Nickel(II) Complexes of Chiral Tripodal N,O,S-Ligands: Square-Planar vs. pseudo-Octahedral Coordination in the Solid State and in Solution, Metal-Induced Racemization of the Ligand

Albrecht Berkessel*[a][+], Jan W. Bats[b], Michael Bolte[b], Thomas Neumann[b], and Lutz Seidel[a]

Organisch-Chemisches Institut der Universität Heidelberg[a],
Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

Institut für Organische Chemie der Universität Frankfurt/Main[b],
Marie-Curie-Straße 11, D-60439 Frankfurt/Main, Germany

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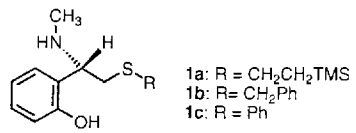
The complexation behavior of three chiral, tripodal N,O,S-ligands with nickel(II) salts was examined. It was found that the coordination mode of the ligands (bidentate N,O and N,S; tridentate N,O,S) and of the central nickel ion (square-planar vs. pseudo-octahedral) is not simply an intrinsic property of the ligand-metal combination, but also a function of the counter ions and of the solvent of crystallization. In the case of one ligand, a diamagnetic square-planar and a paramagnetic pseudo-octahedral form could be switched back and forth, by just changing the solvent of crystallization from methanol to ethanol. By using an enantiomerically pure tripodal N,O,S−ligand, a metal induced racemization was unveiled which would have otherwise remained undetected.

As a part of our continuing efforts to model [Ni,Fe]-hydrogenases with complexes of nickel(II) ions carrying oligodentate N,O,S-ligands[1-3], we recently reported a synthetic approach to the tridentate ligands *rac*-**1b**[1], *rac*-**1c**[2], and **1c**[2]. Herein we describe the synthesis of the trimethylsilyl thioether ligand *rac*-**1a** and the complexation of *rac*-**1a**−**c** and **1c** with nickel(II) salts. As it turned out, the coordination mode of the resulting chelates *in the crystalline state* proved to be a function of both the anions introduced by the nickel salts employed, and by the solvent of crystallization. Furthermore, by using the enantiomerically pure ligand **1c** as a stereochemical probe, a metal-induced racemization process was discovered which would otherwise have remained undetected.



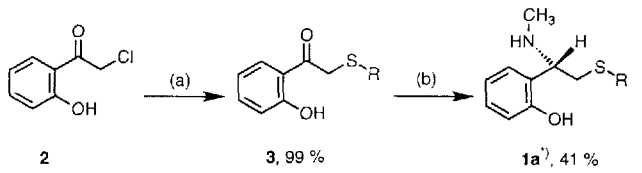
1a: R = CH_2CH_2TMS
1b: R= CH_2Ph
1c: R = Ph

Results and Discussion

Synthesis

Our two-step synthesis of the ligand *rac*-**1a** is depicted in Scheme 1. In the first step, 2-chloro-1-(2-hydroxyphenyl)-ethanone[4] (**2**) was reacted with the thiolate anion generated from 2-(trimethylsilyl)ethanthiol, and the resulting thioether **3** was isolated in virtually quantitative yield. The reductive amination of the intermediate **3** finally afforded the racemic ligand *rac*-**1a** in a yield of 41%.

Scheme 1



2 **3**, 99 % **1a***), 41 %

a: $(CH_3)_3Si-CH_2-CH_2-S^- Na^+$, EtOH, 1,4-dioxane.- R = $-CH_2-CH_2-Si(CH_3)_3$
b: H_2N-CH_3, $NaBH_4$, EtOH.- *) racemic mixture

Complexation with Nickel Ions

As shown in equation 1, the reaction of the N,O,S-ligand *rac*-**1a** with anhydrous nickel(II) chloride afforded the *meso*-complex **4** in a yield of 89%. The elemental composition of **4** could be derived from its elemental analysis. The isolated material contained the ligand, nickel, and chloride in a ratio of 2:1:2. In other words, the ligand must be bound to the metal in intact form, and no deprotonation of the acidic phenol groups had taken place. As indicated by the high-spin nature of the complex (μ_{eff} = 3.21 B.M.), the formation of an octahedral nickel chelate appeared most likely. Luckily, single crystals suitable for X-ray structural analysis could be grown from **4**. The result is shown in Figure 1. As anticipated, the phenol groups of the two

[+] New address: Institut für Organische Chemie der Universität zu Köln, Greinstr. 4, D-50939 Köln, Germany, Telephone: (internat.) +49(0)221-470-3283, Fax. (internat.) +49(0)221-470-5102, E-mail: berkessel@uni-koeln.de

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ligand molecules are not deprotonated, and they do not participate in the coordination of the metal ion. Instead, the equatorial coordination sites at the nickel ion are occupied by the N- and S-heteroatoms of the two enantiomeric ligand moieties. The two chloride ions are located at the axial sites of the pseudo-octahedrally coordinated nickel ion. The metal-heteroatom bond lengths observed in **4** (Figure 1, Table 1) are "normal" and well in the range of Ni–Cl,S,N bonds found in other Ni^{II} high-spin chelates[5].

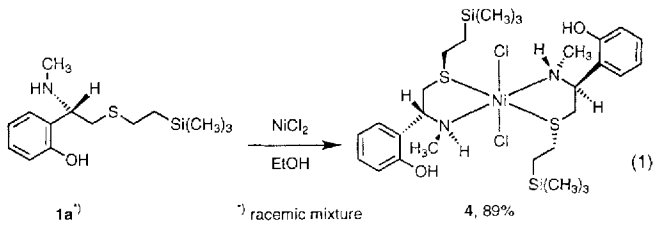
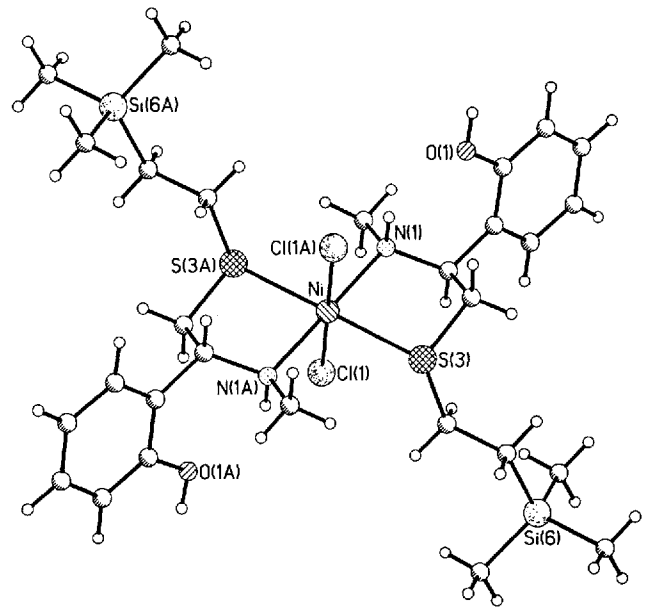


Figure 1. X-Ray crystal structure of the nickel complex **4**. See Table 1 for bond lengths and bond angles



In order to force a deprotonation of the ligand *rac*-**1a**, and thus to induce binding of the phenolate substructures to the metal, we employed nickel(II) acetate instead of nickel(II) chloride. However, in the absence of chloride anions, and under a variety of experimental conditions (e.g., addition of bases), no complex formation could be observed. In all cases, the unchanged ligand *rac*-**1a** could be isolated from the reaction mixtures.

In the same way, the ligand *rac*-**1b** was treated with both nickel chloride and with nickel acetate. In the former case, a crystalline material (**5**) was isolated from the reaction of *rac*-**1b** with anhydrous nickel(II) chloride in ethanol as solvent. Again, as in the case of **4** (eq. 1, Figure 1), the elemental composition indicated the presence of two chloride anions and a ligand-to-metal ratio of 2:1. Furthermore, **5** also proved to be a high-spin complex (μ_{eff} = 3.17 B.M.). Unfortunately, no single crystals suitable for X-ray crystallography could be obtained from **5**. Nevertheless, in analogy to **4** (Figure 1), the structure shown for **5** in Scheme 2 is proposed. Again, the phenol units *must* be in a protonated state, and two enantiomorphic ligand moieties are assumed to equatorially coordinate the metal ion in a *trans*-fashion.

Table 1. Selected bond lengths [Å] and angles [°] of the nickel chelates **4**, **6**, **7**, and **9**

	4	**6**	**7**	**9**
Ni–N1	2.126(2)	2.100(3)	1.914(2)	1.924(1)
Ni–O1		2.013(2)	1.840(2)	1.839(1)
Ni–S3	2.453(1)	2.539(1)		
Ni–Cl1	2.402(1)			
N1–Ni–S3	85.2(1)	83.0(1)		
N1–Ni–S3A	94.8(1)	97.0(1)		
O1–Ni–N1		87.2(1)	94.34(8)	95.1(1)
O1–Ni–N1A		92.8(1)	85.66(8)	84.9(1)
S3–Ni–O1		91.0(1)		
S3A–Ni–O1		89.0(1)		
Cl1–Ni–Cl1A	180.0(1)			
S3–Ni–Cl1A	95.2(1)			
S3A–Ni–Cl1	84.8(1)			
N1–Ni–Cl1A	89.0(1)			
N1–Ni–Cl1	91.0(1)			
N1–Ni–N1A	180.0(1)			
S3–Ni–S3A	180.0(1)	180.0(1)		
O1–Ni–O1A		180.0(1)	180.0(0)	180.0(1)
N1–Ni–N1A		180.0(1)	180.0(0)	180.0(1)

In an attempt to obtain crystals of **5** suitable for X-ray analysis, the turquoise microcrystalline material was recrystallized from methanol. To our surprise, the light-blue crystals thus obtained no longer contained chloride, but still proved paramagnetic (μ_{eff} = 3.40 B.M.). Besides proving the absence of chloride, the elemental analysis revealed that the ligand-to-metal ratio was still 2:1, but that in addition, two moles of methanol were present in this crystalline material (rel. to nickel). Luckily, the crystals obtained from methanol (**6**) proved suitable for X-ray analysis, and the result is shown in Figure 2. Obviously, the central nickel ion is now coordinated by two enantiomeric molecules of the ligand *rac*-**1b** in a pseudo-octahedral fashion. The amine nitrogen atoms and the deprotonated phenolic oxygen atoms form the equatorial coordination sphere, whereas the thioether sulfur atoms occupy the axial positions. Moreover, the two molecules of the solvent methanol are well localized, held as they are by two hydrogen bonds, each between the amine-NH and the phenolate-O atoms (Figure 2). Overall, a centrosymmetric *meso*-structure is formed. Again, the bonding distances between the nickel ion and the heteroatoms of the ligand in **6** (Table 1) are well within the range of "normal" bond lengths in high-spin nickel(II) chelates of N,O,S-ligands[5].

When the ligand *rac*-**1b** was treated with nickel(II) acetate instead of nickel chloride, the *diamagnetic* 2:1-complex **7** (Scheme 2) was obtained. Again, crystals suitable for X-ray structural analysis could be grown and the result is shown in Figure 3. The nickel ion is coordinated in a four-

Scheme 2

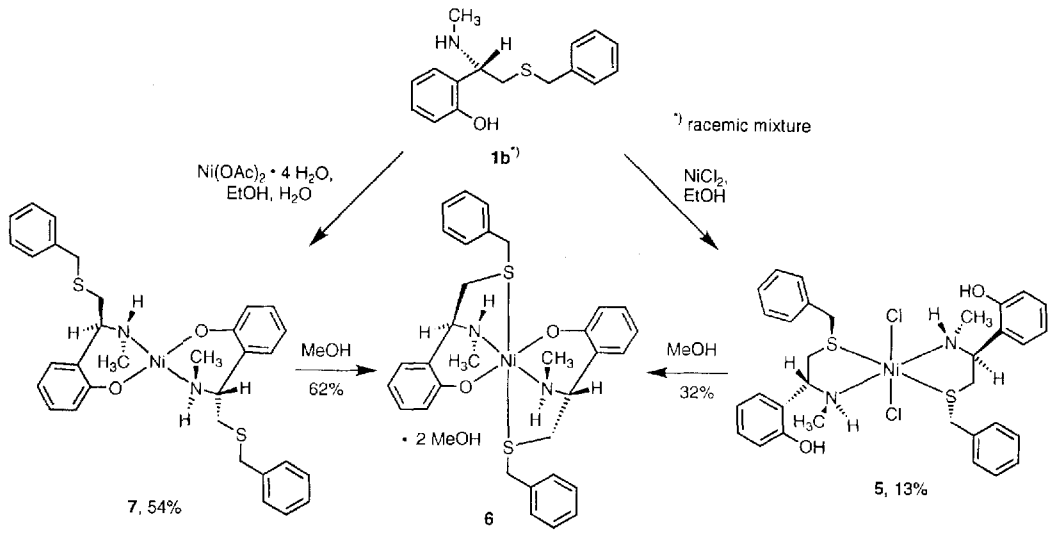
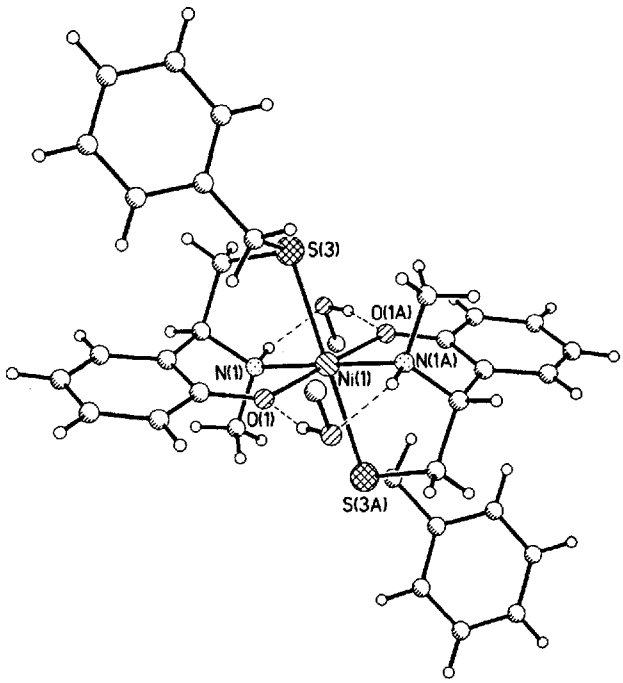
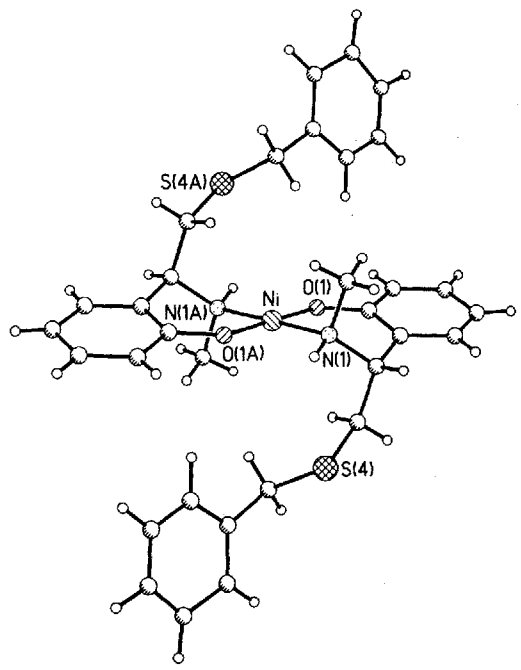


Figure 2. X-Ray crystal structure of the nickel complex **6**. Hydrogen atoms at the methanol carbon atoms are omitted for clarity. See Table 1 for bond lengths and bond angles



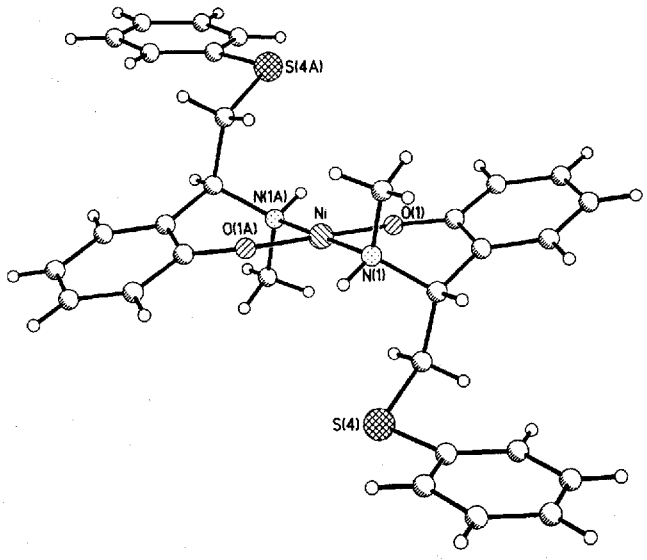
fold, square-planar manner by two enantiomeric molecules of the ligand *rac*-**1b** – a centrosymmetric *meso*-structure results. The enantiomeric molecules **1b**/*ent*-**1b** are deprotonated, they act as N,O–(amine, phenolate) bidentate ligands and chelate the central nickel ion in a *trans*-fashion. The thioether sulfur atoms do not participate in the coordination of the metal ion. The square-planar complex **7** described so far was purified by recrystallization from ethanol (see Experimental Section). Interestingly, when **7** was crystallized from *methanol* instead of ethanol, the pseudo-octahedral complex **6** was isolated in a yield of 62% (Scheme 2). On the other hand, when the paramagnetic nickel complex **6** was dissolved in a mixture of $CDCl_3$ and [D_6]benzene, a well-resolved ^{1}H-NMR spectrum was obtained which closely resembled that of **7** – except for the additional CH_3-signal due to the co-solvate methanol. In other words, the pseudo-octahedral complex **6** adopts the low-spin square-planar coordination mode of **7** in solution.

Figure 3. X-Ray crystal structure of the nickel complex **7**. See Table 1 for bond lengths and bond angles



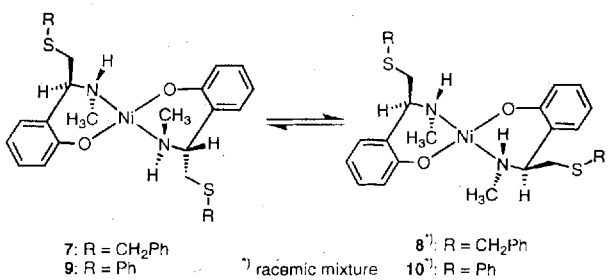
The NMR-spectrum of the nickel chelate **7** requires further comment. As listed in the Experimental Section, it revealed the presence of not only one species (as in crystalline **7**), but of two species in a ratio of ca. 1:1. The reso-

Figure 4. X-Ray crystal structure of the nickel complex **9**. See Table 1 for bond lengths and bond angles

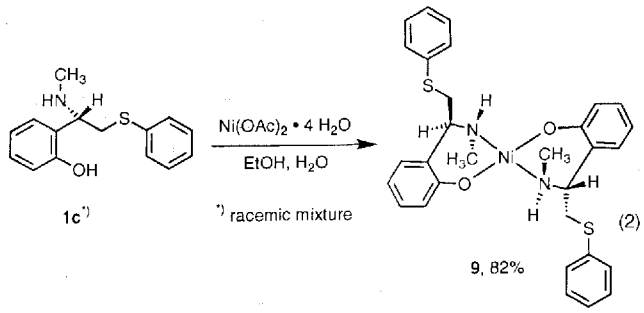


nances could unambiguously be assigned to one or the other species by H,H-COSY spectra. The two sets of signals closely resemble each other both in terms of chemical shifts and coupling patterns. The most reasonable explanation for this phenomenon is the assumption of an equilibrium between the *meso*-complex **7** and the racemic mixture of the diastereomeric chelates **8**/*ent*-**8** (Scheme 3)[6]. In principle, an epimerization at the N atom(s) might account for this observation as well. However, in all of our nickel dihydrosalen chelates carrying the substructures of **1b, c**, a *trans* arrangement of the thioether side chain and the *N*-methyl group was always found[7]. In these complexes – which contain one single ligand molecule – more than one set of NNR signals was never observed[7].

Scheme 3



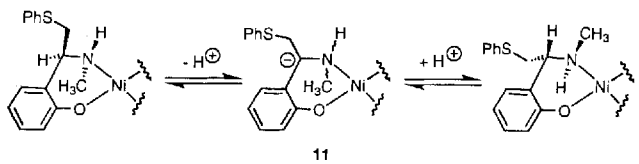
We reasoned that the most rigorous way of testing this hypothesis would be the complexation of nickel(II) with the enantiomerically pure ligand **1b**. In this case, the C_2-symmetric chelate **8** should result exclusively. Due to the ready availability[2] of the enantiomerically pure and very similar ligand **1c** (a phenyl thioether instead of a benzyl thioether), we decided to tackle the problem using **1c**. First, nickel(II) acetate was treated with two equivalents of the racemic ligand *rac*-**1c**. As it turned out, the crystalline, diamagnetic 2:1-complex **9** was obtained in a yield of 82% (eq. 2). Again, single crystals could be grown, and the X-ray crystal structure of **9** is shown in Figure 4. As expected, the overall structure and the coordination mode of the nickel ion in particular, closely resemble that of the *meso*-chelate **7** (Figure 3, Table 1).



We were also pleased to find that the *meso*-complex **9** exhibits two sets of ^{1}H-NMR signals in solution, albeit in a different ratio (ca. 9:1). Next, nickel(II) acetate was treated with the enantiomerically pure ligand **1c**. To our surprise, the two sets of ^{1}H-NMR signals were observed again, but in a ratio of ca. 1:1. In other words, the minor (ca. 10%) component obtained in solution from the pure *meso*-complex **9** was now present in ca. 50%. Except for the relative ratios of the two components, the spectra were identical to those obtained from **9**. This observation indicated that at least a partial racemization of the ligand **1c** must have taken place when complexed to nickel(II). In fact, when the ligand was reisolated by H_2S-treatment of the complex, its enantiomeric composition was found to be 3:1 [**1c**/*ent*-**1c** (by chiral HPLC)]. This result is (a) consistent with the NMR observation of a 1:1 ratio of the complexes **9** and **10** (Scheme 3) and (b) allows for the assignment of the two sets of ^{1}H-NMR resonances to **9** and **10**: The minor component observed in the equilibrium mixture obtained from pure **9** *must* be the racemate **10**/*ent*-**10**.

At the moment, we can only speculate about the mechanism of racemization. Nevertheless, it is clear that a deprotonation/reprotonation, as shown in Scheme 4, most likely accounts for the observed loss of enantiomeric purity. Due to the coordination to the Lewis-acidic nickel ion, the amine-nitrogen atom carries a partial positive charge and thus facilitates deprotonation at the neighboring carbon atom, affording the N-ylide-like structure **11**. Furthermore, due to the conjugation with the benzene ring, the deprotonation of the benzylic position of the ligand **1c** is additionally favored.

Scheme 4



In summary, we have described a number of examples of novel nickel(II) complexes of tridentate N,O,S-ligands showing that the mode of coordination (type, number, and protonation state of the heteroatoms of the ligands, square-planar vs. pseudo-octahedral coordination of the nickel ions) can be a delicate balance of experimental parameters such as counter ions and solvent of crystallization. It is obvious from our study that the coordination behavior of a given combination of ligand and metal ion may not thoroughly be defined by just one crystal structure. Furthermore, using an enantiomerically pure ligand as stereochemical probe, we have unveiled a metal-induced racemization process which would otherwise have remained undetected. The latter finding may have implications for both the use and limitations of chiral N,O-ligands similar to ours in asymmetric catalysis[8,9]. In a consecutive step, one may consider such metal-induced changes of configuration at carbon as a means for the *deracemization* of substrates using configurationally stable templates.

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Experimental Section

General: ^{1}H-NMR spectra were recorded at 270 MHz with a Bruker WH 270 or at 300 MHz with a Bruker AM 300 spectrometer. The spectra were calibrated relative to the chemical shifts of the solvent protons or to tetramethylsilane as internal standard. – FT-IR spectra were obtained using a Perkin Elmer 1600 Series instrument. – UV/VIS spectra were recorded on a Beckmann DU 640 instrument. – Magnetic susceptibility measurements at an applied magnetic field of 1.56 T were performed using a Faraday-type magnetometer, equipped with a Cahn D-200 micro balance and a Bruker B-MN 200/60 electromagnet[10]. $HgCo(SCN)_4$ was used as calibrant. – Elemental analyses were performed by the Mikroanalytisches Laboratorium der Chemischen Institute, Heidelberg, with a Heraeus CHN-Rapid instrument or an Elementar vario EL instrument. – Analytical HPLC was carried out on a Merck/Hitachi HPLC system with a L-6200-A pump and a L-4500 diode array detector. For flash chromatography, silica gel 60 (40–63 mesh, E. Merck) was used.

Substances: 2-Chloro-1-(2-hydroxyphenyl)ethanone (**2**) was prepared according to a literature procedure[4]. (±)-2-[2-(Benzylthio)-1-(methylamino)ethyl]phenol (*rac*-**1b**), (±)-2-[2-(Phenylthio)-1-(methylamino)ethyl]phenol (*rac*-**1c**) and enantiomerically pure **1c** were prepared as reported by us earlier[1,2].

1-(2-Hydroxyphenyl)-2-[2-(trimethylsilyl)ethylthio]ethanone (**3**): A solution of 3.15 g (18.5 mmol) of the ketone **2** in 8 ml of 1,4-dioxane was placed into a 100-ml flask under nitrogen. Sodium (430 mg, 18.4 mmol, 1.00 equiv.) was dissolved in 12 ml of abs. ethanol under nitrogen with ice cooling, and 3.00 ml (2.47 g, 18.4 mmol, 1.00 equiv.) of 2-(trimethylsilyl)ethanethiol was added. The solution of **2** was stirred vigorously, and the thiolate solution was added dropwise at room temperature. After completion of the addition, the solution was stirred for another 1 h at room temperature. It was then poured into 200 g of ice water and extracted with dichloromethane. The combined organic layers were dried with anhydrous sodium sulfate, filtered, and evaporated. Flash chromatography (*n*-hexane/dichloromethane, 2:1) gave 4.90 g (99%) of a slightly yellow oil. – IR (film): $\tilde{\nu}$ = 3047 cm^{-1}, 1635, 1613, 1579, 1487, 1248, 1233, 859, 840, 752. – ^{1}H NMR ($CDCl_3$): δ = 0.02 [s, 9H, $(CH_3)_3Si$], 0.85–0.91 (m, 2H, SCH_2-CH_2-Si), 2.61–2.67 (m, 2H, $S-CH_2-CH_2Si$), 3.79 (s, 2H, 2-H), 6.83–7.72 (m, 4H, aryl H), 12.06 (s, 1H, OH). – $C_{13}H_{20}O_2SSi$ (268.45): calcd. C 58.16, H 7.51; found C 58.10, H 7.56.

(±)-2-{1-(Methylamino)-2-[2-(trimethylsilyl)ethylthio]ethyl}-phenol (*rac*-**1a**): An aqueous solution of methylamine (8.03 M, 930 µl, 7.47 mmol, 1.00 equiv.) was added to a stirred solution of 2.00 g (7.45 mmol) of the ketone **3** in 15 ml of abs. ethanol. After 30 min, 150 mg (3.97 mmol, 0.53 equiv.) of sodium borohydride were added. After 1 h, the solution was acidified with conc. hydrochloric acid to pH 2, and the solvent was evaporated. The residue was taken up in 100 ml of water. The aqueous phase was extracted with ether (4 × 80 ml) and the extract was discarded. The aqueous phase was then adjusted to pH 10 by addition of solid potassium hydroxide and extracted with dichloromethane. The combined dichloromethane layers were dried with anhydrous potassium carbonate, filtered, and evaporated. Flash chromatography (ethyl acetate/methanol, 1:1) yielded 0.86 g (41%) of a slightly yellow oil. – IR (film): $\tilde{\nu}$ = 3298 cm^{-1}, 1588, 1492, 1249, 858, 839, 753. – ^{1}H NMR ($CDCl_3$): δ = 0.04 [s, 9H, $(CH_3)_3Si$], 0.77–0.98 (m, 2H, SCH_2-CH_2-Si), 2.44 (s, 3H, $N-CH_3$), 2.53–2.60 (m, 2H, $S-CH_2-CH_2Si$), 2.79 (dd, *J* = 13.9 Hz, *J* = 11.0 Hz, 1H, 2-H), 2.93 (dd, *J* = 13.9 Hz, *J* = 3.9 Hz, 1H, 2-H), 3.63 (dd, *J* = 11.0 Hz, *J* = 3.9 Hz, 1H, 1-H), 6.76–7.25 (m, 4H, aryl H). – $C_{14}H_{25}NOSSi$ (283.51): calcd. C 59.31, H 8.89, N 4.94; found C 59.61, H 8.62, N 5.14.

[OC-6-1'2'-(R,S*)]-Dichlorobis[2-{1-(methylamino)-2-[2-(trimethylsilyl)ethylthio]ethyl}phenol-N,S]nickel* (**4**): Anhydrous nickel(II) chloride (70.0 mg, 0.54 mmol, 0.51 equiv.) was added to a solution of 300 mg (1.06 mmol) of the ligand *rac*-**1a** in 10 ml of abs. ethanol under argon. The suspension was refluxed for 3 h, filtered, and concentrated to ca. 4 ml. The green solution was kept at ca. –20°C for 24 h. The green precipitate was filtered off, washed with ether, and dried in vacuo. Recrystallization from ethyl acetate yielded 330 mg (89%) of a light-green powder, m.p. 187°C. Single crystals suitable for X-ray structural analysis were obtained by slow cooling of a hot, saturated solution of **4** in ethyl acetate. – IR (KBr): $\tilde{\nu}$ = 3251 cm^{-1}, 2952, 2930, 1597, 1481, 1459, 857, 840, 750. – UV ($CHCl_3$): λ_{max} (lg ε) = 281 nm (3.86). – Magnetic susceptibility: μ_{eff} (295 K) = 3.21 B.M. – $C_{28}H_{50}Cl_2N_2NiO_2S_2Si_2$ (696.21): calcd. C 48.30, H 7.18, N 4.02; found C 47.83, H 7.34, N 3.79.

[OC-6-1'2'-(R,S*)]-Dichlorobis[2-{1-(methylamino)-2-[(phenylmethyl)thio]ethyl}phenol-N,S]nickel* (**5**): A dry 500-ml flask, equipped with a stirring bar, was charged under nitrogen with a solution of 3.01 g (11.0 mmol) of the ligand *rac*-**1b** in 235 ml of abs. ethanol. Anhydrous nickel(II) chloride (710 mg, 5.50 mol, 0.5 equiv.) was added to the stirred solution. The reaction mixture was refluxed for 3 h and filtered. the filtrate was concentrated to ca. 100 ml and kept at ca. –40°C for 10 h. The blue precipitate was filtered off and washed with abs. ethanol. Drying at 70°C in vacuo afforded 468 mg (13%) of the complex **5** as a turquoise microcrystalline solid, m.p. 235°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3222 cm^{-1}, 1596, 1455, 957, 755. – Magnetic susceptibility: μ_{eff} (295.6 K) = 3.17 B.M. – $C_{32}H_{38}Cl_2N_2NiO_2S_2$ (676.39): calcd. C 56.82, H 5.66, N 4.14, Cl 10.48; found C 56.71, H 5.82, N 4.20, Cl 10.47.

[OC-6-1'2'-(R,S*)]-Bis[2-{1-(methylamino)-2-[(phenylmethyl)thio]ethyl}phenolato-N,O,S]nickel-methanol (1:2)* (**6**):

Table 2. Crystal data and details of the X-ray structural analyses for the nickel chelates **4**, **6**, **7**, and **9**[a]

	4	**6**	**7**	**9**
formula	$C_{28}H_{50}Cl_2N_2NiO_2S_2Si_2$	$C_{34}H_{44}N_2NiO_2S_2$	$C_{32}H_{36}N_2NiO_2S_2$	$C_{30}H_{32}N_2NiO_2S_2$
M_r	696.21	667.54	603.17	575.41
crystal dimensions [mm]	0.05 × 0.05 × 0.20	0.10 × 0.10 × 0.30	0.10 × 0.20 × 0.20	0.20 × 0.20 × 0.30
crystal system	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a [Å]	8.828(2)	8.562(3)	8.649(1)	10.710(1)
b [Å]	14.932(1)	10.165(3)	17.837(2)	9.983(1)
c [Å]	14.151(3)	11.212(3)	10.0485(7)	13.741(1)
α [°]	90	65.37(3)	90	90
β [°]	92.00(1)	87.02(2)	106.00(1)	109.49(1)
γ [°]	90	67.97(3)	90	90
V [Å^3]	1864.2(6)	815.9(4)	1490.1(6)	1385.0(7)
$\rho_{calcd.}$ [g·cm^{-3}]	1.241	1.359	1.345	1.380
Z	2	1	2	2
radiation	Cu-K_α	Cu-K_α	Cu-K_α	Cu-K_α
scan mode	ω	ω	ω	ω
$2\theta_{max}$ [°]	100	120	120	120
unique reflections	1868	2406	2203	2048
observed reflections	1729	2257	2179	2035
absorption correction	empirical	empirical	empirical	empirical
$R(F)$	0.033	0.037	0.043	0.33
$R_w(F)$	0.030	0.051	0.040	0.045
ρ_{fin}(max) [e·Å^{-3}]	0.18	0.25	0.48	0.31
CSD depository no.	58426	58426	58426	58426

[a] An Enraf Nonius CAD4 diffractometer was used for the crystal structure determinations. Further details of the crystal structure investigations are available on request from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, by quoting the depository numbers (see above), the names of the authors, and the journal citation.

Recrystallization of 56.9 mg of the nickel complex **5** from 40 ml of abs. methanol gave 18 mg (32%) of **6** as light blue crystals, suitable for X-ray structural analysis, m.p. 176°C. – IR (KBr): $\tilde{\nu}$ = 3211 cm^{-1}, 1594, 1477, 1452, 1302, 1285, 758, 708. – ^{1}H NMR ($CDCl_3$/[D_6]benzene, 1:4): δ = 1.91 (br. m, 2H, NH or CH), 2.31 (s, 6H, CH_3), 2.35–2.50 (br. m, 2H, NH or CH), 2.97 (m, 2H, 2-H), 3.09 (s, 6H, HO–CH_3), 3.62 (s, 4H, CH_2–Ph), 4.81–4.89 (m, 2H, 2-H), 6.38–7.16 (m, 18H, aryl-H). The chemical shifts were found to be very susceptible to the composition of the solvent mixture. – Magnetic susceptibility: μ_{eff} (280 K) = 3.40 B.M. – $C_{34}H_{44}N_2NiO_4S_2$ (667.54): calcd. C 61.18, H 6.64, N 4.20; found C 60.80, H 6.54, N 4.41.

The recrystallization of 85 mg of the nickel complex **7** from methanol and drying in air for 2 days afforded 58 mg (62%) of **6**, m.p. 175–177°C. – IR and ^{1}H-NMR spectra were identical to those described above. – $C_{34}H_{44}N_2NiO_4S_2$ (667.54): calcd. C 61.18, H 6.64, N 4.20; found C 61.21, H 6.69, N 4.33.

[SP-4-1'-(R,S*)]-Bis[2-{1-(methylamino)-2-[(phenylmethyl)-thio]ethyl}phenolato-N,O]nickel* (**7**): A 100-ml flask, equipped with an addition funnel and a stirring bar, was charged with a solution of 1.00 g (4.02 mmol) of nickel(II) acetate tetrahydrate in 5 ml of dist. water. The solution was vigorously stirred and a hot solution of 2.20 g (8.05 mmol, 2.00 equiv.) of the ligand *rac*-**1b** in ethanol was added dropwise. Stirring was continued for 1 h, and the reaction mixture was heated to reflux several times. After cooling to ca. –20°C, the light blue precipitate was filtered off, washed with water, and dried over phosphorus pentoxide in vacuo. Recrystallization from abs. ethanol and drying in vacuo at 10^{-5} Torr afforded 1.30 g (54%) of the complex **7** as a grey microcristalline powder, m.p. 185°C. Crystals suitable for X-ray structure determination were obtained by recrystallization from di-*n*-butyl ether. – IR (KBr): $\tilde{\nu}$ = 3227 cm^{-1}, 1595, 1493, 1476, 1453, 1301, 1283, 1238, 1162, 758, 713. – UV ($CHCl_3$): λ_{max} (lg ε) = 335 nm (3.08), 484 (2.00), 575 (1.95). – ^{1}H NMR ($CDCl_3$/[D_6]benzene, 1:4): δ = 2.07–2.15 (br. m, 2H, NH or CH), 2.34 (s, 6H, CH_3), 2.56–2.68 (br. m, 2H, NH or CH), 3.20 (dd, J = 14.5 Hz, J = 3.2 Hz, 2H, 2-H), 3.92, 3.97 (AB-system, J = 13.9 Hz, 4H, CH_2–Ph), 4.78–4.91 (m, 2H, 2-H), 6.27–7.26 (m, 18H, aryl-H); peak assignments were based on H,H-COSY spectra. – Magnetic susceptibility: μ_{eff} (293.4 K) = 0.62 B.M. – $C_{32}H_{36}N_2NiO_2S_2$ (603.17): calcd. C 63.72, H 5.97, N 4.65; found C 63.60, H 6.10, N 4.68.

A second set of NMR signals was observed (ca. 50% rel. intensity): ^{1}H NMR ($CDCl_3$/[D_6]benzene, 1:4): δ = 1.89 (d, J = 5.5 Hz, 2H, NH), 2.08–2.15 (m, 2H, CH), 2.18 (d, J = 6.0 Hz, 6H, CH_3'), 2.44 (s, 6H, CH_3), 2.54–2.59 (m, 2H, NH'), 3.00 (dd, J = 14.5 Hz, J = 4.2 Hz, 2H, 2-H), 3.15–3.31 (m, 4H, 2-H', 1-H'), 3.51, 3.56 (AB-system, J = 13.6 Hz, 4H, CH'_2–Ph), 3.99, 4.04 (AB-system, J = 14.0 Hz, 4H, CH_2–Ph), 4.81–4.95 (m, 4H, 2-H, 2-H'), 6.27–7.27 (m, 36H, aryl–H, aryl–H'). See text for the assignment of these resonances.

[SP-4-1'-(R,S*)]-Bis[2-[1-(methylamino)-2-(phenylthio)-ethyl]phenolato-N,O]nickel* (**9**): A 50-ml flask, equipped with an addition funnel and a stirring bar, was charged with a solution of 240 mg (0.97 mmol) of nickel(II) acetate tetrahydrate in 5 ml of dist. water. The solution was heated to 40°C, and a hot solution of 500 mg (1.93 mmol, 2.00 equiv.) of the ligand *rac*-**1c** in 5 ml of ethanol was added dropwise with vigorous stirring. The product separated as a black oil. The aqueous phase was decanted from the black, oily residue and 10 ml of ethanol were added. The mixture was refluxed for 1 h. During this time, the oily complex turned into a brown powder. This brown solid was filtered off and washed with ethanol. Drying in vacuo over phosphorus pentoxide afforded 455

mg (82%) of a brown microcrystalline powder. Recrystallization from chloroform/methanol gave crystals suitable for X-ray structure determination. – IR (KBr): $\tilde{\nu}$ = 3240 cm^{-1}, 1590, 1565, 1475, 1450, 1410, 1300, 1280, 1155, 1035, 890, 745, 730, 670. – UV ($CHCl_3$): λ_{max} (lg ε) = 346 nm (3.10), 482 (2.03), 561 (1.96). – ^{1}H NMR ($CDCl_3$): δ = 2.45 (d, *J* = 6.1 Hz, 6H, CH_3), 2.68 (mc, 2H, CH), 2.77–2.84 (m, 2H, NH), 3.66 (dd, *J* = 14.4 Hz, *J* = 3.3 Hz, 2H, 2-H), 5.23 (dd, *J* = 14.4 Hz, *J* = 11.1 Hz, 2H, 2-H), 6.40–7.61 (m, 18H, aryl H). – $C_{30}H_{32}N_2NiO_2S_2$ (575.41): calcd. C 62.62, H 5.61, N 4.87; found C 62.52, H 5.61, N 4.86.

A second set of NMR signals (ca. 10% rel. intensity) was observed: ^{1}H NMR ($CDCl_3$): δ = 2.55 (d, *J* = 6.2 Hz, 6H, CH_3), 2.68 (mc, 2H, CH), 2.77–2.84 (m, 2H, NH), 3.54 (dd, *J* = 14.5 Hz, *J* = 3.5 Hz, 2H, 2-H), 5.07 (dd, *J* = 14.5 Hz, *J* = 11.1 Hz, 2H, 2-H) 6.40–7.61 (m, 18H aryl H). See text for the assignment of these resonances.

^{13}C NMR (signals of both species) ($CDCl_3$): δ = 36.37, 36.43 (q, CH_3), 40.14, 40.85 (t, CH_2), 60.95, 61.21 (d, CH), 114.84, 115.03 (d, aryl–CH), 120.43, 120.73 (d, aryl–CH), 122.88, 123.02 (s, aryl–C), 127.08, 127.22 (d, aryl-CH), 129.30, 129.31, 129.54, 129.62, 130.51, 130.81, 131.27 (all d, aryl–CH), 134.52, 134.93 (s, aryl-C), 160.09, 160.28 (s, aryl–C).

Complexation of Nickel(II) with the Enantiomerically Pure Ligand (**1c**) *and Reisolation of the Partially Racemized Ligand* (**1c**/*ent*-**1c**): A 10-ml flask, equipped with an addition funnel and a stirring bar, was charged with a solution of 72 mg (289 μmol) of nickel(II) acetate tetrahydrate in 2 ml of dist. water. The solution was heated to 50°C, and a hot solution of 150 mg (578 μmol, 2.00 equiv.) of the ligand **1c** in 2 ml of ethanol was added dropwise with vigorous stirring. The mixture was refluxed for 1 hour. The aqueous phase was decanted from the black, oily residue and 1 ml of ethanol was added. The mixture was again refluxed for 1 hour and then kept at 0°C for 48 h. The precipitate was filtered off and washed with ethanol. Drying in vacuo over phosphorus pentoxide afforded 36 mg (21%) of a black microcrystalline powder. – ^{1}H NMR ($CDCl_3$): identical to that of **9** except for the ratio of the two components (ca. 1:1).

For the reisolation of the ligand **1c**, 36 mg of the above black, microcrystalline complex was dissolved in 5 ml of a mixture of dichloromethane/chloroform (1:1) and the solution was saturated with hydrogen sulfide. The black precipitate was filtered off. Evaporation of the filtrate and drying in vacuo afforded 8 mg (50%) of the ligand **1c**/*ent*-**1c** as a slightly yellow oil. – ^{1}H-NMR ($CDCl_3$): identical to that of **1c**/*rac*-**1c**. – The ratio of the enantiomers **1c**/*ent*-**1c** = 3:1 was determined by analytical HPLC [250 × 4 mm 9521-A column (Bayer), eluent hexane/isopropanol, 7:3]: t_R [(*S*), **1c**] = 11.0 min., t_R [(*R*), *ent*-**1c**] = 14.2 min.

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