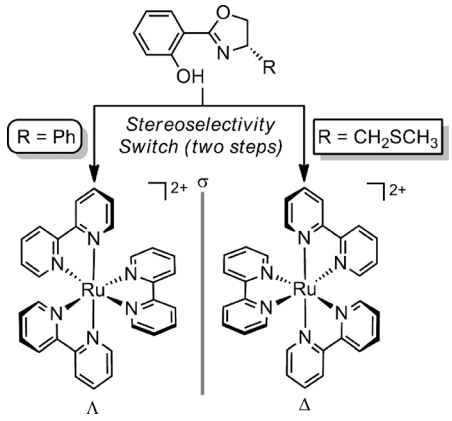
CHEMISTRY
AN ASIAN JOURNAL

DOI: 10.1002/asia.201200532

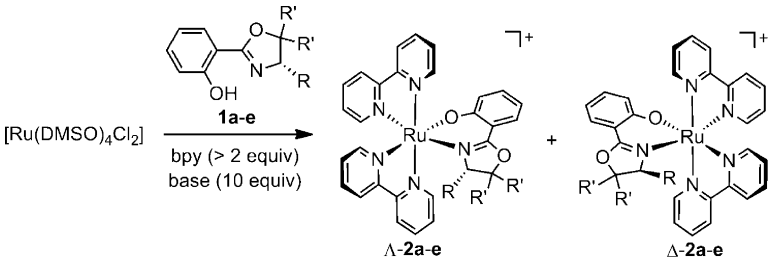
# Active *versus* Passive Substituent Participation in the Auxiliary-Mediated Asymmetric Synthesis of an Octahedral Metal Complex

**Liang-An Chen,[a] Jiajia Ma,[a] Mehmet Ali Celik,[b] Hong-Lang Yu,[a] Zexing Cao,[a] Gernot Frenking,[b] Lei Gong,*[a] and Eric Meggers*[a, b]**

Over the last few decades organic chemistry has developed highly sophisticated synthetic tools for the stereocontrol of chemical transformations.[1] However, most of the synthetic strategies can be traced back to just two basic effects that often lead to opposite stereochemical outcomes: On the one hand steric hindrance based on repulsive nonbonding interactions and on the other hand stereochemical reactions that proceed through a preassociation by attractive forces (electrostatic interaction, hydrogen bonding, Lewis acid-base adducts, coordinative bonds, or covalent bonds).[2] We here wish to report that these general concepts of passive and active substituent control in stereochemical transformations can be applied to the asymmetric synthesis of coordination complexes.[3] In the herein discussed example, a surprising reversal of chirality transfer from carbon to metal occurs—leading to either the Λ- or Δ-enantiomer of $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine)—solely depending on the chemical composition of the side chain of a salicyloxazoline auxiliary (Scheme 1).[4]




Scheme 1. Controling chirality-at-metal by the substituent of a salicyloxazoline auxiliary.




Scheme 2. Diastereoselective one-pot formation of salicyloxazolinate complexes **2a**–**2e**. See Table 1 for more details.

In the quest for straightforward and economical asymmetric syntheses of chiral octahedral metal complexes, we found that the reaction of the readily accessible ruthenium precursor complex $[Ru(DMSO)_4Cl_2]$[5] with (*S*)-5-phenyl-2-(2′-hydroxy phenyl)oxazoline (**1a**) in the presence of 2,2′-bipyridine (8 equiv) and $K_2CO_3$ (10 equiv) in $C_6H_5Cl$/DMF (8:1) at 140 °C for 2 hours afforded, in a one-pot procedure, complex Λ-**2a** (59 %) with high diastereocontrol (52:1 d.r.) (Table 1, entry 1; Scheme 2). However, to our surprise, when we employed the oxazoline derivative **1b** instead, in which the phenyl substituent is replaced by a thioether, the stereochemical outcome of this reaction was completely switched, providing the Δ-diastereomer (Δ-**2b**) smoothly in 83 % yield with 66:1 d.r. under optimized conditions with EtOH as the solvent, $Et_3N$ (10 equiv) as the base, and reflux overnight (Table 1, entry 2). Additional methyl groups at the 4-position of the oxazoline moiety (auxiliary **1c**, 66 % yield, 31:1 d.r.) somewhat reduced yields and diastereoselectivity (Table 1, entry 3). Most interestingly, replacing the sulfur atom of **1b** by a methylene group (**1d**) caused the complete loss of diastereoselectivity. Even just changing the position of the thioether (**1e**) strongly abated the outcome of the re-

[a] L.-A. Chen, J. Ma, H.-L. Yu, Prof. Z. Cao, Prof. L. Gong, Prof. Dr. E. Meggers
College of Chemistry and Chemical Engineering
Xiamen University
Xiamen 361005 (P. R. China)
Fax: (+86) 592-2185821
E-mail: meggers@xmu.edu.cn
gongl@xmu.edu.cn

[b] Dr. M. A. Celik, Prof. Dr. G. Frenking, Prof. Dr. E. Meggers
Fachbereich Chemie
Hans-Meerwein-Straße
Philipps-Universität Marburg
35043 Marburg (Germany)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/asia.201200532.

Table 1. Diastereoselectivity of the formation of complexes **2a–e** as a function of the salicyloxazoline substituents.

| Entry | Auxiliaries **1a–e** | Conditions[a] | Product | Yield | Λ:Δ[b] |
|---|---|---|---|---|---|
| 1 | R = $C_6H_5$, R′ = H (**1a**) | PhCl/DMF 8:1[c] | **2a** | 59 % | 52:1 |
| 2 | R = $CH_2SCH_3$, R′ = H (**1b**) | EtOH[d] | **2b** | 83 % | 1:66 |
| 3 | R = $CH_2SCH_3$, R′ = $CH_3$ (**1c**) | EtOH | **2c** | 66 % | 1:31 |
| 4 | R = $CH_2CH_2CH_3$, R′ = H (**1d**) | EtOH | **2d** | 44 % | 1:1.3 |
| 5 | R = $CH_2CH_2SCH_3$, R′ = H (**1e**) | EtOH | many products | | n.d.[e] |

[a] Reaction conditions: $[Ru(DMSO)_4Cl_2]$, auxiliary, bpy, together with a base were heated in the indicated solvent under argon atmosphere in the dark. See the Experimental Section and Supporting Information for more details. [b] Diastereomeric ratios determined by $^1$H NMR. [c] Optimized solvent mixture. In EtOH, yields and d.r. value are reduced. [d] Ethanol is the solvent of choice for this reaction. For example, no main product is formed using the solvent PhCl/DMF (8:1). [e] not determined.

action (Table 1, entry 5), thus revealing that the thioether and its position are essential for the course and stereoselectivity of this reaction.

A crystal structure of the complex Λ-**2a** is shown in Figure 1 and reveals a stacking of the phenyl substituent on

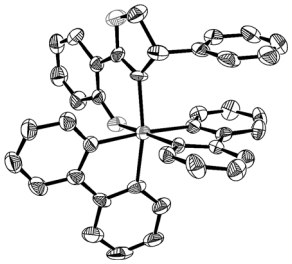


Figure 1. X-ray crystal structure of the salicyloxazolinate complex Λ-**2a**. The hexafluorophoshate counterion and an ether solvent molecule are omitted for clarity. The absolute configuration was determined.

a coordinated 2,2′-bipyridine ligand and the metal-centered configuration Λ (left-handed propeller).[6] The stereochemical outcome of this reaction was expected and consistent with previous results from our group regarding the metal-centered stereocontrol by salicyloxazoline auxiliaries bearing aliphatic or aromatic substituents.[7] The previous reactions were demonstrated to be under thermodynamic control and, in fact, density functional theory (DFT) calculations (M06-2X/6-311+G(3d,p)) reveal that the experimentally observed main diastereomer Λ-**2a** (R = Ph) with its stacked phenyl group is by 1.43 kcal mol$^{-1}$ more stable compared to the trace diastereomer Δ-**2a**.

A crystal structure of the thioether complex Δ-**2b** (R = $CH_2SCH_3$) is displayed in Figure 2.[6] It is noteworthy that this structure was obtained from the crystal structure of the racemic salicyloxazolinate complex **2b** since the pure enantiomer Δ-**2b** did not crystallize in our hands. The structure confirms an opposite stereochemistry with a Δ-configuration at the metal (right-handed propeller), unambiguously demonstrating that the thioether ligand, although essential for the stereochemical outcome of the reaction, is indeed not coordinated to the ruthenium in the product.

However, thioethers are formidable coordinating ligands for transition metals and it can be expected that the thioether substituent of auxiliaries **1b** and **1c** is transiently coordinated to the ruthenium center and thereby controling the stereochemical course of the reaction by temporarily blocking a coordination side.[8–10] In fact, we noticed that reactions with thioether-containing auxilaries **1b** and **1c** proceeded significantly faster compared to auxiliary **1a**, suggesting that the highly nucleophilic thioether attacks the ruthenium first, followed by the formation of a tridentate chelate. Upon coordination to an additional 2,2′-bipyridine ligand, the two intermediates **I** and **II** would be generated (Scheme 3).

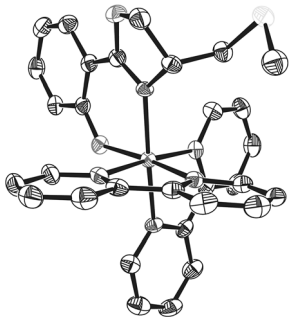
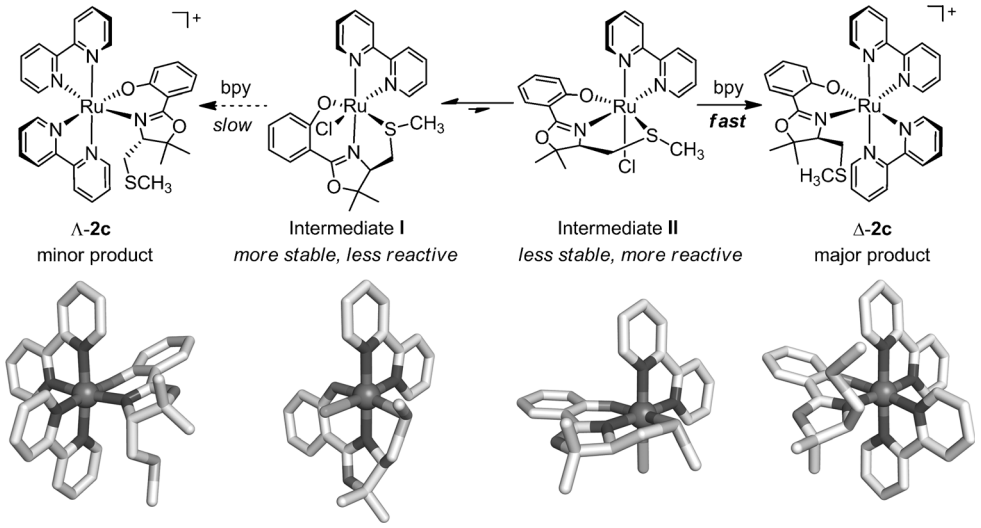


Figure 2. X-ray crystal structure of the racemic salicyloxazolinate complex **2b**. The hexafluorophosphate counterion is omitted for clarity and only the enantiomer Δ-**2b** is shown.

The subsequent substitution of the remaining monodentate ligand (chloride in Scheme 3) and the hemilabile[11,12] thioether in favor of a second 2,2′-bipyridine ligand would provide the Λ-diastereomer from intermediate **I** and the observed Δ-diastereomer from intermediate **II**. DFT calculations at the M05-2X/def2-SVP level reveal that the intermediate **I** is by 2.7 kcal mol$^{-1}$ more stable compared the intermediate **II**. Considering an equilibrium between **I** and **II** through a pentacoordinated intermediate, it is apparently the more reactive intermediate **II** that reacts faster to the observed thermodynamically favored Δ-diastereomer, whereas the more stable tridentate chelate in intermediate **I** blocks a conversion into the unobserved Λ-enantiomer. The fast preequilibrium between the intermediates **I** and **II**, which subsequently react irreversibly to the diastereomers Λ-**2c** and Δ-**2c**, respectively, presumably realizes a Curtin–Hammett-situation where the relative transition state energies for the conversions **I**→Λ-**2c** versus **II**→Δ-**2c** and not the ground state energy differences between the intermediates **I** and **II** determine the product distribution. The proposed mechanism revolving around a fast equilibrium between two intermediates **I** and **II** is consistent with the experimentally observed preference of the solvent ethanol for this reaction (Table 1), as a previous study revealed the establishment of a complete equilibrium of related intermediates in EtOH but not in other solvents such as $C_6H_5Cl$.[7]

CHEMISTRY
AN ASIAN JOURNAL




Scheme 3. Proposed mechanism for the thioether-assisted diastereoselective formation of Δ-isomers. Shown are also the optimized geometries of the proposed intermediates **I** and **II** as well as the reaction products Λ-**2c** and Δ-**2c**, which were all calculated at the M05-2X/def2-SVP level. The Gibbs free energy of intermediate **I** is by 2.7 kcal mol$^{-1}$ lower compared to intermediate **II**, whereas the Gibbs free energies of the products Δ-**2c** and Λ-**2c** differ only by 0.7 kcal mol$^{-1}$ in favor of the observed major reaction product Δ-**2c**.

Furthermore, although we could not detect the proposed reactive intermediates **I** or **II**, we succeeded in demonstrating the capability of the thioether oxazoline **1b** to coordinate transition metals in a meridional tridentate fashion, as shown in Figure 3 with a crystal structure of [PdCl(**1b**-H)].[13,14]

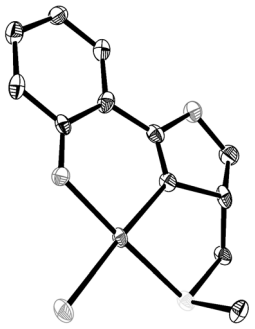


Figure 3. X-ray crystal structure of the complex [PdCl(**1b**-H). Only one of two independent Pd complexes is shown.

Finally, in order to demonstrate that the salicyloxazolinate ligands serve as true auxiliaries, complexes Λ-**2a** and Δ-**2b** were subjected to TFA treatment in the presence of 2,2′-bipyridine to provide [Ru(bpy)$_3$]$^{2+}$ as Λ- (83%, 98:2 e.r.) and Δ-enantiomer (98%, 98.5:1.5 e.r.), respectively, from substitution of the auxiliaries by 2,2′-bipyridine under complete retention of configuration.

In conclusion, we here reported a surprising sulfur-effect for the chirality transfer from carbon to metal, most likely relying on the active participation of a transiently coordinating thioether substituent, thus causing a reversal of the stereochemical outcome compared to the commonly applied passive steric control of chiral substituents. This work therefore reveals a new mechanism for the stereocontrolled synthesis of octahedral metal complexes. From a purely practical perspective, the here reported reaction sequence provides a highly convenient access to nonracemic ruthenium polypyridyl complexes starting from the common precursor [Ru(DMSO)$_4$Cl$_2$], which can be synthesized from RuCl$_3$ in a single step.[15] A better understanding of the stereocontrolled synthesis of octahedral metal complexes will be crucial to fully exploit the opportunities provided by the rich stereochemistry of octahedral coordination geometries for applications in the life sciences.[16]

## Experimental Section

*Stereoselective Synthesis of Λ-**2a**.*

[Ru(DMSO)$_4$Cl$_2$] (20.0 mg, 0.041 mmol) together with oxazoline **1a** (9.9 mg, 0.041 mmol), 2,2′- bipyridine (51.2 mg, 0.33 mmol), and $K_2CO_3$ (56.7 mg, 0.41 mmol) was heated in PhCl/DMF (8:1, 2.2 mL) at 140 °C under argon atmosphere for two hours. The crude material was purified by silica gel column chromatography using $CH_3CN/H_2O$/sat.$KNO_3$ (150:3:1). Eluents were concentrated to dryness, the resulting material was dissolved in minimal amounts of ethanol/water, and the product precipitated upon addition of excess solid $NH_4PF_6$. The precipitate was centrifuged, washed twice with water, and dried under high vacuum to afford a purple solid (19.7 mg, 59%) with 52:1 d.r. $^1$H NMR (400 MHz, $CD_3CN$): $\delta$ = 8.94 (d, $J$ = 5.7 Hz, 1H), 8.76 (d, $J$ = 5.6, 1H), 8.40 (d, $J$ = 8.1 Hz, 1H), 8.29 (d, $J$ = 8.1 Hz, 1H), 7.99 (td, $J$ = 7.7, 1.4 Hz, 1H), 7.89 (d, $J$ = 5.6 Hz, 1H), 7.76 (m, 3H), 7.70 (m, 2H), 7.61 (m, 2H), 7.52 (m, 1H), 7.12 (m, 2H), 7.06 (m, 2H) 6.98 (tt, $J$ = 7.5, 1.2 Hz, 1H), 6.71 (t, $J$ = 7.9 Hz, 2H), 6.41 (m, 2H), 6.10 (d, $J$ = 7.6 Hz, 2H), 5.01 (dd, $J$ = 9.6, 4.1 Hz, 1H), 4.90 (t, $J$ = 8.8 Hz, 1H), 4.16 ppm (dd, $J$ = 8.7, 4.1 Hz, 1H); $^{13}$C NMR (100 MHz, $CD_3CN$): $\delta$ = 171.5, 164.7, 160.7, 159.3, 159.1, 158.3, 153.9, 152.2, 151.5, 150.5, 141.4, 136.8, 136.5, 136.4, 135.4, 134.0, 131.1, 129.5, 128.5, 127.3, 127.2, 127.0, 126.6, 125.9, 124.6, 124.3, 124.2, 124.1, 123.8, 114.0, 110.3, 76.3, 72.5 ppm; IR (film): $\tilde{\nu}$ = 3364, 2956, 2924, 2853, 1659, 1632, 1608, 1461, 1378, 1260, 1092, 1019, 843, 802, 753, 559 cm$^{-1}$; HRMS calcd for $C_{35}H_{28}N_5O_2Ru$ (M-PF$_6$)$^+$ 652.1286, found: 652.1294; CD (MeCN): λ, nm (Δε, M$^{-1}$cm$^{-1}$) 243 (−27), 301 (+105).

*Stereoselective Synthesis of Δ-**2b**.*

[Ru(DMSO)$_4$Cl$_2$] (18.0 mg, 0.037 mmol) together with oxazoline **1b** (9.1 mg, 0.041 mmol), 2,2′-bipyridine (12.7 mg, 0.081 mmol), and triethylamine (53.4 μL, 0.37 mmol) were heated in ethanol (15 mL) under argon atmosphere at reflux overnight. The solvent was removed under reduced pressure and the residue purified by silica gel column chromatography

using $CH_3CN/H_2O$/sat.$KNO_3$ (100:3:1). The eluents were concentrated to dryness, the resulting material dissolved in minimal amounts of ethanol/water, and the product precipitated upon addition of excess solid $NH_4PF_6$. The precipitate was centrifuged, washed twice with water, and dried under high vacuum to afford 23.9 mg (83%) of a brownish solid with 66:1 d.r. $^1$H NMR (500 MHz, $CD_3CN$): $\delta$ = 8.98 (d, $J$ = 5.3 Hz, 1H), 8.79 (d, $J$ = 5.1 Hz, 1H), 8.49 (d, $J$ = 8.2 Hz, 1H), 8.43 (d, $J$ = 8.2 Hz, 1H), 8.35 (dd, $J$ = 8.1, 4.2 Hz, 2H), 8.09 (td, $J$ = 7.9, 1.5 Hz, 1H), 7.97 (m, 2H), 7.82 (td, $J$ = 8.3, 1.4 Hz, 1H), 7.74 (td, $J$ = 8.0, 1.4 Hz, 1H), 7.63 (m, 1H), 7.54 (dd, $J$ = 8.2, 1.9 Hz, 1H), 7.50 (d, $J$ = 5.3 Hz, 1H), 7.44 (m, 1H), 7.11 (m, 2H), 6.99 (m, 1H), 6.35 (m, 2H), 4.39 (dd, $J$ = 9.1, 4.4 Hz, 1H), 4.06 (t, $J$ = 8.4 Hz, 1H), 3.14 (m, 1H), 2.58 (dd, $J$ = 13.1, 10.9 Hz, 1H), 2.42 (dd, $J$ = 13.1, 2.2 Hz, 1H), 1.46 ppm (s, 3H); $^{13}$C NMR (125 MHz, $CD_3CN$) $\delta$ = 170.3, 163.5, 159.7, 158.2, 157.9, 157.6, 154.2, 152.5, 151.3, 150.6, 136.0, 135.9, 135.7, 134.8, 132.7, 129.6, 126.9, 126.2, 125.7, 125.6, 123.8, 123.34, 123.32, 123.2, 122.9, 112.9, 110.1, 71.6, 65.0, 37.2, 13.9 ppm; IR (film): $\tilde{\nu}$ = 3076, 3019, 2964, 2915, 1606, 1536, 1461, 1442, 1418, 1387, 1347, 1260, 1235, 1155, 1070, 1035, 1019, 972, 928, 877, 830, 756, 728, 685, 656, 575, 555 cm$^{-1}$; HRMS calcd for $C_{31}H_{28}O_2N_5RuS$ (M-$PF_6$)$^+$ 636.1002, found: 636.1003; CD (MeCN): λ, nm ($\Delta\varepsilon$, M$^{-1}$cm$^{-1}$) 300 (−108), 286 (+21).

## Acknowledgements

We are grateful for support from the "National Thousand Plan" Foundation of P. R. China and the "985 Program" of the Chemistry and Chemical Engineering disciplines of Xiamen University.

**Keywords:** asymmetric synthesis · chiral auxiliary · coordination chemistry · stereocontrol · sulfur

[1] a) Y. Gnas, F. Glorius, *Synthesis* **2006**, 1899–1930; b) M. A. Rizzacasa, M. Perkins, *Stoichiometric Asymmetric Synthesis* Blackwell, **2000**; c) P. J. Walsh, M. C. Kozlowski, *Fundamentals of Asymmetric Catalysis*, University Science Books, **2009**.

[2] a) A. H. Hoveyda, D. A. Evans, G. C. Fu, *Chem. Rev.* **1993**, *93*, 1307–1370; b) M. T. Reetz, *Acc. Chem. Res.* **1993**, *26*, 462–468; c) G. Rousseau, B. Breit, *Angew. Chem.* **2011**, *123*, 2498–2543; *Angew. Chem. Int. Ed.* **2011**, *50*, 2450–2494.

[3] For reviews on asymmetric coordination chemistry, see: a) J.-L. Pierre, *Coord. Chem. Rev.* **1998**, *178–180*, 1183–1192; b) U. Knof, A. von Zelewsky, *Angew. Chem.* **1999**, *111*, 312–333; *Angew. Chem. Int. Ed.* **1999**, *38*, 302–322; c) H. Brunner, *Angew. Chem.* **1999**, *111*, 1248–1263; *Angew. Chem. Int. Ed.* **1999**, *38*, 1194–1208; d) P. D. Knight, P. Scott, *Coord. Chem. Rev.* **2003**, *242*, 125–143; e) C. Ganter, *Chem. Soc. Rev.* **2003**, *32*, 130–138; f) J. Lacour, V. Hebbe-Viton, *Chem. Soc. Rev.* **2003**, *32*, 373–382; g) H. Amouri, M. Gruselle, *Chirality in Transition Metal Chemistry*, Wiley, Chichester, **2008**; h) E. Meggers, *Eur. J. Inorg. Chem.* **2011**, 2911–2926.

[4] For auxiliary-mediated asymmetric synthesis of metal complexes, see: E. Meggers, *Chem. Eur. J.* **2010**, *16*, 752–758.

[5] I. P. Evans, A. Spencer, G. Wilkinson, *J. Chem. Soc. Dalton Trans.* **1973**, 204–209.

[6] CCDC 883768 and CCDC 883769 contain the supplementary crystallographic data for Λ-**2a** and for the racemic complex **2b**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[7] a) L. Gong, S. P. Mulcahy, K. Harms, E. Meggers, *J. Am. Chem. Soc.* **2009**, *131*, 9602–9603; b) L. Gong, S. P. Mulcahy, D. Devarajan, K. Harms, G. Frenking, E. Meggers, *Inorg. Chem.* **2010**, *49*, 7692–7699.

[8] For somewhat related ONS-ligands which coordinate in a tridentate fashion, see for example: a) G. Rajsekhar, C. P. Rao, P. K. Saarenketo, E. Kolehmainen, K. Rissanen, *Inorg. Chem. Commun.* **2002**, *5*, 649–652; b) S. Dhar, D. Senapati, P. K. Das, P. Chattopadhyay, M. Nethaji, A. R. Chakravarty, *J. Am. Chem. Soc.* **2003**, *125*, 12118–12124; c) S. Dhar, M. Nethaji, A. R. Chakravarty, *Inorg. Chem.* **2006**, *45*, 11043–11050; d) I. D. Kostas, B. R. Steele, A. Terzis, S. V. Amosova, A. V. Martynov, N. A. Makhaeva, *Eur. J. Inorg. Chem.* **2006**, 2642–2646.

[9] The related ligand 2-(2′-hydroxyphenyl)oxazoline-4-carboxylate is capable of serving as a coordinating ON-bidentate or ONO-tridentate ligand. See, for example: M. D. Godbole, M. P. Puig, S. Tanase, H. Kooijman, A. L. Spek, E. Bouwman, *Inorg. Chim. Acta* **2007**, *360*, 1954–1960.

[10] The related natural chiral siderophore desferriferrithiocin has been demonstrated to coordinate metal ions in a tridentate fashion. See: a) K. Langemann, D. Heineke, S. Rupprecht, K. N. Raymond, *Inorg. Chem.* **1996**, *35*, 5663–5673; b) F. E. Hahn, T. J. McMurry, A. Hugi, K. N. Raymond, *J. Am. Chem. Soc.* **1990**, *112*, 1854–1860.

[11] For the concept of hemilability of multidentate ligands, see: a) C. S. Slone, D. A. Weinberger, C. A. Mirkin, *Prog. Inorg. Chem.* **1999**, *48*, 233–355; b) P. Braunstein, F. Naud, *Angew. Chem.* **2001**, *113*, 702–722; *Angew. Chem. Int. Ed.* **2001**, *40*, 680–699.

[12] The lability of the thioether coordination site results from the strain caused by the stereogenic carbon within the oxazoline moiety.

[13] PdCl(**1b**-H)] was synthesized from $PdCl_2$ in methanol (56 mM) by addition of LiCl (3 equiv) followed by addition of oxazoline **1b** (1 equiv).

[14] CCDC 885320 contains the supplementary crystallographic data for [PdCl(**1b**-H)]. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

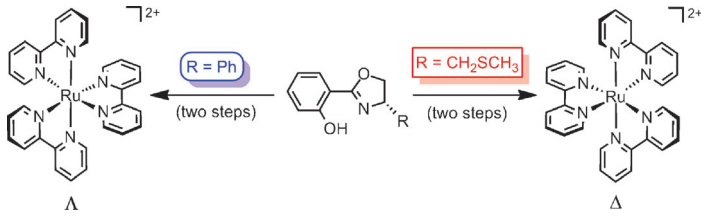
[15] This thioether-assisted asymmetric synthesis can even be executed starting directly from $RuCl_3{\cdot}3H_2O$, albeit in somewhat lower yields. A typical procedure: $RuCl_3{\cdot}3H_2O$ (15.0 mg, 0.057 mmol) together with oxazoline **1b** (14.1 mg, 0.063 mmol), 2,2′-bipyridine (19.6 mg, 0.13 mmol), and triethylamine (82 μL, 0.57 mmol) were heated in ethanol (22 mL) under argon atmosphere at reflux overnight. The solvent was removed under reduced pressure and the residue purified by silica gel column chromatography using $CH_3CN/H_2O$/sat.$KNO_3$ (100:3:1). The eluents were concentrated to dryness, the resulting material dissolved in minimal amounts of ethanol/water, and the product precipitated upon addition of excess solid $NH_4PF_6$. The precipitate was centrifuged, washed twice with water, and dried under high vacuum to afford 23.5 mg of Δ-**2b** (53%) with 36:1 d.r.

[16] E. Meggers, *Chem. Commun.* **2009**, 1001–1010.

Received: June 14, 2012
Published online: ■■ ■■, 0000

# COMMUNICATION




**Ambiguous chirality transfer**: A surprising reversal of chirality transfer from carbon to metal is reported in the asymmetric synthesis of a chiral ruthenium complex, affording the metal-centered configuration Λ or Δ depending only on the chemical composition of the side chain of a chiral salicyloxazoline auxiliary.

**Asymmetric Coordination Chemistry**

*Liang-An Chen, Jiajia Ma, Mehmet Ali Celik, Hong-Lang Yu, Zexing Cao, Gernot Frenking, Lei Gong,* Eric Meggers** ——— ▮▮▮▮–▮▮▮▮

**Active *versus* Passive Substituent Participation in the Auxiliary-Mediated Asymmetric Synthesis of an Octahedral Metal Complex**