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Synthesis of enantiomeric pure lithium and potassium benzamidinate complexes

Paul Benndorf, Corinna Preuß, Peter W. Roesky*

Institut für Anorganische Chemie, Karlsruher Institut für Technologie (KIT), Engesserstraße Geb. 30.45, 76131 Karlsruhe, Germany

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ABSTRACT

A new synthesis leading to the chiral amidines (*S*,*S*)- and (*R*,*R*)-*N*,*N*-bis-(1-phenylethyl)benzamidine ((*S*)- and (*R*)-HPEBA) in good yields is presented. Further reaction of (*S*)-HPEBA with *n*-BuLi gave the chiral lithium salt (*S*)-LiPEBA. Treatment of KH with (*S*)-HPEBA in boiling THF afforded the corresponding potassium salt (*S*)-KPEBA. In contrast by performing the reaction in boiling toluene a fast racemization was observed. In the solid state racemic KPEBA formed a dimer, in which all four nitrogen atoms are in a plane. To each potassium atom a toluene molecule is η^6-coordinated.

1. Introduction

The use of non-cyclopentadienyl ligands in main group and transition metal chemistry resulted some years ago in a renaissance of amido metal complexes [1–6]. Within the broad series of *N*-centered donor ligands the readily accessible amidinate and guanidinate anions play a major role. A number of recent comprehensive reviews in this area cover the rapidly expanding chemistry [7–11]. Today amidinates and guanidinates complexes of the main group and transition metals are used for various applications such as catalysis and materials science [8]. The amidinate anions of the general formula $[RC(NR')_2]^-$ (Scheme 1), which allows an effective tuning of the steric and electronic requirements by varying the substituents R and R′, can be considered as the nitrogen analog of the carboxylate anions.

Due to the large number of publications dealing with amidinates a number of synthesis leading to these kinds of compounds were established [12]. Most of them use either imidoylchlorides (Scheme 2, A) or carbodiimides (Scheme 2, B) as intermediates [13]. Although a huge number of amidinate and guanidinate complexes are known, the amount of reports dealing with chiral amidinates is surprisingly small. Only relatively few complexes of group 4 metals [14–16], molybdenum [17], nickel [17,18], and rhodium [19,20] with chiral amidinate ligands were reported. In most of the published work the chiral amidinates shown in Scheme 3 were used [14–20].

Having all these in mind we were attracted by the chiral compounds (*S*,*S*)- and (*R*,*R*)-*N*,*N*-bis-(1-phenylethyl)benzamidine ((*S*)- and (*R*)-HPEBA) (Typ **I**, Scheme 3), which were published about 30 years ago by H. Brunner et al. [17,19]. Chiral complexes of composition $[(\eta^5\text{-}C_5H_5)(CO)_2Mo(PEBA)]$ were synthesized and then combined with rhodium complexes to form enantioselective catalysts for the hydrogenation of prochiral olefins. Unfortunately, the benzamidines (*S*)- and (*R*)-HPEBA, which were obtained via the imidoylchloride route, were described as oily compounds and used without any purification. The crystal structure of (*S*)-HPEBA was established by I. Bernal et al. [21], but no new synthesis was mentioned. In 2006 E. Yashima et al. published a new synthesis to HPEBA based on the carbodiimide route. The disadvantage of this new synthesis is a laborious purification of the products by column chromatography [22].

Herein we now report a new and convenient approach to (*S*)- and (*R*)-HPEBA as well as the synthesis of the lithium and potassium derivatives.

2. Results and discussion

2.1. Synthesis of (R)- and (S)-HPEBA

Based on the original synthesis by H. Brunner et al. we developed a significantly modified procedure to (*R*)- (**1a**) and (*S*)-HPEBA (**1b**) (Scheme 4). In the first step benzoylchloride (**2**) was treated with enantiomerically pure (*R*)- or (*S*)-1-phenylethylamine to give (*R*)- or (*S*)-*N*-(1-phenylethyl)benzamide (**3**) in good yield. Further

* Corresponding author. Tel.: +49 721 608 6117; fax: +49 721 608 4858.
E-mail address: roesky@kit.edu (P.W. Roesky).

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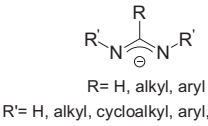
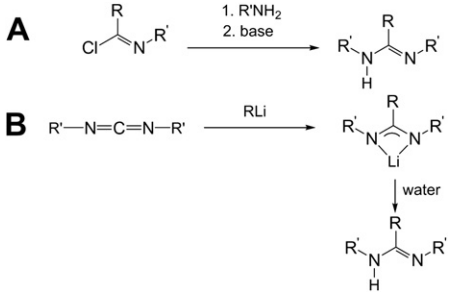


Scheme 1. The amidinate anion.

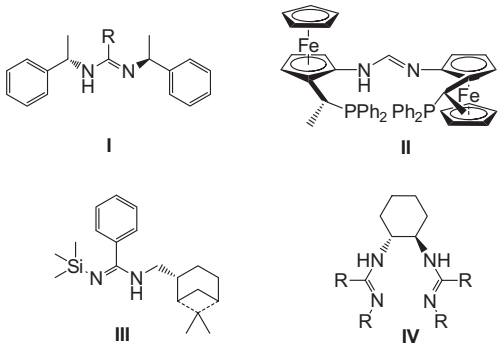
reaction of **3** with oxalylchloride and lutidine in CH_2Cl_2 resulted in (*R*)- or (*S*)-*N*-(1-phenylethyl)benzimidoylchloride (**4**). The second step is based on a method published by R. F. Cunico et al. [23]. The standard procedure chlorinating agents, which are either PCl_5 or thionylchloride, resulted in a significant amount of by-products, which hampers purification of the final product [23,24]. In the third step compound **4** was heated in toluene with (*R*)- or (*S*)-1-phenylethylamine to give the adducts (*R*)- or (*S*)-HPEBA·HCl as an oily compound, which was transformed to **1a,b** by treatment with $NaHCO_3$. After crystallization from ethanol **1a,b** were isolated as analytical pure crystals. Both compounds were obtained as enantiomeric pure products, which have been characterized by standard analytical/spectroscopic techniques. The results are in agreement with the data available from the literature [22].

As a result of the (*Z*)/(*E*) isomerism and tautomerism the NMR spectra of compounds **1a,b** are complex and strongly depend on the nature of the solvent used and the measuring temperature. For **1a,b** only broad and non-characteristic signals were observed in the ^{1}H NMR spectrum by using $CDCl_3$ as solvent (Fig. 1). In contrast, by measuring **1a,b** in d_6-DMSO the proton exchange rate is slowed down and the expected set of signals can be observed (Fig. 1) [25]. Two sets of signals are seen for the methyl (δ(d_6-DMSO) = 5.16, 4.06 ppm) and the methine groups (δ(d_6-DMSO) = 1.40, 1.20 ppm) in the ^{1}H NMR spectrum. The low field shifted set of signals can be assigned to the substituent forming the Schiff-base function. Consistent with these observations are the four signals observed in the ^{13}C{^{1}H} NMR spectrum for the aliphatic carbon atoms (δ(d_6-DMSO) = 57.2, 50.1, 27.3, 23.6 ppm).

The solid state structure of compound **1a** was also established by single crystal X-ray diffraction (Fig. 2). Compound **1a** crystallizes in the orthorhombic space group $P2_12_12_1$ having four molecules of **1a** in the unit cell. The data is consistent with the earlier published single crystal X-ray structure of the enantiomer **1b** [21]. Therefore only a brief structural discussion is given here. **1a** crystallizes in a *E-syn* configuration, which is typical for amidines in the solid state [26,27]. The imine (C1–N1 1.276(2) Å) and the amine bond length (C1–N2 1.374(2) Å) are in the expected range observed for amidines [13]. The N1–C1–N2 bond angle (119.7(2)°) is almost ideal for an sp^2 hybridized carbon atom. The N2–C1–C2–C3 torsion angle between the central phenyl group and the heteroallylic NCN unit is 66.7(2)°. This value, which is typical for benzamidines, shows that there is not a conjugated system between the aromatic ring and the



Scheme 2. Imidoylchloride (A) and carbodiimide route (B) leading to amindines and amidinates.



Scheme 3. Known chiral amidines.

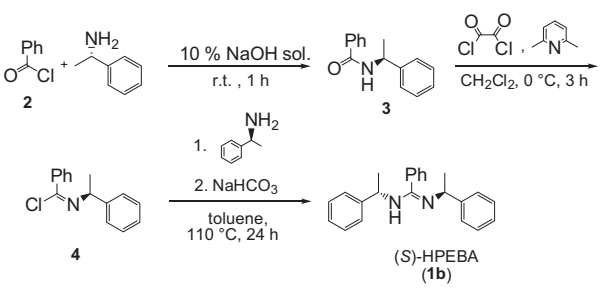
heteroallylic NCN unit. As a result of the steric demand of the phenyl rings a dimerization via hydrogen bonds is prevented [27].

2.2. Metal complexes

The reaction of **1b** with a slight excess of *n*-butyl lithium in THF resulted in the metallated compound lithium-*N*,*N*′-bis-((*S*)-1-phenylethyl)benzamidinate ((*S*)-LiPEBA) (Scheme 5). (*S*)-LiPEBA was isolated as an orange-red solid, which was characterized by standard analytical/spectroscopic techniques. As a result of the deprotonation, the symmetry of (*S*)-LiPEBA increases in comparison to the starting material **1b** in solution. Thus only one set of signals is observed for the phenylethyl substituent. In compound (*S*)-LiPEBA both methine protons are homotop giving only one signal at δ = 4.32 ppm in the ^{1}H NMR spectrum. Consequently only one doublet is seen for the methyl groups at δ = 1.41 ppm (^3J = 6.5 Hz).

Treatment of **1b** with potassium hydride in boiling THF afforded the corresponding potassium salt (*S*)-KPEBA in high yields as an orange solid (Scheme 6). In comparison with many other deprotonation reactions the appropriate reaction temperature for the synthesis of (*S*)-KPEBA is essential. Running the reaction at room temperature did not result in a complete conversion and afforded a sticky product, which was a mixture of **1b** and (*S*)-KPEBA. In contrast by performing the reaction in boiling toluene a fast racemization was observed. This observation is not very surprising because enantiomeric pure 1-phenyletyhlamine undergoes racemization in the presence of catalytic amounts of sodium amide or sodium hydride within minutes in the temperature range of 70–150 °C [28].

(*S*)-KPEBA has been characterized by standard analytical/spectroscopic techniques. The signals in the ^{1}H NMR spectrum of (*S*)-KPEBA are slightly broader at room temperature than those of (*S*)-LiPEBA. The signals of the methyl (δ = 4.22 ppm) and the methine group (δ = 1.30 ppm) of (*S*)-KPEBA are slightly upfield



Scheme 4. Synthesis of (*S*)-HPEBA (**1b**).