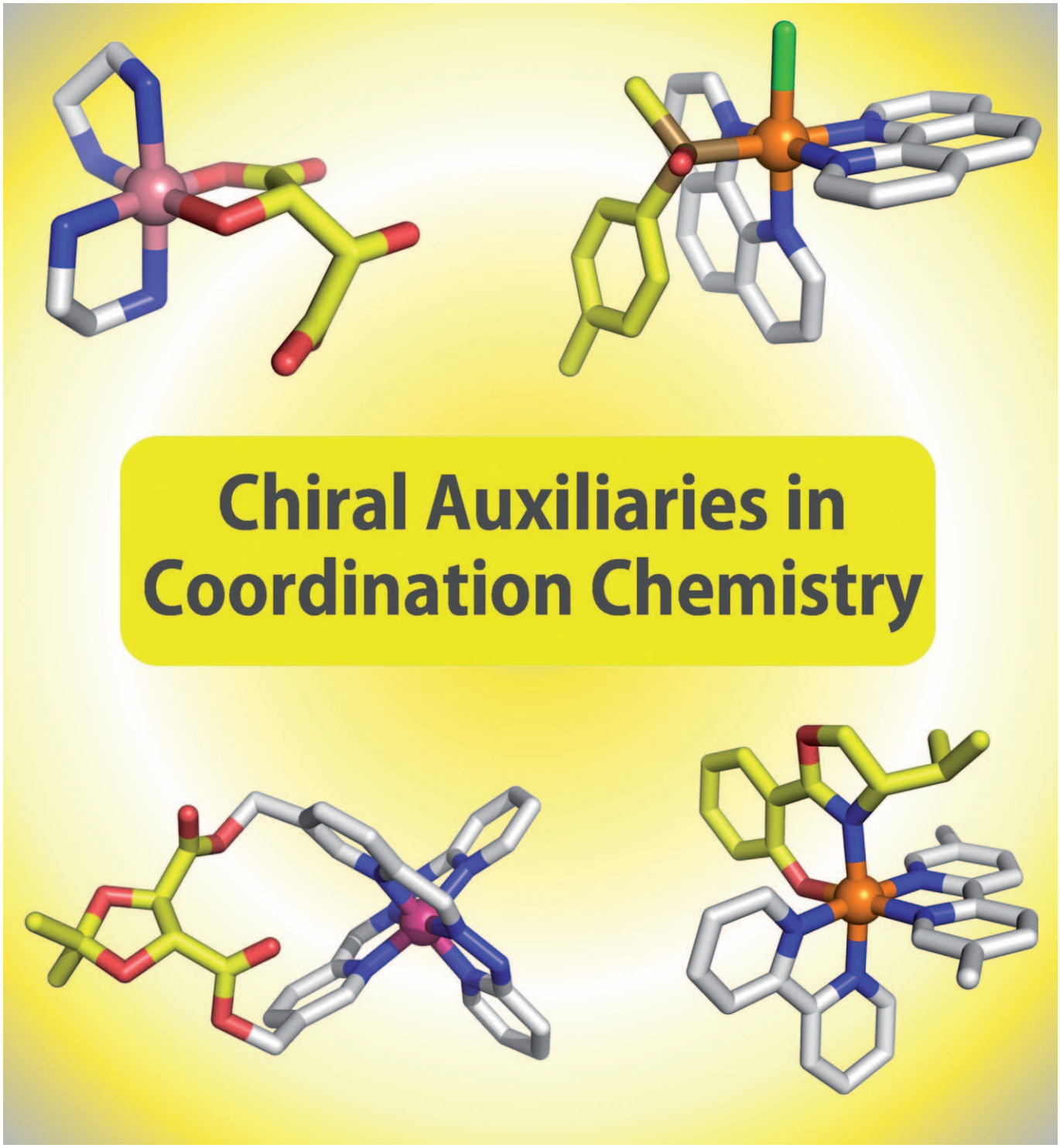
CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200902652

Chiral Auxiliaries as Emerging Tools for the Asymmetric Synthesis of Octahedral Metal Complexes

Eric Meggers*[a]



Abstract: New methods for the stereocontrolled synthesis of octahedral metal complexes are needed in order to fully exploit the stereochemical richness of the octahedron in the fields of catalysis, materials sciences, and life sciences. Whereas a large body of work exists regarding the diastereoselective coordination chemistry with chiral ligands, such efforts are restricted to certain carefully designed chiral ligands which remain in the coordination sphere. The emerging strategy of chiral-auxiliary-mediated asymmetric synthesis holds promise to solve the problem of controlling relative and absolute configuration in octahedral metal complexes in a general fashion, thus hopefully in the future providing access to any desired optical active octahedral metal complex without the need for chiral separations. This short review will summarize reported examples of chiral auxiliaries applied to the asymmetric synthesis of octahedral metal complexes.

Keywords: asymmetric synthesis · chiral auxiliaries · diastereoselectivity · octahedral metal complexes · optical activity

Introduction

A key difference between organic and inorganic structures is manifested in the geometry of their main building blocks: whereas inorganic chemistry is dominated by the octahedral metal coordination, organic chemistry is ruled by the tetrahedral carbon. Strikingly, the octahedron permits a much larger structural complicatedness than the tetrahedron, which can be illustrated by the number of possible stereoisomers; a tetrahedron is capable of building a maximum of two enantiomers, in comparison to an octahedron which can form up to 30 stereoisomers, 15 diastereomers as pairs of Δ- and Λ-enantiomers.

Organic chemistry has developed sophisticated synthetic strategies and methods to control the relative and absolute stereochemistry at tetrahedral carbon atoms and this has tremendously advanced our ability to synthesize structurally complicated optically active molecules in an economical fashion. However, this is not the case for the octahedron. The enormous potential opportunities of octahedral metal complexes to serve as functional structural scaffolds, for example, in catalysis, the materials sciences, and life sciences, are offset by the difficulties to control the relative stereochemistry in the course of the coordination chemistry, which often results in the formation of undesired or unseparable mixtures of stereoisomers. The same holds true for the synthesis of optically pure octahedral complexes.[1,2] Here also, general methods to control the metal-centered chirality are scarce and if enantiomers are desired, racemic mixtures are typically resolved by chiral separation techniques.

A following brief example will illustrate the scope and limitations of octahedral metal complexes as structural scaffolds in the life sciences. My lab demonstrated over the last few years that inert metal complexes can serve as highly potent and selective inhibitors for protein kinases.[3] We are convinced that octahedral metal coordination geometries in particular offer new opportunities to design rigid, globular molecules with defined shapes that can fill protein pockets, such as enzyme active sites, in a unique fashion. For example, Figure 1 depicts the octahedral organoruthenium complex Λ-FL172 bound to the ATP-binding site of the protein kinase PAK-1.[4] PAK-1 harbors a particularly open ATP-binding site, making it difficult to target with conventional organic scaffolds, but particularly suitable for filling it with bulky and rigid octahedral complexes. It is worth noting that compared to the Δ isomer, the mirror-imaged complex Λ-FL172, obtained enantiomerically pure by the resolution of a racemic mixture with chiral HPLC, is a significantly stronger binder for PAK-1 by a factor of 27. Furthermore, Λ-FL172 has an improved selectivity profile compared to its

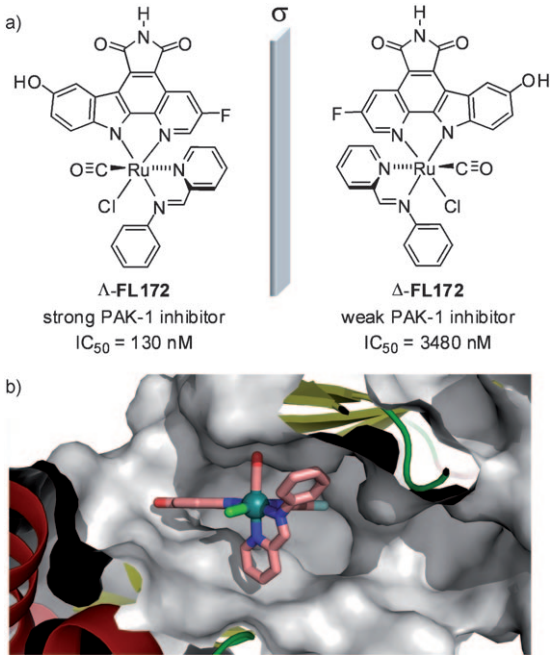


Figure 1. Molecular recognition of an enzyme active site by a chiral octahedral metal complex. a) The ruthenium complex Λ-**FL172** is a selective inhibitor of the protein kinase PAK-1 in contrast to the almost inactive mirror-imaged complex Δ-**FL172** (1 μM ATP). b.) Binding of Λ-**FL172** to the active site of PAK-1.

[a] E. Meggers
Fachbereich Chemie, Philipps-Universität Marburg
Hans-Meerwein-Strasse, 35032 Marburg (Germany)
Fax: (+49) 6421-282-2189
E-mail: meggers@chemie.uni-marburg.de

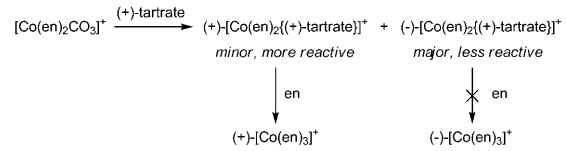
racemic mixture, rendering the enantiopure ruthenium complex a very desirable probe for studying biological processes involving PAK-1. However, currently no method exists to synthesize complexes such as Λ-FL172 in an asymmetric fashion, making the large scale production of such octahedral compounds impractical.

Thus, more than 100 years after the discovery of the octahedral coordination geometry by Alfred Werner, a demand exists for more sophisticated and general synthetic methods to control relative and absolute stereochemistry at octahedral metal centers in order to gain the opportunity to fully exploit the stereochemical richness of the octahedron. This short review will focus on a promising emerging strategy in asymmetric coordination chemistry, which is the use of chiral auxiliaries to influence metal centered chirality in octahedral complexes. Reported examples exploit one of three distinct strategies: the temporary coordination of chiral monodentate or bidentate ligands, the attachment of cleavable chiral groups to the periphery of coordinating ligands, and the utilization of chiral counterions.

Tartrate as the First Chiral Auxiliary Used for Asymmetric Coordination Chemistry

Chiral auxiliaries are utilized extensively as work horses in organic synthesis to access enantiomerically pure compounds in a predictable and time-efficient fashion.[5] In this strategy, an enantiomerically pure compound or moiety, the chiral auxiliary, is temporarily linked to a substrate so that it can control the stereochemical course of a diastereoselective reaction, before it is cleaved-off afterwards.

Applied to metal complexes, a chiral auxiliary can constitute a coordinating chiral ligand that controls the course of ligand exchange reactions in the coordination sphere of a metal complex, until it gets replaced by another achiral ligand, leaving behind an enantiomerically enriched metal complex. A significant body of work has been devoted to the diastereoselective coordination chemistry with chiral ligands and this important research has given us insight into strategies to control metal-centered chirality.[1,2] However, the current challenge lies in the ability to remove such directing ligands afterwards without compromising the metal-centered configuration. The first example of such a strategy was reported in pioneering work by Bailar and co-workers, who published in 1948 the first asymmetric synthesis of (+)-$[Co(en)_3]^{3+}$, (+)-$[Co(en)_2Cl_2]^+$ and (+)-$[Co(en)_2(NO_2)_2]^+$ (en = 1,2-ethylenediamine) by using (*R*,*R*)-(+)-tartrate as a coordinating chiral auxiliary.[6] Accordingly, the reaction of $[Co(en)_2CO_3]^+$ with (*R*,*R*)-(+)-tartrate resulted in the formation of $[Co(en)_2\{(R,R)$-(+)-tartrate$\}]^+$ as an unequal mixture of Λ and Δ isomers, which reflected the relative thermodynamic stabilities of the two formed diastereomers.[7] When the mixture was subsequently reacted with en, the complex (+)-$[Co(en)_3]^{3+}$ (the Λ enantiomer)[8] was obtained with an enantiomerically purity of up to 90%. After careful investigations, Bailar et al. came to the conclusion that this asymmetric formation of (+)-$[Co(en)_3]^{3+}$ was the result of a faster reaction of the more reactive diastereomer (+)-$[Co(en)_2\{(R,R)$-(+)-tartrate$\}]$ with en, while the more stable diastereomer (−)-$[Co(en)_2\{(R,R)$-(+)-tartrate$\}]$ remained unreacted in solution. This reaction is therefore an early example of a kinetic resolution (Scheme 1). Furthermore,



Scheme 1. Bailar's asymmetric synthesis of (+)-$[Co(en)_3]^+$ (en = 1,2-ethylenediamine).

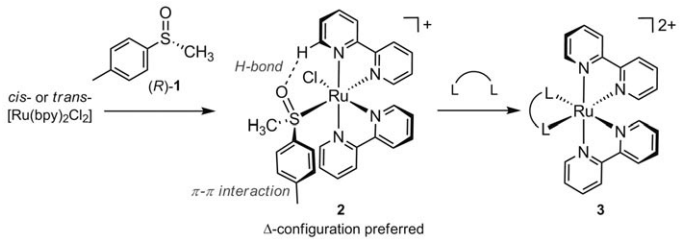
starting with racemic $[Co(en)_2CO_3]^+$, (+)-$[Co(en)_3]^{3+}$ was synthesized in a yield of up to 70%, thus demonstrating that some of the (−)-$[Co(en)_2\{(R,R)$-(+)-tartrate$\}]$ converted slowly in solution into the (+)-enantiomer as the latter was depleted in the course of the reaction with en. Analogously, (+)-$[Co(en)_2(NO_2)_2]^+$ and (+)-$[Co(en)_2Cl_2]^+$ were synthesized in an asymmetric fashion.[6]

In 1964 Bailar also demonstrated the first asymmetric synthesis of enantiomerically enriched configurationally inert $[Ru(bpy)_3]^{2+}$(bpy=2,2′-bipyridine), by reacting first K_2RuCl_5 hydrate with (*R*,*R*)-(+)-tartrate, affording in situ an undefined "tartratoruthenium complex", followed by the addition of an excess of bpy to yield the ruthenium complex $[Ru(bpy)_3]^{2+}$ with an enantiomeric ratio of 63:37.[9,10] In an analogous fashion, enantiomerically enriched $[Ru(phen)_3]^{2+}$ (phen = 1,10-phenanthroline) and $[Os(bpy)_3]^{2+}$ were synthesized.[9]

Eric Meggers received his Diploma degree in chemistry from the University of Bonn in 1995 and a Ph.D. from the University of Basel in 1999, contributing to the long-range charge hopping mechanism in DNA under the guidance of Professor Bernd Giese. After postdoctoral research on artificial metal-mediated base pairs in DNA with Professor Peter G. Schultz at the Scripps Research Institute in La Jolla (USA), he became in 2002 an Assistant Professor in the Chemistry Department at the University of Pennsylvania. Since 2007, Eric Meggers is Professor and Chair of Chemical Biology at the Philipps-University Marburg. His current main research interest is the design of biologically active inert metal complexes and their stereoselective synthesis.

Chiral Monodentate Sulfoxides as Auxiliaries

Inoue and co-workers reported the use of monodentate chiral sulfoxides as chiral auxiliaries.[11,12] For example, starting from $[Ru(pp)_2Cl_2]$, the reaction with (*R*)-(+)-methyl *p*-tolyl sulfoxide, (*R*)-**1**, in DMF at 120°C afforded *cis*-$[Ru(pp)_2\{(R)\text{-}\mathbf{1}\}Cl]Cl$ with a Δ:Λ ratio of 2.8:1 (48% *de*) for pp = bpy (complex **2**) and a Δ:Λ ratio of 4:1 (60% *de*) for pp = 4,4′-dimethyl-2,2′-bipyridine (Scheme 2). This diastereoselectivity was independent of the choice of the *cis* (chiral, racemic) or *trans* (achiral) starting material, implying a thermodynamic control with the diastereomeric ratio determined by the stability differences of the formed sulfoxide complexes. Based on NMR experiments, molecular modeling, and the X-ray crystallographic analysis of related sulfoxide complexes,[13] Inoue and co-workers concluded that the higher stability of the major diastereomer can be rationalized by a hydrogen bond between the sulfoxide oxygen and a pyridyl *ortho*-proton in combination with π–π interactions between the tolyl group of the sulfoxide and one of the bpy ligands.[11] These intramolecular interactions were shortly thereafter confirmed by Aït-Haddou and co-workers with a crystal structure of the analogous 1,10-phenanthroline complex *cis*-Δ-$[Ru(phen)_2\{(R)\text{-}\mathbf{1}\}Cl]Cl$ (the preferred diastereomer), whereas *cis*-Δ-$[Ru(bpy)_2\{(S)\text{-}\mathbf{1}\}Cl]Cl$ (the minor diastereomer) only has a S–O···H hydrogen bond, but not the attractive π–π interaction (Figure 2).[14] Aït-Haddou improved the asymmetric induction by performing the reactions under microwave irradiation to afford *de* values of up to 76% (Δ:Λ = 7.3:1) starting from racemic *cis*-$[Ru(pp)_2Cl_2]$. Overall achieved yields of up to 99% demonstrate that under the reaction conditions the ruthenium-centered configuration is labile, supporting the conclusion that the products are in a thermodynamic equilibrium during the synthesis through inversion of the metal centered configuration. In addition, importantly for practical reasons, Aït-Haddou reported that the two sulfoxide diastereomers differ significantly in their solubilities, thus allowing us to improve the optical purity of the major isomer by washing or crystallization protocols. Finally, as demonstrated by Inoue and co-workers, the optically active sulfoxide complexes can be converted with bidentate ligands to tris-heteroleptic ruthenium complexes under release of the chiral sulfoxide and almost complete retention of the metal-centered configuration (**2**→**3** in Scheme 2).[15] Thus, in this overall reaction sequence the chiral sulfoxide ligand serves as a chiral auxiliary for controlling the metal-centered chirality, although the diastereoselectivities are only modest.



Scheme 2. Methyl *p*-tolyl sulfoxide as a chiral auxiliary for the synthesis of tris-heteroleptic ruthenium complexes.

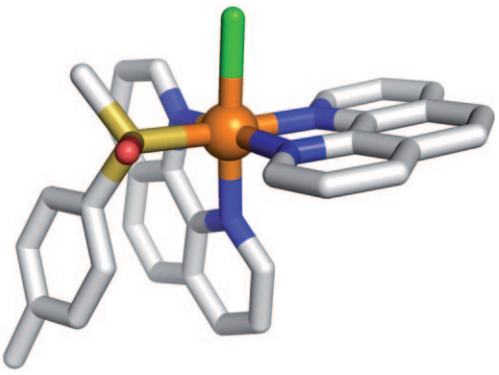
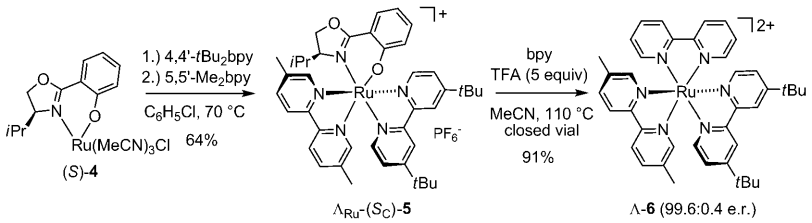


Figure 2. Crystal structure of *cis*-Δ-$[Ru(phen)_2\{(R)\text{-}\mathbf{1}\}Cl]^+$ showing the favorable π–π stacking in the more stable diastereomer.

Chiral Salicycloxazolines as Chelating Auxiliaries

Compared to monodentate ligands, chiral bidentate chelates are usually superior for asymmetric coordination chemistry due to a restricted rotation around the M–L coordinative bonds that fixes the position of the stereocenter(s) relative to the remaining coordination sites, thus often providing high diastereoselectivities.[1,2] However, such chiral chelates bind much tighter to the metal center and the challenge remains to develop chiral bidentate ligands, which can be removed afterwards under relatively mild conditions without isomerization of the metal-centered configuration. Meggers and co-workers reported recently that this is in fact possible with salicyloxazolines and they demonstrated the advantage of bidentate chiral auxiliaries for the asymmetric synthesis of enantiopure tris-heteroleptic ruthenium polypyridyl complexes $[Ru(pp)(pp')(pp'')]^{2+}$, with pp, pp′, pp″ = achiral 2,2′-bipyridines.[16] For example, starting from complex (*S*)-**4**, which harbors a deprotonated (*S*)-5-isopropyl-2-(2′-hydroxyphenyl)oxazoline ligand in addition to three acetonitriles and one chloride, the chiral salicyloxazolinate ligand provided an excellent asymmetric induction in the course of the substitution of the ligands for two bipyridine ligands and, importantly, could thereafter become substituted stereospecifically under complete retention of configuration in the presence of trifluoroacetic acid (TFA; Scheme 3). The reaction of (*S*)-**4** with first one equivalent of 4,4′-di-*tert*-butyl-2,2′-bipyridine (4,4′-tBu$_2$bpy) in chlorobenzene at 70°C and subsequent with one equivalent of 5,5′-dimethyl-2,2′-bipyridine (5,5′-Me$_2$bpy) again in chlorobenzene at 70°C afforded complex Λ_{Ru}-(S_C)-**5** with virtually complete diastereoselectivity (diastereopurity > 99.5%). Finally, treatment of Λ_{Ru}-(S_C)-**5** with bpy in acetonitrile at 110°C in a closed vial in the presence of 5 equivalents of TFA afforded the tris-heter-



Scheme 3. Example of the asymmetric synthesis of a tris-heteroleptic ruthenium complex utilizing a chiral salicyloxazolinate as chiral auxiliary.

oleptic complex Λ-**6** under replacement of the salicyloxazolinate by bpy with complete retention of configuration and a high enantiopurity of 99.6:0.4 e.r. (Scheme 3). In this case it appears that the protonation of the phenolate oxygen is responsible for affecting the coordinative strength of the salicyloxazoline ligand.

The diastereoselectivities are only marginally reduced if sterically less demanding bipyridines are employed. For example, the reaction of (*S*)-**4** with first bpy followed by 5,5′-Me_2bpy afforded complex Λ_{Ru}-(S_C)-**7** with a diastereopurity of 98.4% out of four possible diastereomers. A crystal structure of the monocation Λ_{Ru}-(S_C)-**7** is shown in Figure 3 and

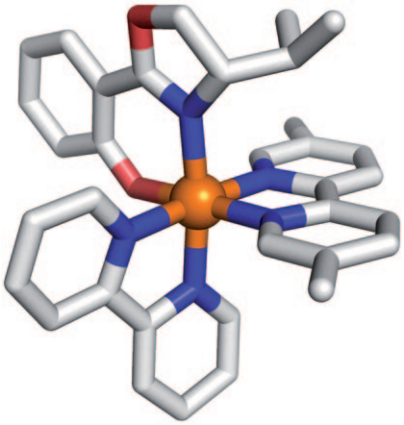
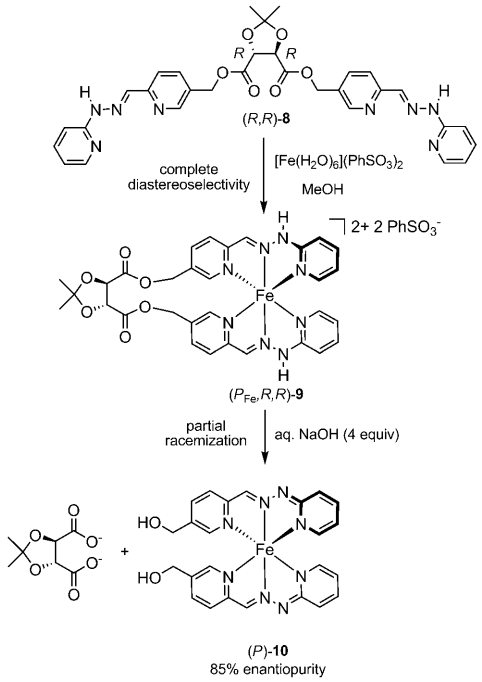


Figure 3. Crystal structure of the monocation Λ_{Ru}-(S_C)-**7**.

reveals that the *i*Pr group sterically interferes with the Me_2bpy ligand. Thus, the formation of Λ_{Ru}-(S_C)-**7** can be rationalized by the stereoselective incorporation of the first added ligand (bpy) at the two coordination sites pointing the farthest away from the *i*Pr group, with the following second bidentate ligand (5,5′-Me_2bpy) filling the remaining two vacant coordination sites.

Cleavable Chiral Linkers as Auxiliaries

Wild and co-workers recently introduced a different strategy in which the chiral auxiliary is not directly coordinated to the metal center but instead linked between two ligands.[17,18] Scheme 4 shows the C_2-symmetrical hexadentate ligand (*R*,*R*)-**8**, in which two tridentate pyridine-2-aldehyde 2′-pyridylhydrazones are tethered by a base-cleavable chiral (*R*,*R*)-tartrate linker.[17] When reacted with iron(II), the hexadentate ligand (*R*,*R*)-**8** afforded an octahedral, two-bladed propeller complex (P_{Fe},*R*,*R*)-**9** with complete diastereoselectivity



Scheme 4. Synthesis of an octahedral chiral two-bladed propeller complex by taking advantage of a chiral tartrate linker as the chiral auxiliary. The metal-centered configuration is described with the helix nomenclature.

(Scheme 4, Figure 4). Unfortunately, removal of the auxiliary by hydrolysis of the ester linkages and deprotonation of the hydrazone NH groups provided the corresponding neutral iron complex (*P*)-**10** only with e.r. = 85:15. The loss of configurational integrity during the cleavage step was attributed to partial racemization of the metal-centered configu-

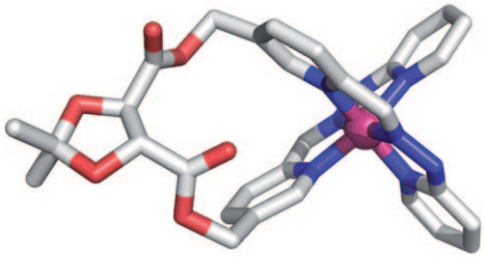
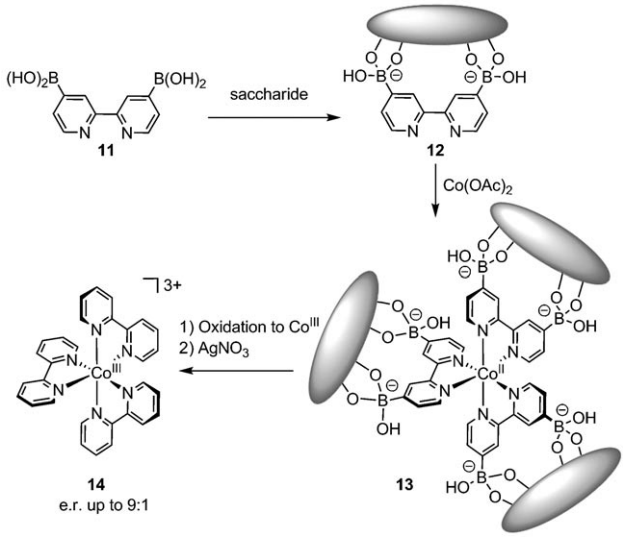


Figure 4. Crystal structure of one conformer of iron complex (P_{Fe},*R*,*R*)-**9**.

ration in the configurationally labile iron complex. It would be interesting to apply this strategy to configurationally more stable metal complexes.

Asymmetric Synthesis Through Boronic Acid–Saccharide Interactions

Shinkai and co-workers used saccharides as chiral auxiliaries for asymmetric coordination chemistry.[19] 2,2′-Bipyridine-4,4′-diboronic acid (**11**) forms cyclic 1:1 complexes with monosaccharides through the formation of boronic esters **12** (Scheme 5). The bpy–sugar complexes **12** were then reacted

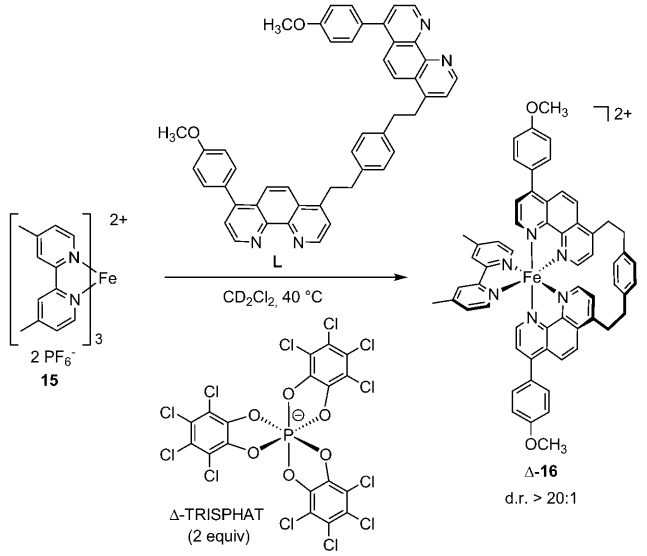


Scheme 5. Saccharides as chiral auxiliaries for the asymmetric synthesis of $[Co(bpy)_3]^{3+}$. Using D-glucose as the chiral auxiliary, Δ-$[Co(bpy)_3]^{3+}$ was synthesized with 9:1 e.r. when the reactions were performed at −25 °C.

with $Co(OAc)_2$ to afford the tris-heteroleptic cobalt(II) complex **13**. Complex **13** was subsequently oxidized with oxygen to form configurationally stable Co^{III}, followed by a removal of the chiral auxiliary through reductive cleavage of the C–B bonds with $AgNO_3$ to yield $[Co(bpy)_3]^{3+}$ (**14**). The enantiomeric excess was dependent on the type of saccharide and the reaction temperature, with highest stereoselectivity obtained with D-glucose. When the reactions were performed at −25 °C, Δ-**14** was obtained with 79% *ee*. The authors suggest that the chiral twist in the bpy ligand induced by the saccharide is the main contributor for the asymmetric induction.

Chiral Anion Mediated Asymmetric Synthesis

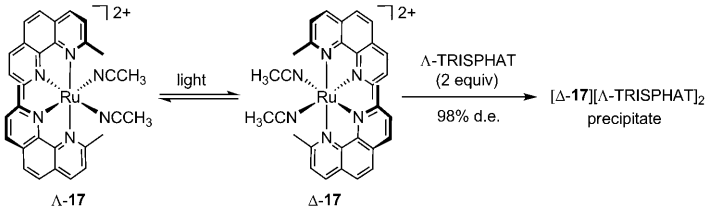
Since metal complexes are often charged, chiral counterions can be used as auxiliaries to control the stereoselectivity of coordination chemistry.[20,21] Scheme 6 shows a recent exam-



Scheme 6. Ion pair mediated asymmetric synthesis of a tris(diimine) iron complex that is configurationally stable at room temperature.

ple from Lacour and co-workers, in which $[Fe(dmbp)_3]^{2+}$ (**15**, dmbp = 4,4′-dimethyl-2,2′-bipyridine), when complexed with the chiral counter ion Δ-TRISPHAT, resulted in the formation of the iron complex Δ-**16** upon reaction with the tetradentate ligand **L** in CD_2Cl_2 at 40 °C with high diastereoselectivity.[22] Since the iron complex is configurationally stable at room temperature, the TRISPHAT counter ion can be removed without loss of stereochemical information, thus constituting a real chiral auxiliary.[23] The authors demonstrated that this reaction is under thermodynamic control. For example, when the reaction was performed at 20 °C, as opposed to 40 °C, no asymmetric induction was observed at all because Λ-**16** and Δ-**16** cannot reach an equilibrium. Apparently, the observed stereoselectivity results from the preferred homochiral association of the three-bladed propellers Δ-**16** and Δ-TRISPHAT as opposed to the heterochiral propellers Λ-**16** and Δ-TRISPHAT. The authors note that this is a rare example of a high selectivity in an asymmetric synthesis of a configurationally relatively stable coordination complex by using diastereoselective interactions restricted to intermolecular forces.[22]

In a related strategy of anion mediated asymmetric synthesis, Fontecave and co-workers exploited the low solubility of TRISPHAT-containing ion pairs in crystallization-induced asymmetric transformations.[24] For example, irradiation of a racemic mixture of $[Ru(dmp)_2(MeCN)_2][PF_6]_2$ (dmp = 2,9-dimethyl-1,10-phenanthroline; [**17**][PF_6]$_2$) with a 40 W tungsten filament lamp for 3 h in CH_2Cl_2 and in the presence of [nBu$_3$NH][Λ-TRISPHAT] (2.1 equiv) afforded a suspension in which the racemic ruthenium complex was completely converted to precipitated virtually optically pure [Δ-**17**][Λ-TRISPHAT]$_2$ (Scheme 7). This method relies on the photochemical racemization of the ruthenium precursor complex, probably induced by the photodissociation of one



Scheme 7. Crystallization-induced asymmetric synthesis with the chiral anion Λ-TRISPHAT as the chiral auxiliary.

MeCN, in combination with the low solubility of the heterochiral ion pair [Δ-**17**][Λ-TRISPHAT]$_2$ in CH_2Cl_2.

Conclusions and Outlook

The here discussed examples of chiral-auxiliary-mediated asymmetric synthesis of octahedral metal complexes point into a promising direction of modern, more sophisticated stereocontrolled coordination chemistry, by using chiral counterions, cleavable chiral linkers, maybe even traceless linkers, and temporary chiral ligands in which the coordinative strength can be varied. However, there are significant challenges lying ahead in the field of stereocontrolled coordination chemistry and I would like to highlight two key points:

1) It is useful to distinguish between configurationally labile and inert metal complexes. Whereas labile metal complexes allow thermodynamic control with the metal-centered configurations being in equilibrium even under mild reaction conditions, this strategy cannot be implemented as straightforward for the more challenging asymmetric synthesis of kinetically inert complexes of Ru, Os, Rh, and Ir. However, such complexes are of particular interest since they can store stereochemical information permanently.
2) Relative and absolute metal-centered configuration must be controlled at the same time. It is of note that all here discussed strategies were applied to simple octahedral complexes that lack additional diastereomers. Considering that for complicated octahedral metal complexes with low symmetry a large number of diastereomers are possible, more sophisticated auxiliaries or even combinations of auxiliaries will be necessary to solve this problem in a general fashion.

The stereocontrolled synthesis of octahedral metal complexes is a central and exciting problem of modern coordination chemistry and will ultimately allow us to fully exploit the rich stereochemistry provided by octahedral complexes.

[1] For chiral coordination compounds, see: a) A. von Zelewski, *Stereochemistry of Coordination Compounds*, Wiley, New York, **1996**; b) H. Amouri, M. Gruselle, *Chirality in Transition Metal Chemistry: Molecules, Supramolecular Assemblies and Materials*, Wiley, New York, **2008**.
[2] Reviews on stereoselective synthesis in coordination chemistry: a) U. Knof, A. von Zelewsky, *Angew. Chem.* **1999**, *111*, 312–333; *Angew. Chem. Int. Ed.* **1999**, *38*, 302–322; b) P. D. Knight, P. Scott, *Coord. Chem. Rev.* **2003**, *242*, 125–143.
[3] E. Meggers, G. E. Atilla-Gokcumen, H. Bregman, J. Maksimoska, S. P. Mulcahy, N. Pagano, D. S. Williams, *Synlett* **2007**, 1177–1189.
[4] J. Maksimoska, L. Feng, K. Harms, C. Yi, J. Kissil, R. Marmorstein, E. Meggers, *J. Am. Chem. Soc.* **2008**, *130*, 15764–15765.
[5] For chiral auxiliaries in organic synthesis, see for example: Y. Gnas, F. Glorius, *Synthesis* **2006**, 1899–1930.
[6] H. B. Jonassen, J. C. Bailar, E. H. Huffman, *J. Am. Chem. Soc.* **1948**, *70*, 756–758.
[7] The authors reported that final diastereomeric ratio was independent of the optical activity of the carbonate starting compound.
[8] Y. Saito, K. Nakatus, M. Shiro, H. Kuroya, *Bull. Chem. Soc. Japan* **1957**, *30*, 795–799.
[9] C. F. Liu, N. C. Liu, J. C. Bailar, *Inorg. Chem.* **1964**, *3*, 1085–1087.
[10] R. D. Gillard, R. E. E. Hill, R. Maskill, *J. Chem. Soc. A* **1970**, 707–710.
[11] D. Hesek, Y. Inoue, S. R. L. Everitt, H. Ishida, M. Kunieda, M. G. B. Drew, *Inorg. Chem.* **2000**, *39*, 317–324.
[12] D. Hesek, Y. Inoue, H. Ishida, S. R. L. Everitt, M. G. B. Drew, *Tetrahedron Lett.* **2000**, *41*, 2617–2620.
[13] D. Hesek, Y. Inoue, S. R. L. Everitt, H. Ishida, M. Kunieda, M. G. B. Drew, *Dalton Trans.* **1999**, 3701–3709.
[14] F. Pezet, J.-C. Daran, I. Sasaki, H. Aït-Haddou, G. G. A. Balavoine, *Organometallics* **2000**, *19*, 4008–4015.
[15] D. Hesek, Y. Inoue, S. R. L. Everitt, H. Ishida, M. Kunieda, M. G. B. Drew, *Chem. Commun.* **1999**, 403–404.
[16] G. Lei, S. P. Mulcahy, K. Harms, E. Meggers, *J. Am. Chem. Soc.* **2009**, *131*, 9602–9603.
[17] R. J. Warr, A. C. Willis, S. B. Wild, *Inorg. Chem.* **2006**, *45*, 8618–8627.
[18] R. J. Warr, A. C. Willis, S. B. Wild, *Inorg. Chem.* **2008**, *47*, 9351–9362.
[19] T. Mizuno, M. Takeuchi, I. Hamachi, K. Nakashima, S. Shinkai, *J. Chem. Soc. Perkin Trans. 1* **1998**, 2281–2288.
[20] For an early report, see: P. Pfeiffer, K. Quehl, *Chem. Ber.* **1931**, *64*, 2667–2671.
[21] J. Lacour, R. Frantz, *Org. Biomol. Chem.* **2005**, *3*, 15–19.
[22] D. Monchaud, J. J. Jodry, D. Pomeranc, V. Heitz, J.-C. Chambron, J.-P. Sauvage, J. Lacour, *Angew. Chem.* **2002**, *114*, 2423–2425; *Angew. Chem. Int. Ed.* **2002**, *41*, 2317–2319.
[23] This is in contrast to examples where the chiral counter ion is controlling the metal-centered chirality of configurationally labile metal complexes. For example, it was recently shown that chiral TRISPHAT acts as an effective asymmetry inducer on racemic [Fe(dmbp)$_3$]$^{2+}$: when associated with the labile cationic guest, Δ-TRISPHAT controls its configuration with high diastereoselectivity in $CDCl_3$ in favor of Δ-[Fe(dmbp)$_3$]$^{2+}$ (d.r. > 49:1). J. Lacour, J. J. Jodry, C. Ginglinger, S. Torche-Haldimann, *Angew. Chem.* **1998**, *110*, 2522–2524; *Angew. Chem. Int. Ed.* **1998**, *37*, 2379–2380.
[24] O. Hamelin, J. Pécaut, M. Fontecave, *Chem. Eur. J.* **2004**, *10*, 2548–2554.

Published online: December 10, 2009

