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Enantiopure amidinate complexes of lutetium☆

Tobias S. Brunner, Peter W. Roesky*

Institute of Inorganic Chemistry, Karlsruhe Institute of Technology (KIT), Engesserstraße 15, 76131 Karlsruhe, Germany

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ABSTRACT

Two new enantiomeric pure amidinates *N,N'*-bis-((*R*)-1-cyclohexylethyl)benzamidinate ((*R*)-CEBA)$^-$ and *N,N'*-bis-((*S*)-1-phenylethyl)acetamidinate ((*S*)-PEAA)$^-$ were synthesized by two different synthetic pathways. The chiral amidine (*R*)-HCEBA was synthesized via the so-called imidoylchloride route. The corresponding lithium derivative (*R*)-LiCEBA was best obtained by deprotonation of the amidinate hydrochloride (*R*)-HCEBA·HCl. In contrast (*S*)-LiPEAA was most efficiently accessed by reaction of methyllithium with bis-((*S*)-1-phenylethyl)carbodiimide. Further reactions of these lithium salts with $LuCl_3$ in a 2:1 ratio resulted in the enantiomeric pure bisamidinate lutetium complexes $[\{(R)\text{-CEBA}\}_2\text{Lu-}\mu\text{-Cl}]_2$ and $[\{(S)\text{-PEAA}\}_2\text{LuCl(thf)}]$, which are either dimeric or monomeric in the solid state.

1. Introduction

Recently, we introduced chiral amidinates into the coordination chemistry of the rare earth elements and reported mono-, bis-, and tris(amidinate) complexes of these metals [1–3]. Whereas achiral amidinates of the general formula $[RC(NR')_2]^-$ and the closely related guanidinates $[R_2NC(NR')_2]^-$ are a well-established class of *N*-chelating ligands, which form complexes with almost every metal of the periodic table [4–10], chiral amidinates are far less common. Besides our contribution in rare earth chemistry only a few group 4 metal [11–14], molybdenum [15,16], rhodium [17,18], and nickel [19] complexes with chiral amidinates are known. In rare earth chemistry achiral amidinates, e.g. *N,N'*-bis-(trimethylsilyl)-benzamidinate [20,21], have been found to stabilize lanthanide compounds in all three common oxidation states (+II, +III, +IV) [5,6,22–26]. The pioneering work has been performed by Edelmann et al. in the 1990s [22,27] followed by contributions from Deacon and Junk et al. [28–33]. Selected amidinate complexes have been used as homogeneous catalysts for the polymerization of ethane [34] and isoprene [35,36], ring opening polymerization of polar monomers (e.g. ε-caprolactone and trimethylene carbonate), hydroboration, hydrosilylation and intramolecular hydroamination/cyclization [37] reactions [22,23,37].

We recently published an improved synthesis of the chiral amidine *N,N'*-bis-(1-phenylethyl)benzamidine (HPEBA; Scheme 1) [38], which was reported for the first time about 35 years ago by H. Brunner et al. [15,18]. In 2011, we also reported the synthesis of the first rare earth metal complexes ligated by the corresponding chiral amidinate (PEBA)$^-$. For catalytic applications chiral mono(amidinate) bisborohydride complexes were used as initator for the ring opening polymerization of *rac*-lactide [39]. Moreover, bis(amidinate) amido complexes with yttrium and lutetium $[\{(S)\text{-PEBA}\}_2\text{Ln}\{N(SiMe_3)_2\}]$ (Ln = Y, Lu) were used as catalysts in the enantioselective hydroamination reaction [1,2]. Since the coordination chemistry of the lanthanides is strongly influenced by the steric demand of the ligand, we started modifying the bite angle and the substituents of the chiral amidinate ligands slightly. In a recent approach we substituted the phenyl group in the (PEBA)$^-$ ligand backbone by the bulkier *t*Bu group. This resulted in the chiral amidine (*S,S*)-*N,N'*-bis-(1-phenylethyl)pivalamidine ((*S*)-HPETA) (Scheme 1). Furthermore, a number of (*S*)-PETA rare-earth element complexes including amides and alkyl compounds, which were applied as catalysts in enantioselective intramolecular hydroamination reactions of non-activated terminal amino olefins were reported [40]. It was shown by us that the substituent in the backbone of the amidinate has an influence on the bite angle of the ligand and thus also influences the catalytic activity [40].

Also the naphthyl substituted ligand (*S,S*)-*N,N'*-bis-(1-(2-naphthyl)ethyl)benzamidine ((*S*)-HNEBA) (Scheme 1) and a series of the corresponding enantiomerically pure homoleptic rare earth metal complexes $[Ln\{(S)\text{-NEBA}\}_3]$ (Ln = Y, Sm, Tb, Dy, Er, Yb, Lu) are known [41].

☆ Dedicated to Prof. Richard D. Adams on the occasion of his 70th birthday.

* Corresponding author.
E-mail address: roesky@kit.edu (P.W. Roesky).

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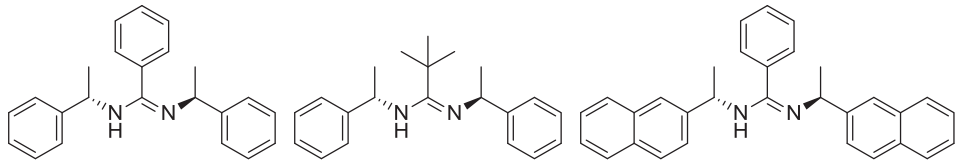


Scheme 1. Chiral amidines which were recently used by us (*S*)-HPEBA, (*S*)-HPETA, and (*S*)-HNEBA for the synthesis of enantiomerically pure rare earth metal complexes [1–3], [40,41].

Herein, we now describe the synthesis of two other chiral amidinates as well as their lithium and lutetium complexes. For the design of the first ligand *N,N'*-bis-((*R*)-1-cyclohexylethyl)benzamidine ((*R*)-HCEBA) (Scheme 2), we used in comparison to HPEBA a cyclohexyl group instead of a phenyl group on the side function of the amidine. In the second ligand, *N,N'*-bis-((*S*)-1-phenylethyl) acetamidine ((*S*)-HPEAA) (Scheme 2), we altered the group at the ligand backbone by using a small methyl group instead of a phenyl group in HPEBA or a *t*Bu group in HPETA.

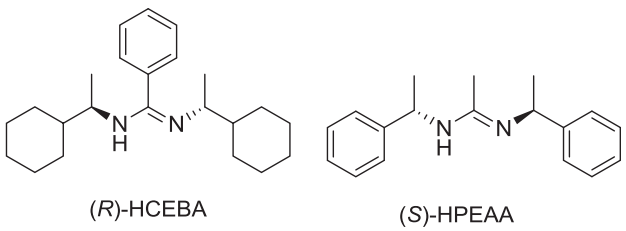
2. Results and discussion [42]

The new enantiomerically pure amidine (*R*)-HCEBA was synthesized in a similar way as the previously described (*S*)-HPEBA [43] (Scheme 3). In the first step benzoylchloride was reacted with enantiomerically pure (*R*)-1-cyclohexylethylamine to give *(R)-N*-(1-cyclohexylethyl)benzamide (**I**) in high yields. Treatment of **I** with oxalylchloride and 2,6-lutidine in CH_2Cl_2 resulted in the second step in (*R*)-*N*-(1-cyclohexylethyl)benzimidoylchloride (**II**), which was further reacted without further purification and analysis. In the third step, compound **II** and (*R*)-1-cyclohexylethylamine were heated in toluene. The resulting amidine hydrochloride ((*R*)-HCEBA·HCl) precipitates from the hot reactions mixture. It was recrystallized from toluene as analytically pure white crystals in an overall yield of 63%.

Symmetrical patterns of the 1-cyclohexylethyl substituents were observed in the NMR spectra. The signals of both N-H protons are seen at 10.46 ppm as a doublet, whereas all other signals are multipletts. In the $^{13}C\{^1H\}$-NMR spectrum, the peak of the NCN unit shows a characteristic down field shift at 166.1 ppm whereas the signals of the N*C*H and *C*H_3 groups were detected in the expected region at 56.7 ppm and 19.1 ppm. ESI-MS spectra and elemental analysis support the proposed composition.

In contrast to the synthesis of (*S*)-HPEBA or (*S*)-HPETA, the deprotonation of the hydrochloride (*R*)-HCEBA·HCl with $NaHCO_3$ or NaOH in aqueous alkaline solution did not lead to a clean product. In contrast by using one equiv *n*-butyllithium as base in toluene and subsequent workup, the desired product, the neutral amidine (*R*)-HCEBA, was obtained in almost quantitative yield (97%) (Scheme 4). The overall yield over all four steps thus is 61%.

As a result of the E/Z isomerization and the asymmetry of the compound, the ^1H NMR spectrum of (*R*)-HCEBA is rather complex [10,44]. Mainly relatively broad peaks are observed. By using DMSO-d_6 as solvent the proton exchange is altered and better resolved spectra were obtained. Due to the asymmetry, two signals are seen for the NCH groups at 3.85 and 2.67 ppm. The signals of the methyl groups are covered partly by the resonances of the cyclohexyl rings. In contrast to the ^1H NMR spectrum, the corresponding $^{13}C\{^1H\}$-NMR spectrum is much better resolved, e.g. four signals, which can be assigned to the methyl and methine groups, are observed at 57.9, 48.9, 21.2 and 16.7 ppm.



Scheme 2. The chiral amidines ((*R*)-HCEBA and ((*S*)-HPEAA).

Since (*R*)-HCEBA is an oily compound, which is hard to transfer, we decided to generate the corresponding lithium salt (*R*)-LiCEBA directly from the hydrochloride (*R*)-HCEBA·HCl. Reaction of (*R*)-HCEBA·HCl with two equiv of *n*-buthyllithium resulted directly in a double deprotonation. As product the lithium salt was obtained in 74% yield (Scheme 5). The desired compound was obtained as a colorless solid, which includes one equivalent of lithium chloride. Upon further reaction, the remaining lithium chloride was removed at the next step. In contrast to (*R*)-HCEBA and in agreement with (*R*)-HCEBA·HCl, the lithium salt shows a symmetric pattern in the NMR spectra. Thus, the protons of the methine group show a well resolved multiplett at 2.91 ppm ($^3J_{H,H}$ = 4.5 Hz). Also only one resonance is seen in the $^{13}C\{^1H\}$ NMR spectrum for the methine (56.8 ppm) and methyl groups (22.4 ppm), each. The characteristic signal for the NCN unit is seen at 176.8 ppm, which corresponds to a low field shift in comparison of the hydrochloride (166.1 ppm) of 20 ppm.

As second ligand system, we investigated *N,N'*-bis-((*S*)-1-phenylethyl)acetamidine ((*S*)-HPEAA). As mentioned in the introduction, we intended to alter the bite angle of the ligand and to draw a comparison to the previously used systems (S)-HPEBA and (S)-HPETA. To access the ligand, we chose a different strategy. Similar to the synthesis of HPETA, we reacted methyllithium with the corresponding chiral carbodiimide bis-((*S*)-1-phenylethyl)carbodiimide ((*S*)-PEC) [40,45–48] to obtain pure lithium-bis-((*S*)-1-phenylethyl)acetamidinate ((*S*)-LiPEAA) in good yields (85%) (Scheme 6). In contrast, for the synthesis of (*R*)-HCEBA this simpler reaction pathway resulted in low yields only [49]. The reaction of carbodiimides with lithium alkyls to give lithium amidinates is a well-established synthetic procedure [6,22,50,51]. As other alternative for the ligand synthesis, L. R. Sita described the reaction of [$CpTiMe_3$] with the carbodiimide(*R*)-PEC. Upon insertion of the carbodiimide into the Ti-Me bond the titanium complex [{(*R*)-PEAA}$CpTiMe_2$] was formed [13].

The ^1H NMR spectrum of (*S*)-LiPEAA shows well resolved signals. As expected the methine proton is coupled to a quartet at 4.41 ppm ($^3J_{H,H}$ = 6.6 Hz) and for the corresponding methyl group a doublet at 1.21 ppm ($^3J_{H,H}$ = 6.6 Hz) is observed. In contrast, a sharp singlet is seen for the methyl group bound to the NCN unit at 1.58 ppm. In the $^{13}C\{^1H\}$ NMR spectrum the methine group and the corresponding methyl group of the chiral side chain are observed at 57.5 ppm and 29.1 ppm. The signal of the NCN unit was detected at

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