# Predetermined Helical Chirality in Octahedral Complexes with a Novel Pentadentate $C_2$-Symmetrical Chiral Bis(oxazoline) Ligand

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Dedicated to Dr. Joe P. Richmond on the occasion of his 60th birthday.

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**Abstract:** The first example of the pentadentate bis(oxazolines) has been synthesized using a modular approach that readily provides access to this ligand class. This ligand allows the controlled transfer of carbon-centered to octahedral, metal-centered chirality, as demonstrated both in the solid state as well as in solution. The characteristic CD band has been identified for dicationic, octahedral transition metal complexes with the $\Delta_2$-configuration.

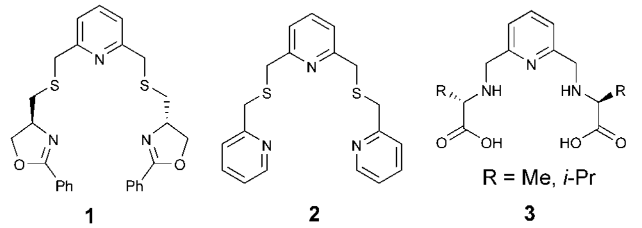
**Keywords:** chirality; circular dichroism; helical structures; structure elucidation; transition metals

Many molecules containing the oxazoline motive have proved to be outstanding ligands for asymmetric catalysis.[1] Metal complexes of $C_2$-symmetrical bis(oxazolines) and pyridine-(bisoxazolines) excel in a great number of enantioselective transformations with unprecedented selectivity.[2] Extending their scope on the basis of our previous work,[3] we wanted to design pentadentate bis(oxazoline) ligands that can provide a $C_2$-symmetrical octahedral environment for a metal, leaving one coordination site open for substrate/reagents. This approach appears to be especially attractive since a chiral metal center can be created in this way by a helical fold of such ligands, transferring the chirality from the chiral, non-racemic organic ligand to a metal center.[4] Various pentadentate ligand systems have been developed as a model system for bleomycin,[5] known to activate dioxygen and catalyze oxidation reactions of non-activated organic substrates. We sought to develop new chiral variants of such catalysts, following the design concept described in this paper.

To the best of our knowledge, no other pentadentate bis(oxazolines) have been reported to date. In order to arrive at such ligands we combined the design of Newkome's ligand **2** [$C_2$-symmetry of Co(II) complexes][6] and Bernauer's ligand **3** (predetermination of the helical chirality)[7] to the new model compound **1**.

***Ligand synthesis:*** A modular synthesis could be developed for **1** (Scheme 1) starting from (*S*)-serine methyl ester hydrochloride (**4**) and commercially available ethyl benzimidate hydrochloride to yield the known oxazoline **5**.[8] Reduction to the alcohol **6** on a 250 mmol-scale proceeded smoothly without detectable racemization using $LiAlH_4$ in THF at −30 °C instead of the rather expensive DIBAL-H recommended in the literature.[8] Tosylation was achieved according to a literature procedure to yield **7**.[9] Preparation of the air-sensitive dithiol **10** started from commercially available 2,6-bis(hydroxymethyl)pyridine (**8**), following a procedure reported by Chiotellis et al.[10] The final combination of the two precursors **7** and **10** by nucleophilic substitution yielded the new ligand **1**. Since only two compounds, **1** and **6**, have to be purified by column chromatography, this synthetic route can be conveniently carried out on a large scale, affording **1** in multigram quantities.

***Metal complexes – solid and solution state structures:*** Given the significance of cobalt (II) for dioxygen activation[11] and its preference to form octahedral complexes, we investigated the complex-formation of **1** with this metal. Complexation of Co(II) at ambient temperature and under anhydrous conditions required the use of non-coordinating counterions. The metal precursor of



**1** **2** **3**

**Figure 1.** Design of the new ligand **1** based on known **2** and **3**.

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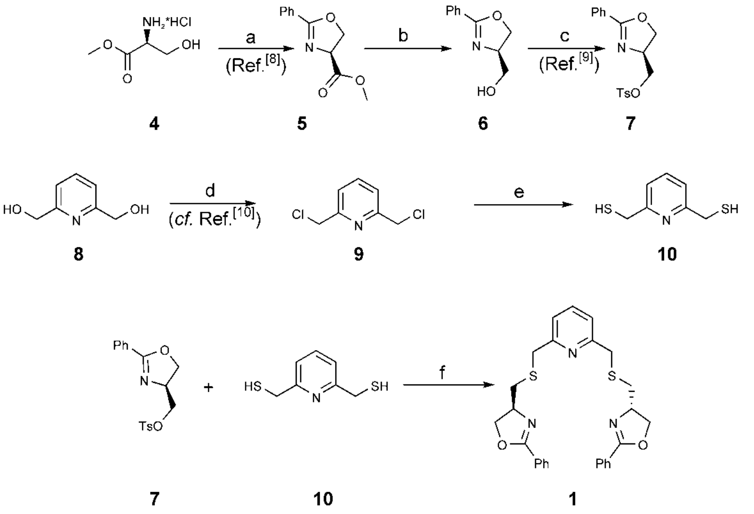


**Scheme 1.** Synthesis of ligand **1**. Conditions: a) Ethyl benzimidate (0.91 equivs.), 1,2-dichloroethane, 20 h, reflux, 90%; b) $LiAlH_4$ (0.55 equivs.), THF, −35 °C, 45 min, 0 °C 30 min, 64%; c) Ts-Cl (1.1 equivs.), $NEt_3$ (2.2 equivs.), $CHCl_3$, 0 °C to rt, 20 h, 78%; d) (i) $SOCl_2$ (2.2 equivs.), $Et_2O$, 0 °C to rt, 18 h; (ii) $NaHCO_3$ (aq.), $CH_2Cl_2$, 93% (2 steps); e) Ar atmosphere, thiourea (2.0 equivs.), EtOH, reflux, 1 h, (ii) NaOH (4.0 equivs.), $H_2O$, reflux, 4 h, 64% (2 steps); f) **7** (2.1 equivs.), NaH (2.1 equivs.), **10** (1.0 equivs.), DMF, 0 °C to rt, 18 h, 72%.

$$\text{Co dust} \xrightarrow[\text{CH}_3\text{CN, reflux, 2 h, 81\%}]{\text{anhyd. CF}_3\text{SO}_3\text{H (2.1 equivs.)}} \underset{\mathbf{11}}{\text{Co(OTf)}_2(\text{CH}_3\text{CN})_2}$$

$$\mathbf{1} \xrightarrow[\text{THF, rt, 3 h, 68\%}]{\mathbf{11}\text{ (1.0 equivs.)}} \underset{\mathbf{12}}{[\text{Co}^{\text{II}}(\mathbf{1})(\text{THF})](\text{OTf})_2}$$

**Scheme 2.** Synthesis of complex **12**.

our choice was $Co(OTf)_2(CH_3CN)_2$ (**11**), prepared in an analogous manner compared to the known anhydrous Fe(II) triflate.[12] Combining ligand **1** and the cobalt salt **11** in THF yielded the pink solid **12**, which precipitated from the reaction mixture.

Single crystals suitable for X-ray analysis were obtained by vapor diffusion of diethyl ether into a solution of **12** in acetonitrile. The structure (Figure 2) shows a pseudo-$C_2$-symmetrical, distorted octahedral Co(II) complex. THF is coordinating as the sixth ligand in a *trans*-position to the pyridine ring, the triflate anions are non-coordinating. The two phenyl rings provide a rather tight chiral pocket for the metal, effectively shielding two opposite quadrants of the accessible front space of the complex.

The configuration at the metal center is exclusively $\Delta_2$. The corresponding $\Lambda_2$-complex would be less favored, since the phenyl rings attached to the oxazolines would be placed directly above and below the ligand backbone (see Ru complexes, Figure 4).

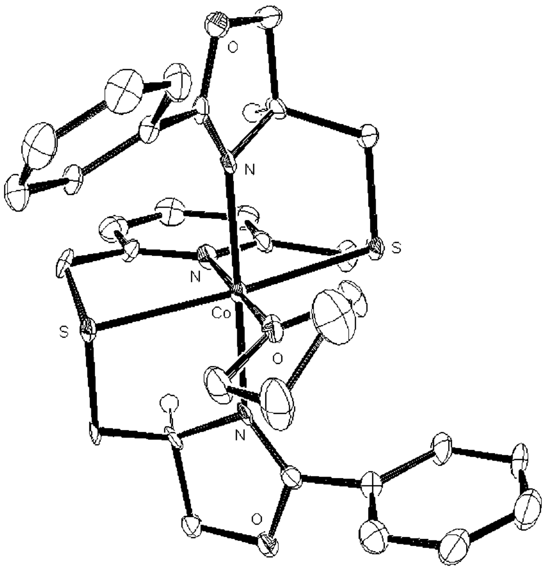


**Figure 2.** Thermal ellipsoid plot for the cation of **12** (CCDC No. 216870). The displacement ellipsoids are drawn at the 50% probability level. Except for the atoms attached to the chiral centers of the oxazolines, all other hydrogens have been omitted for clarity. Crystal data for **12** (for more detailed information see the supporting information): $C_{33}H_{35}CoF_6N_3O_9S_4$, M = 918.81, monoclinic space group $P2_1$, $a = 11.481(3)$ Å, $b = 8.809(2)$ Å, $c = 18.976(4)$ Å, $ß = 105.688(5)°$, $V = 1847.7(7)$ Å$^3$, $T = 100(2)$ K, $Z = 2$, $F(000) = 942$, $\mu(\text{Mo-K}_\alpha) = 0.779\ \text{mm}^{-1}$, 10392 reflections measured, 5661 unique ($R_{int} = 0.0439$), 5392 observed ($I > 2\sigma(I)$), 505 parameters refined, R1 = 0.0710 (observed data), $wR(F^2) = 0.1866$ (all data), S = 1.047.

$$\underset{\mathbf{13}}{[\text{RuCl}_2(\text{benzene})]_2} \xrightarrow[\substack{\text{1. EtOH, reflux, 10 h} \\ \text{2. CH}_2\text{Cl}_2}]{\mathbf{1}\text{ (2.0 equivs.)}} \underset{\mathbf{14}}{[\text{Ru}^{\text{II}}(\mathbf{1})(\text{CH}_2\text{Cl}_2)]\text{Cl}_2} + \underset{\mathbf{15}}{[\text{Ru}^{\text{II}}(\mathbf{1})\text{Cl}]\text{Cl}} \quad (7:3)$$

**Scheme 3.** Synthesis of the Ru(II) complexes **14** and **15**.

The structure of **12** clearly shows the validity of the ligand design for the construction of a well-defined helical-chiral environment, at least in the solid state. Nevertheless, in solution the behavior can be different. Therefore, it was desirable to investigate appropriate complexes by NMR spectroscopy. The best candidate in our view was diamagnetic Ru(II), because of its high tendency for octahedral coordination geometries and the great stability of the expected 18-electron species. Refluxing ligand **1** and Ru(II) precursor **13**[13] in anhydrous ethanol and filtration through Celite using $CH_2Cl_2$ yielded a brown solid with practically quantitative conversion (Scheme 3). This material consists of two symmetric, diamagnetic Ru(II) complexes as shown by $^1H$ NMR spectroscopy (Figure 3), which were assigned to the species $[Ru(\mathbf{1})(CH_2Cl_2)]Cl_2$ (**14**)[14] and $[Ru(\mathbf{1})Cl]Cl$ (**15**) on the basis of proton-NMR and mass spectrometry.

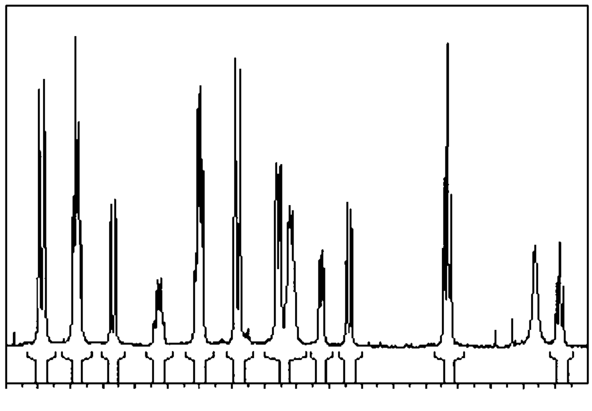


**Figure 3.** $^1$H NMR ($CDCl_3$, 600 MHz) spectra of the mixture of Ru(II) complexes of **1** between 5.2 and 1.6 ppm. For the full spectrum see the supporting information.

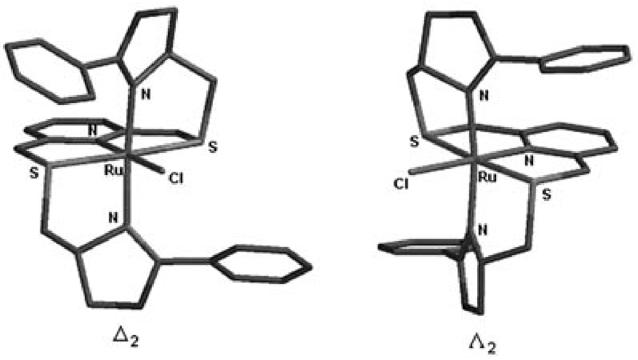


**Figure 4.** Molecular modelling of the favored $\Delta^2$- and disfavored $\Lambda^2$-configuration of **15** (PM3-TM, Titan 1.0.5, Schrödinger Inc.).

The Ru(II) species show well resolved proton signals, indicating a rather rigid structure. The most prominent feature is that **14** and **15** have two groups of benzylic signals (doublets at $\delta = 4.98$, 3.76 ppm and 4.54, 3.08 ppm) showing geminal coupling ($J \approx 18$ Hz). In distinct contrast, the spectrum of the free ligand **1** exhibits only one singlet for all four benzylic protons.

For the symmetrical species **14** and **15**, only two modes of ligand complexation, $\Delta_2$ and $\Lambda_2$, are possible (Figure 4). Several arguments point towards the assignment to only one single configuration: a) The NMR spectra of **14** and **15** exhibit very similar, only shifted signal patterns, which indicates an analogous spatial arrangement of the ligand around the metal. b) Mass spectrometry (ESI, $CH_3CN$) clearly shows two cationic species, $[Ru(\mathbf{1})Cl]^+$ and $[Ru(\mathbf{1})CH_3CN]^{2+}$, explaining the rather large NMR shift of the signal patterns by the mono- and dicationic nature of the complexes. c) Molecular modelling of the possible $\Delta_2$- and $\Lambda_2$-species on a semi-empirical level indicates the greater stability ($\Delta E \approx 3$ kcal/mole) of the expected $\Delta_2$-configuration of **15** (Figure 4).

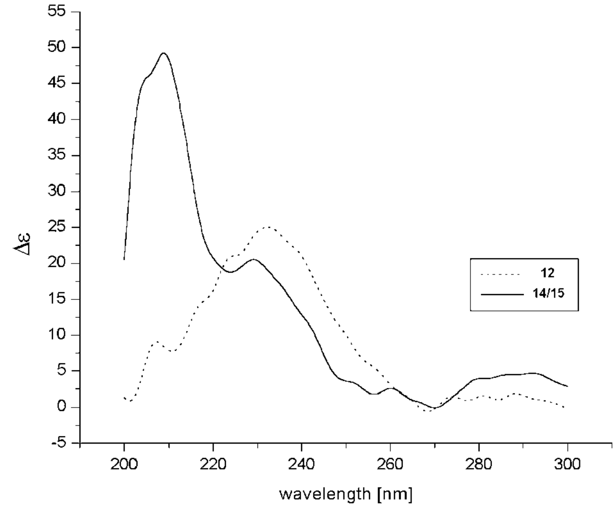
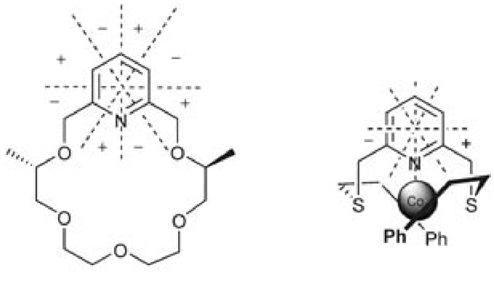


**Figure 5.** CD spectra of Co complex **12** and Ru complexes **14/15** were recorded in acetonitrile (Figure 5).



**16**

cation of **12** (schematic)

**Figure 6.** Pyridine crown ether **16** and proposed sector rules for n → π* transitions by Palmer et al. (+ and – correspond to the sign of the CD signal for the presence of substituents *above* the pyridine ring; *below* this plane the signs are inverted).

In order to further investigate the solution structures, CD spectra of **12** and **14/15** were recorded in acetonitrile (Figure 5).

Both spectra show strong CD bands (**12**: 232 nm, **14/15**: 229 nm/209 nm). Since ligand **1** alone exhibits no detectable CD signals, the observed bands can clearly be attributed to the corresponding complexes. The signals are assigned to the corresponding n→π* transitions of the pyridine chromophore, following the analysis of the reported $C_2$-symmetrical pyridine crown ether **16** (Figure 6) by Palmer et al.[15] Their sector rules for $C_2$-symmetrical pyridine derivatives predict a positive CD band (n→π*) for $\Delta_2$-configurations and a negative signal for $\Lambda_2$.

Since all CD bands observed for **12** and **14/15** show only positive signs, we conclude that these complexes should reside in the $\Delta_2$-configuration (*vide supra*). Moreover, the dicationic species **12** and **14** show very similar maxima (**12**: 232 nm and **14**: 229 nm[16]). This indicates that the solid state structure of **12** is retained in solution, a finding which is not trivial.

In conclusion, we have shown that the design of ligand **1** is appropriate to obtain a well-defined helical-chiral environment with exclusive $\Delta_2$-configuration. For the cobalt complex **12**, the solid and the solution state structure must be very similar. Furthermore, it was possible to identify the characteristic CD bands for an octahedral $\Delta_2$-arrangement in dicationic transition-metal complexes. On the basis of this finding, the prediction of solution-state structures of other dicationic transition-metal complexes (Mn, Fe, Ni, Cu, Zn...) should be possible.

The elucidation of the structures of the complexes should allow a rational approach for the testing of their catalytic activity in various transformations. These investigations are currently under way.

## Experimental Section

### General Remarks

Only procedures for new compounds are mentioned here. For a more detailed experimental description of the full synthetic route, NMR spectra and crystal structure data for **12** see the Supporting Information.

All reactions were carried out under a dry, oxygen-free atmosphere of $N_2$ using Schlenk techniques. Commercially available reagents were used as received. DMF, $CH_3CN$ and $CH_2Cl_2$ were distilled over $P_4O_{10}$ and stored under $N_2$ over molecular sieves 3 Å. EtOH was dried over Mg and stored under $N_2$. THF and $Et_2O$ were dried with Na/benzophenone and stored over Na wire under $N_2$. EtOAc and hexanes for chromatographic separations were distilled before use. For column chromatography silica gel Geduran 60 (Merck, 0.063–0.200 mm) was used. TLC analysis was done on silica gel 60 $F_{254}$ (Merck) coated on aluminum sheets.

NMR spectra were recorded on Bruker Avance 300 ($^1$H: 300 MHz, $^{13}$C: 75.5 MHz) and Bruker Avance 600 ($^1$H: 600 MHz) spectrometers with TMS as internal standard. IR spectroscopy was done on a Mattson Genesis Series FT-IR (sample preparation as indicated). X-Ray analysis was performed by the Crystallography Laboratory (University of Kansas, D. R. Powell) on a Bruker APEX ccd area detector(1) mounted on a Bruker D8 goniometer using graphite-monochromated Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å). Elemental analysis (Heraeus elementar vario EL III) and mass spectrometry (Finnigan ThermoQuest TSQ 7000) were done by the Central Analytical Laboratory (Universität Regensburg). CD spectra were recorded on a Jasco J-710 spectropolarimeter using $CH_3CN$ solutions (HPLC grade) in 1 mm cuvettes (cylindrical).

### Ligand 1

2,6-Bis(mercaptomethyl)pyridine (**10**; 2.12 g, 12.4 mmol, 1.0 equiv.)[10] was dissolved in 100 mL dry DMF under $N_2$ and cooled to 0 °C. An NaH suspension (60% in mineral oil; 1.04 g, 26.0 mmol, 2.1 equivs.) was added in portions and the mixture was stirred until the evolution of hydrogen had ceased. (*S*)-2-Phenyl-4-tosyloxymethyl-oxazoline (**7**; 8.60 g, 26.0 mmol, 2.1 equivs.) [9] was added as a solid and the ice bath was removed. Stirring was continued at ambient temperature overnight. Then 100 mL water and 200 mL $CH_2Cl_2$ were added and the phases were separated. The organic layer was extracted with 4 × 100 mL water and dried ($MgSO_4$). After removal of the solvent under vacuum, the residue was purified by column chromatography ($SiO_2$, hexanes/EtOAc 1:1 to hexanes/EtOAc 3:7) to afford the slightly yellow oil **1** that solidified after several days to give a waxy slightly brown solid; yield: 4.36 g (72%); mp 59–61 °C; $[\alpha]_D^{20}$: +21.6 (*c* 1.16, $CH_2Cl_2$); $^1$H NMR (300 MHz, $CDCl_3$): $\delta = 7.98-7.85$ (m, 4H), 7.60 (t, $J = 7.7$ Hz, 1H), 7.53–7.32 (m, 6H), 7.25 (d, $J = 7.7$ Hz, 2H), 4.57–4.39 (m, 4H), 4.29–4.15 (m, 2H), 3.89 (s, 4H), 2.94 (dd, $J = 13.3$, 4.8 Hz, 2H), 2.65 (dd, $J = 13.3$, 7.8 Hz, 2H); $^{13}$C NMR (75.5 MHz, $CDCl_3$): $\delta = 164.5$, 158.2, 137.4, 131.5, 128.3 (2 peaks), 127.6, 121.4, 72.0, 66.5, 38.3, 36.6; IR (film): $\nu = 3074$, 2978, 2930, 2910, 1970, 1912, 1820, 1731, 1646, 1589, 1573, 1495, 1453, 1418, 1360, 1306, 1264, 1177, 1084, 1063, 1029, 967, 909, 818, 782, 751, 694 cm$^{-1}$; MS (ESI): *m/z* (%) = 491.2 (34), 490.1 (100); HRMS (EI): calcd. for $C_{27}H_{27}N_3O_2S_2$ $[M]^+$: 489.1545; found: 489.1541.

### $Co(OTf)_2(CH_3CN)_2$ (11)

Cobalt (935 mg, 15.9 mmol, 1.0 equiv.; Aldrich, >99.9%, <100 mesh) was suspended in 16 mL anhydrous $CH_3CN$. The mixture was cooled to 0 °C and 5.0 g (33.3 mmol, 2.1 equivs.) triflic acid (Merck, >98%) were added dropwise in the course of 3 min. The ice-bath was removed and stirring was continued for 30 min. After heating the mixture for 2 h under reflux, the solvent and excess triflic acid were removed under reduced pressure. The solid was dissolved in dry $CH_3CN$ and residual cobalt was removed by filtration through a pad of Celite 535 (Fluka). The resulting red solution was concentrated under reduced pressure until crystallization began. The solid was redissolved by adding a minimum amount of dry $CH_3CN$. This solution was layered with approximately twice its volume of dry $Et_2O$ and allowed to stand at room temperature for two days. The formed slightly sticky crystals were collected , washed with $Et_2O$ and dried under vacuum to constant weight to give the pink amorphous powder **11** that was stored under $N_2$; yield: 5.67 g (81%). IR (nujol): $\nu = 3172$, 2726, 2675, 2319, 2292, 1310, 1213, 1185, 1039, 722, 642, 516 cm$^{-1}$; MS (ESI, $CH_3CN$): *m/z* (%) = 330.8 (100, $[Co(CH_3CN)_3(OTf)]^+$), 289.7 (74, $[Co(CH_3CN)_2(OTf)]^+$); anal. calcd. for $C_6H_6CoF_6N_2O_6S_2$ (439.18): C 16.41, H 1.38, N 6.38, S 14.60; found: C 16.63, H 1.47, N 6.61, S 14.46.

### $[Co(1)(THF)](OTf)_2$ (12)

Compounds **1** (113 mg, 231 μmol, 1.0 equiv.) and **11** (101 mg, 231 μmol, 1.0 equiv.) were dissolved separately in 2.5 mL dry THF each. The cobalt solution was added to the ligand solution. A pink solid formed almost immediately. The mixture was stirred for additional 3 h. The solid was collected and washed with dry THF. Drying the complex under reduced pressure yielded the pink solid **12** that was stored under $N_2$; yield: 145 mg (68%). Single-crystals suitable for X-ray analysis were obtained by vapor diffusion of $Et_2O$ into a $CH_3CN$-solution of the title compound. For crystal data (CCDC 216870) see Figure 2 and for a more detailed description the supporting information. IR (nujol): $\nu = 3162, 2725, 2672, 1304, 1154, 1122, 1028, 967, 722, 636\ cm^{-1}$; MS (ESI, $CH_3CN$): *m/z* (%) = 274.1 (100, $[M - THF]^{2+}$): anal. calcd. for $C_{33}H_{35}CoF_6N_3O_9S_4$ (918.81): C 43.14, H 3.84, N 4.57, S 13.96; found: C 43.04, H 3.80, N 4.60, S 13.98.

### Ruthenium Complexes 14 and 15

Under $N_2$ a Schlenk flask was charged with 55.7 mg (111 μmol, 1.0 equiv.) $[RuCl_2(benzene)]_2$ (**13**)[13] and 15 mL anhydrous EtOH were added. The suspension was treated with 109.1 mg (222.7 μmol, 2.0 equivs.) of **1** and the mixture was heated to reflux for 10 h. After cooling down to ambient temperature the solvent was removed under vacuum (4 h) and the residue was taken up in 5 mL dry $CH_2Cl_2$. The resulting yellow-brown solution was passed through a pad of Celite 535 (Fluka) and the solvent was removed under reduced pressure again to yield 161 mg of a dark-yellow solid, that consisted of two symmetric diamagnetic $Ru^{II}$ complexes as shown by $^1H$ NMR. The two species are presumably $[Ru(\mathbf{1})(CH_2Cl_2)]Cl_2$ (**14**)[14] and $[Ru(\mathbf{1})Cl]Cl$ (**15**) (ratio 7:3), supported also by ESI-MS: MS (ESI, $CH_3CN$): *m/z* (%) = 315.6 (8, $[Ru(\mathbf{1})(CH_3CN)]^{2+}$), 626.2 (100, $[Ru(\mathbf{1})Cl]^+$).

**$[Ru(1)(CH_2Cl_2)]Cl_2$ (14):** $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$ = 8.27 (d, *J* = 7.3 Hz, 4H), 7.72–7.34 (m, 9H), 5.30 (s, 2H), 4.98 (d, *J* = 18.0 Hz, 2H), 4.82–4.69 (m, 2H), 4.06–3.94 (m, 2H), 3.76 (d, *J* = 18.0 Hz, 2H), 3.59–3.37 (m, 4H), 2.51–2.41 (m, 2H).

**$[Ru(1)Cl]Cl$ (15):** $\delta$ = 8.00 (d, *J* = 7.5 Hz, 4 H), 7.72–7.34 (m, 9H), 4.82–4.69 (m, 2H), 4.54 (d, *J* = 17.0 Hz, 2 H), 4.30–4.20 (m, 2 H), 4.06–3.94 (m, 2 H), 3.28–3.20 (m, 2 H), 3.08 (d, *J* = 17.0 Hz, 2H), 1.82–1.72 (m, 2H).

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