distances between **5c** [1.5746(15) Å] and **6** [1.551(3) Å] demonstrates the special electron-withdrawing effect of molybdenum. Otherwise, the structure of ligands **4a,c** turns out to be rather similar when coordinated to the metals of **5c** and **6** and also in comparison to free sulfoximines. This is in line with previously obtained results giving only “minor structural changes”¹⁵ on coordination to copper,^{15,62} zinc,⁶² palladium,¹⁹ or rhodium.¹²

Catalytic Effects. Molybdenum coordination compounds are known to catalyze the epoxidation of alkenes by hydroperoxides.^{31–34} This invited to test the molybdenum/sulfoximine complexes (**5**) as catalysts in the epoxidation of various alkenes. An attractive feature should be that coordination compounds (**5**) dissolve well in unpolar organic solvents such as chloroform or toluene. The optimum reaction conditions were found using cyclooctene (**8**) as substrate (Scheme 3). All complexes (**5**) turned out to catalyze the epoxidation of **8** by *tert*-butyl hydroperoxide efficiently at the low catalyst concentration of 0.5 mol %. In chloroform at 55 °C or in toluene at 85 °C, yields in the 90–95% range within 30

Scheme 3. Epoxidation of Alkenes Catalyzed by Coordination Compounds (**5**)



min are observed. This means that our molybdenum complexes (**5**) are among the best-performing epoxidation catalysts.³¹ A comparison of turnover numbers (TON) shows that the efficiency of the catalyst is improved by longer carbon chains on the sulfoximine sulfur: in toluene, the TONs increase from 1900 to almost 2700 h⁻¹ on going from the *S*-methyl (**5a**) via the *S*-butyl (**5c**) to the *S*-decyl residue (**5d**). In contrast, the branched and so sterically more demanding *S*-isopropyl compound **5b** gives a TON of only 1460 h⁻¹. The variation of the substrate revealed that monosubstituted alkenes **10** are conveniently oxidized to oxiranes **11**. In toluene at 100 °C and employing catalyst **5a**, styrene (**10a**), allylbenzene (**10b**), and 1-octene (**10c**) give 52, 53 and 64% of epoxidation products (**11**) (Scheme 3). Also, the allylic alcohol **12** is successfully epoxidized to **13** in 61% yield. In contrast, all attempts to use complex **5a** incorporating the optically active ligand (*R*)-(-)-**4a** in enantioselective epoxidation gave no significant asymmetric induction. Iron complex **6** was tested as a catalyst in the cyclodimerization of simple dienes, which is known to proceed well in the presence of an iron/1,4-diaza-1,3-diene catalyst,⁶³ but turned out to have no catalytic effect.

CONCLUSIONS

Both metal ions Mo⁶⁺ and Fe²⁺ undergo a smooth reaction with sulfoximines (**4**) to give coordination compounds **5** and **6**, respectively. In contrast to the mononuclear complex **5c**, the chlorine atoms in **6** lead to a dimeric structure. Within the N–M–N unit, the Mo complex **5c** shows a pronounced difference in the M–N bond lengths, which reflects the mixed axial/equatorial “trans” position of the N atoms. In contrast, in the Fe complex **6**, the M–N distances are rather similar. Except for the S=N bond in the sulfoximine unit, the bond lengths within the sulfoximine ligands in **5c** and **6** are rather similar to those reported for free sulfoximines.^{5,12,15} It appears that the sulfoximines are “innocent spectator ligands”,⁶⁴ though they obviously modulate the catalytic efficiency of the metals. Actually, the synthetic experience shows that for satisfying catalytic efficiency in the promotion of reactions and of enantioselective product formation fine-tuning of the ligands is required,^{15,19,22} but the crystal structures do not clearly reflect these effects. Thus, various coordination compounds of optically active sulfoximines with copper(II) give widely varying enantioselectivities in halogenations reactions,²² but the available structural data of copper complexes give no straightforward rationale.¹⁵ Similarly, a rhodium complex with an optically active sulfoximine gives normal structural data and promotes the hydrosilylation of acetophenone but does not allow enantioselectivity.¹² This is also seen for complexes (**5**), which in our exploratory experiments are good catalysts for the epoxidation of alkenes, but a modification with optically active **4a** as ligand is not efficient in the asymmetric version.

ASSOCIATED CONTENT

Supporting Information

Spectroscopic and analytical data of **1c**, **1d**, **3d**, **4c**, **4d**, **5a**, **5b**, and **5d**. For **5c** and **6**, CIF files giving crystal data and tables, and text giving crystallographic details, all bond lengths and angles, atomic coordinates, and thermal parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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