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Stabilization of the Labile Metal Configuration in Half-Sandwich Complexes with Tripod Ligands

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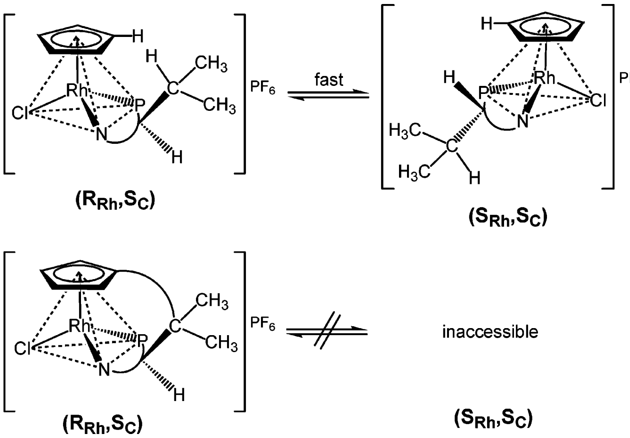
Summary: In contrast to bidentate ligands, e.g. PN, the tripod ligands CpPN$^-$ predetermine a single metal configuration, preventing formation of the opposite metal configuration.

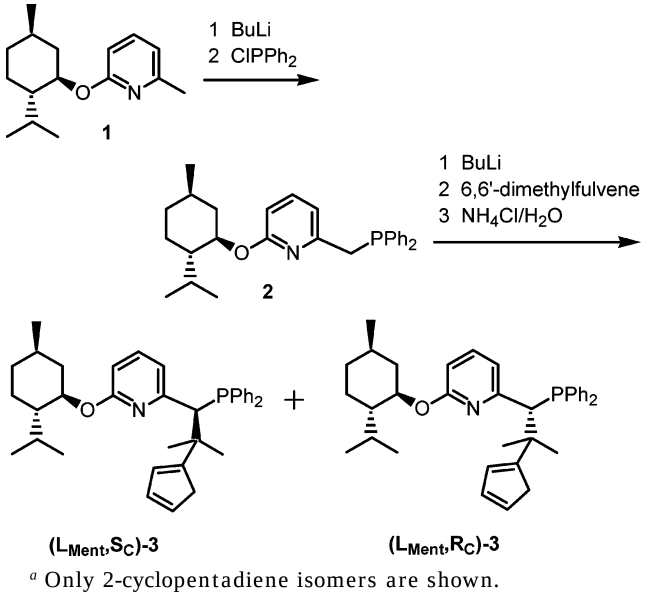
In three-legged piano-stool complexes of the type [(η^n-Ar)M(LL′)X] (L−L′ = unsymmetrical chelate ligand and X = monodentate ligand) the metal atom is a chiral center. With an enantiomerically pure chelate ligand, e.g. an ^{i}Pr-substituted S_C-configured PN ligand, the two diastereomers R_{Rh},S_C and S_{Rh},S_C arise in compounds of the type [(η^5-C_5H_5)Rh(PN)Cl]PF_6 (Scheme 1, top), which only differ in the metal configuration.[1−3] In solution these compounds epimerize by a change of the labile metal configuration initiated by dissociation of the monodentate ligand or by chelate ring opening.[4,5] Compounds of this type are catalysts in organic transformations, such as transfer hydrogenation, Diels−Alder reactions, isomerization reactions, etc.[6−8]

As usually the epimerization at the metal atom is faster than the catalytic reaction, two diastereomeric catalysts participate in product formation.[7,8] It is known that the stereochemistry of reactions occurring at a metal center strongly depends on the metal configuration.[9] Thus, reaction channels with diastereomeric catalysts differing in the metal configuration tend to produce products with opposite configuration. Therefore, it would be desirable to control the metal configuration such that only a catalyst with a single metal configuration is present during catalysis. In this paper we present a new tripod ligand of the type MentCpH(PN) which fixes the metal chirality, inhibiting any configurational change (Scheme 1, bottom). This ligand has three different binding sites, a cyclopentadiene system (CpH), a diphenylphosphanyl group (P), and a pyridine ring (N) connected by a resolved asymmetric carbon atom (Scheme 2).

Scheme 1. Stabilization of the Metal Configuration with the Tripod Ligand CpPN$^-$



Scheme 2. Synthesis of the Tripod Ligands (L_{Ment},S_C)-3 and (L_{Ment},R_C)-3 with Three Different Binding Sites[a]



[a] Only 2-cyclopentadiene isomers are shown.

Substitution of the bromo substituent in 2-bromo-6-methylpyridine[10] for the anion of L-(−)-menthol afforded 2-menthoxy-6-methylpyridine (**1**).[11] The methyl group in the α-position of the pyridine ring was deprotonated with n-BuLi and reacted with $ClPPh_2$ to introduce the

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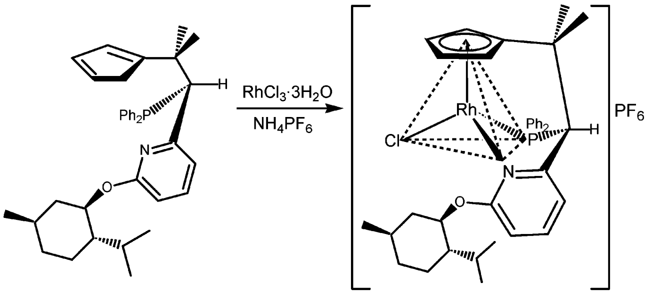
Scheme 3. Synthesis of $(\text{L}_{\text{Ment}},S_{\text{C}},R_{\text{Rh}})$-4



$(\text{L}_{\text{Ment}},S_{\text{C}})$-3 **$(\text{L}_{\text{Ment}},S_{\text{C}},R_{\text{Rh}})$-4**

diphenylphosphanyl group to give 6-[(diphenylphosphanyl)methyl]-2-menthoxypyridine (**2**). The next deprotonation with n-BuLi was performed without isolating **2**. Addition of 6,6'-dimethylfulvene and hydrolysis gave the tripod ligand **3**, containing a new asymmetric carbon atom at the branching point of the three different binding sites CpH, P, and N. Due to the L-menthyl substituent, two diastereomers were formed in the ratio $(\text{L}_{\text{Ment}},R_{\text{C}})$-**3**:$(\text{L}_{\text{Ment}},S_{\text{C}})$-**3** = 60:40. From a concentrated pentane solution of the 60:40 mixture only the $\text{L}_{\text{Ment}},S_{\text{C}}$ diastereomer (the "40% isomer") crystallized at −30 °C. The $\text{L}_{\text{Ment}},R_{\text{C}}$ diastereomer (the "60% isomer") remained in solution. Thus, it was possible to prepare the tripod ligand $(\text{L}_{\text{Ment}},S_{\text{C}})$-**3** with a resolved branching position in an operationally simple way in multigram quantities. The synthesis of the menthyl-substituted ligands **3** is an extension of our previous work with racemic (CpH)PN ligands.[12] An X-ray structure analysis of single crystals of $(\text{L}_{\text{Ment}},S_{\text{C}})$-**3** established the absolute configuration of the newly generated asymmetric carbon atom as S_{C}. Only the 2-cyclopentadiene isomer was found in the crystal. In solution the cyclopentadiene isomers interchange. Therefore, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of both diastereomers are broad at room temperature.

Complexation of $(\text{L}_{\text{Ment}},S_{\text{C}})$-**3** with $\text{RhCl}_3\cdot 3\text{H}_2\text{O}$ in ethanol in the presence of NH_4PF_6 gave the chiral-at-metal complex $(\text{L}_{\text{Ment}},S_{\text{C}},R_{\text{Rh}})$-**4** (Scheme 3). It was soluble in polar solvents, such as alcohols or chlorinated solvents, and it was air stable in the solid state and in solution.

The cyclopentadiene isomerism present in ligand $(\text{L}_{\text{Ment}},S_{\text{C}})$-**3** disappeared on complexation to $(\text{L}_{\text{Ment}},S_{\text{C}},R_{\text{Rh}})$-**4**, because a cyclopentadienyl system devoid of stereogenicity was formed. Consequently, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $(\text{L}_{\text{Ment}},S_{\text{C}},R_{\text{Rh}})$-**4** in CDCl_3 showed only one doublet at 72.6 ppm with a P−Rh coupling of 145 Hz.

Remarkably, the $\text{L}_{\text{Ment}},S_{\text{C}}$ diastereomer of ligand **3** can only form the complex $(\text{L}_{\text{Ment}},S_{\text{C}},R_{\text{Rh}})$-**4**. The S_{Rh} configuration is inaccessible for the metal atom (Scheme 1, bottom). Thus, the S_{C} configuration of the α-carbon of the ligand predetermines the R_{Rh} configuration of the metal atom.[13] Even if ligand arms dissociate from the metal atom, the chirality at the metal center does not get lost, because on coming back the original R_{Rh} configuration inevitably is restored. Clearly, the opposite metal configuration (S_{Rh}) is only accessible with the other ligand diastereomer $(\text{L}_{\text{Ment}},R_{\text{C}})$-**3**. Recently, there has been a different approach to fix the metal configuration in (η^6-arene)ruthenium complexes using planar chirality.[14,15] The synthesis of chiral (CpH)PP′ and (IndH)PP′ ligands has been described.[16] However, they have been used in complexation studies unresolved with respect to the branching position.

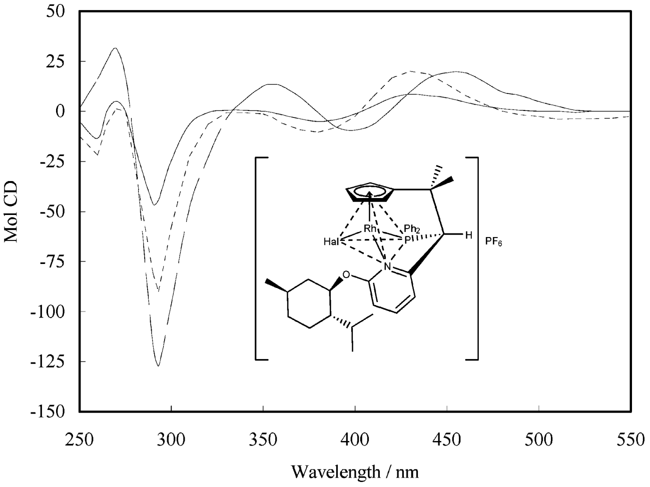


Figure 1. CD spectra of $(\text{L}_{\text{Ment}},S_{\text{C}},R_{\text{Rh}})$-**4** (—; $c = 2.4 \times 10^{-4}$ mol L^{-1}), of its Br analogue (- - -; $c = 2.3 \times 10^{-4}$ mol L^{-1}) and of its I analogue (— — —; $c = 2.2 \times 10^{-4}$ mol L^{-1}) in CH_2Cl_2.

The predetermination of the metal configuration by the tripod ligand $(\text{L}_{\text{Ment}},S_{\text{C}})$-**3** implies that substitution reactions of the chloro ligand in $(\text{L}_{\text{Ment}},S_{\text{C}},R_{\text{Rh}})$-**4** must occur with retention of the metal configuration. Stirring $(\text{L}_{\text{Ment}},S_{\text{C}},R_{\text{Rh}})$-**4** with an excess of NaBr or NaI in methanol at room temperature afforded the corresponding bromo and iodo derivatives. The similarity of the CD spectra in Figure 1 is in accordance with these expectations.

Formal cleavage of the C−C bond between the cyclopentadienyl ring and the CMe_2 group of the tether to the branching position in $(\text{L}_{\text{Ment}},S_{\text{C}},R_{\text{Rh}})$-**4** results in a combination of a Cp ligand and a bidentate PN ligand carrying an ^{i}Pr substituent. As shown in Scheme 1 (top), for such a ligand combination the two different metal configurations R_{Rh} and S_{Rh} are possible. As the pentamethylcyclopentadienyl (Cp*) compounds of rhodium are more stable than the cyclopentadienyl (Cp) compounds, the comparison was carried with $(\text{L}_{\text{Ment}},S_{\text{C}},R_{\text{Rh}})$-[(CpPN)RhCl]PF$_6$ (**4**; fixed metal configuration) on the one side and the pair $(\text{L}_{\text{Ment}},S_{\text{C}})(R_{\text{Rh}})$- and $(\text{L}_{\text{Ment}},S_{\text{C}})(S_{\text{Rh}})$-[Cp*(PN)RhCl]PF$_6$ (**7**; both metal configurations possible) on the other side (Scheme 4).

Reaction of $[\text{Cp*RhCl}_2]_2$ with the 1:1 diastereomer mixture of the bidentate PN ligand $(\text{L}_{\text{Ment}},R_{\text{C}})$-/$(\text{L}_{\text{Ment}},S_{\text{C}})$-2-[1-(diphenylphosphanyl)-2-methylpropyl]-6-menthoxypyridine (**5**) gave the two diastereomers $(\text{L}_{\text{Ment}},R_{\text{C}})$-**6** and $(\text{L}_{\text{Ment}},S_{\text{C}})$-**6**, in which the PN ligand is only P-bonded (Scheme 4). $(\text{L}_{\text{Ment}},R_{\text{C}})$-**6** could be isolated due to its insolubility in ether. $(\text{L}_{\text{Ment}},S_{\text{C}})$-**6** was obtained in pure form by chromatography. The absolute configurations

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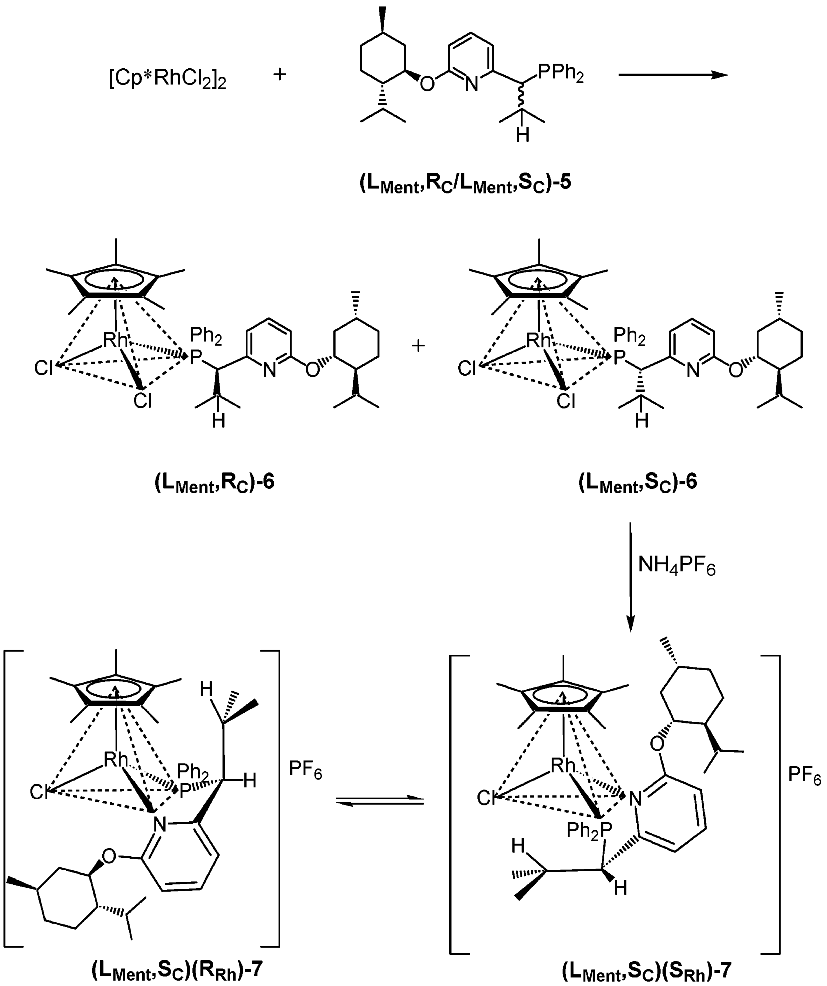
Scheme 4. Complexes $(\text{L}_{\text{Ment}},S_{\text{C}})$-6 and $(\text{L}_{\text{Ment}},R_{\text{C}})$-6 and the Chiral-at-Metal Complexes $(\text{L}_{\text{Ment}},S_{\text{C}})(S_{\text{Rh}})$-7 and $(\text{L}_{\text{Ment}},S_{\text{C}})(R_{\text{Rh}})$-7



of both diastereomers were determined by X-ray crystallography.

Treatment of $(\text{L}_{\text{Ment}},S_{\text{C}})$-**6** with NH_4PF_6 afforded the chiral-at-metal diastereomers $(\text{L}_{\text{Ment}},S_{\text{C}})(S_{\text{Rh}})$- and $(\text{L}_{\text{Ment}},S_{\text{C}})(R_{\text{Rh}})$-[Cp*(PN)RhCl]$PF_6$ (**7**), which equilibrate in CD_2Cl_2 solution (ratio 96:4 at −80 °C, $^{31}P\{^1H\}$ NMR integration). The assignment of the metal configuration in $(\text{L}_{\text{Ment}},S_{\text{C}})(S_{\text{Rh}})$-**7** was possible on the basis of an X-ray structure analysis obtained using crystals with a 1:1 ratio of diastereomers $(\text{L}_{\text{Ment}},S_{\text{C}})(S_{\text{Rh}})$-**7** and $(\text{L}_{\text{Ment}},R_{\text{C}})(R_{\text{Rh}})$-**7**. Surprisingly, in the diastereomer mixture $(\text{L}_{\text{Ment}},S_{\text{C}})(S_{\text{Rh}})$-**7**/$(\text{L}_{\text{Ment}},S_{\text{C}})(R_{\text{Rh}})$-**7** the isomer with S_{Rh} configuration is dominating, because orientation of the ^{i}Pr substituent of the PN ligand toward the large Cp* ligand means more steric hindrance than toward the Cl ligand. Thus, in the tripod complex $(\text{L}_{\text{Ment}},S_{\text{C}},R_{\text{Rh}})$-**4** the "less stable" Rh configuration is stabilized by ligand design.

The complex $(\text{L}_{\text{Ment}},S_{\text{C}},R_{\text{Rh}})$-**4** is air-stable, relatively unreactive, and, thus, not a good catalyst precursor. Addition of $AgPF_6$ might create a Lewis acidic site at the metal atom. Dissociation of the hemilabile pyridine arm might open a second vacant site. For catalyses requiring three empty coordination sites metal atoms with coordination numbers higher than Rh(III), e.g. lanthanoids, could be used. At any rate, tripod ligands such as $(\text{L}_{\text{Ment}},S_{\text{C}})$-**3** fix a specific metal configuration and in enantioselective catalysis should maintain it throughout all the catalytic cycles, preventing participation of diastereomers with opposite metal configurations which would open other reaction channels to probably give the opposite product configurations.[9] Similar to the PN ligands described here, many bidentate ligands can be metalated and additional tripod legs such as the cyclopentadienyl system can be introduced by reaction with fulvenes. Thus, a broad extension of the concept of the chiral tripod ligands and their consequences for the metal configuration is possible. Control of the metal configuration could be a promising improvement in the field of enantioselective catalysis.

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