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Synthesis of enantiomeric pure lithium and potassium benzamidinate complexes

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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

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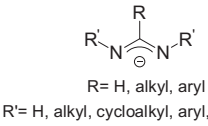
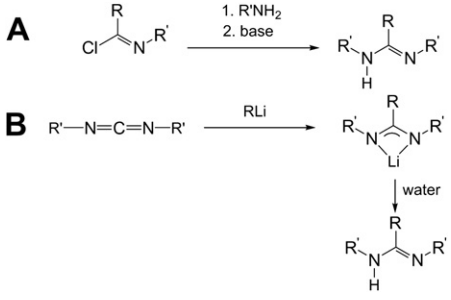


Scheme 1. The amidinate anion.

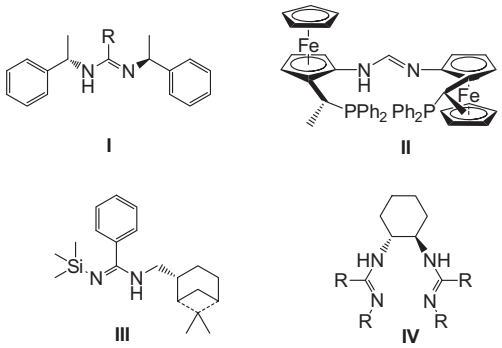
reaction of **3** with oxalylchloride and lutidine in CH_2Cl_2 resulted in (*R*)- or (*S*)-*N*-(1-phenylethyl)benzimidoylchloride (**4**). The second step is based on a method published by R. F. Cunico et al. [23]. The standard procedure chlorinating agents, which are either PCl_5 or thionylchloride, 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.

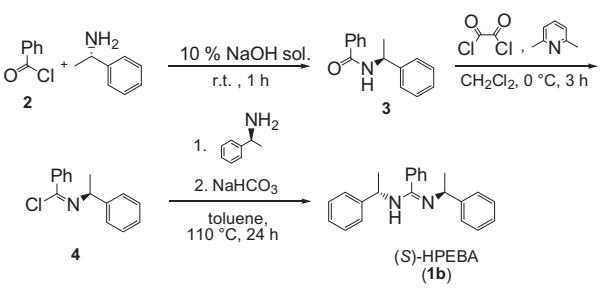
heteroallylic NCN unit. As a result of the steric demand of the phenyl rings a dimerization via hydrogen bonds is prevented [27].

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**).

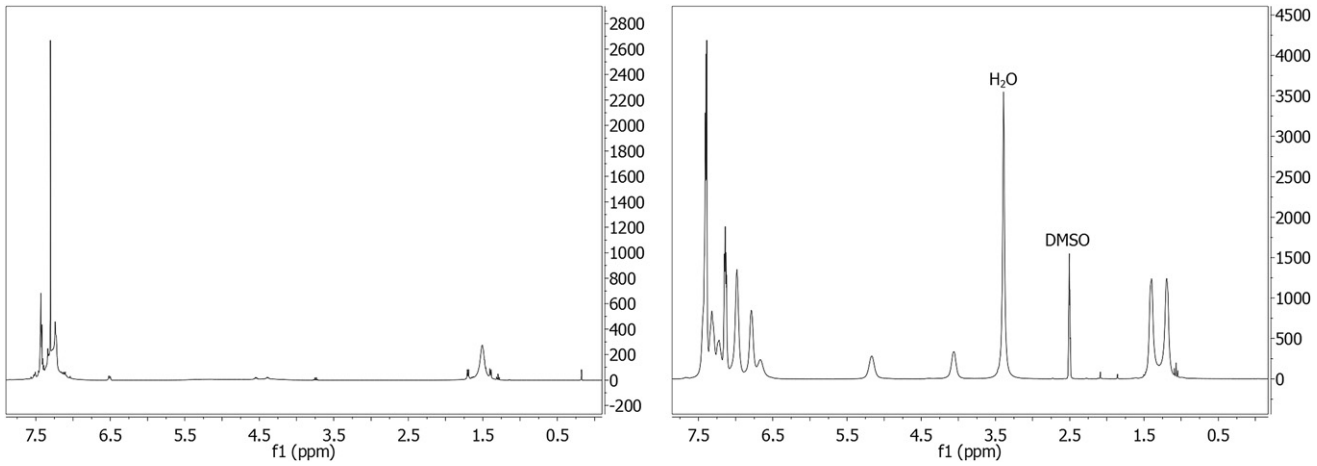


Fig. 1. ^{1}H NMR spectrum of HPEBA in $CDCl_3$ (left) and d_6-DMSO (right).

shifted in comparison to (*S*)-LiPEBA, whereas similar chemical shifts are observed in the $^{13}C\{^{1}H\}$ NMR for both groups (*C*H: δ = 57.2 ppm; CH_3: δ = 22.3 ppm (KPEBA)).

Single crystals of racemic KPEBA ((*rac*)-KPEBA) could be obtained from a toluene/*n*-pentane mixture (Fig. 3). The solid state structure of (*rac*)-KPEBA was established by single crystal X-ray diffraction. (*rac*)-KPEBA crystallizes in the monoclinic space group $P2_1/n$ having four molecules of (*rac*)-KPEBA and four molecules of toluene in the unit cell. In the solid state (*rac*)-KPEBA forms a dimer, in which all four nitrogen atoms form a plane. In the center of this plane a crystallographic inversion center is observed. The potassium atoms, which coordinate to both amidinate ligands in a μ–η^2:η^2 fashion, are symmetrically localized above and below the plane having a K–K′ distance of 3.352(2) Å, which is twice the amount of the ion radius of an eight fold coordinated potassium cation (1.65 Å) [29]. The K–N bond distances of K–N1 2.831(4) Å and K–N2 2.830(4) Å show the symmetric coordination of the potassium atoms. The observed bond distances and angles of the amidinate ligand are in agreement with published data [30–32]. The C–N bond distances within the amidinate ligand are identical within the error range (C1–N1 1.334(5) Å and C1–N2 1.336(5) Å). The N1–C1–N2 angle of 117.2(4)° is about 2° smaller than in **1a**. The N2–C1–C2–C3 torsion angle between the central phenyl group and the heteroallylic NCN unit is 96.6(2)°. This value shows that there is not a conjugated system between the aromatic ring and the heteroallylic NCN unit.

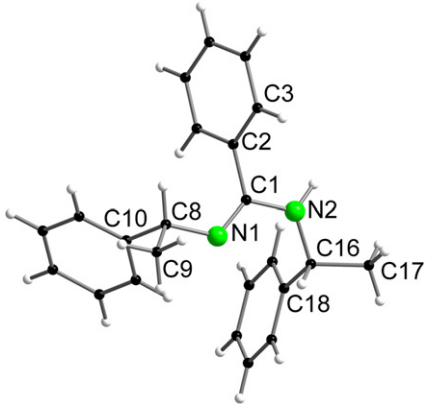


Fig. 2. Solid state structure of **1a**. Selected bond lengths [Å] or angles [°]: N1–C1 1.276 (2), N1–C8 1.457(2), C1–N2 1.374(2), C1–C2 1.500(2), N2–C16 1.454(2), C8–C10 1.518 (3), C8–C9 1.528(3), C16–C17 1.517(3), C16–C18 1.521(3); C1–N1–C8 119.62(14), N1–C1–N2 119.7(2), N1–C1–C2 127.3(2), N2–C1–C2 113.0(2), C1–N2–C16 120.9(2), N1–C8–C10 110.29(14), N1–C8–C9 108.88(15), C10–C8–C9 110.5(2), N2–C16–C17 108.8(2), N2–C16–C18 112.95(14), C17–C16–C18 111.9(2); N2–C1–C2–C3 66.7(2).

Usually potassium amidinates and guanidinates either crystallize with no coordinated solvent molecules or with donor solvents such as THF coordinated to the metal atom [11,30–33]. In some cases polymeric chains are formed [30]. Formamidinates were reported to form *N*:η^6-aryl-coordinated potassium compounds [34,35]. In (*rac*)-KPEBA a toluene molecule is η^6-coordinated to each potassium atom. In this discussion we consider all C–K interactions up to a value of 3.6 Å as bonds, which is a conservative limit for K–C interactions [36,37]. The K–C distances range from 3.349(8)–3.554(7) Å. The difference in the bond distances are a result of a slightly asymmetric coordination of the toluene ring. Moreover, the potassium atoms are also π-coordinated by one carbon atom (C19) of a phenyl ring of the phenylethyl substituents. The K–C19 bond distance of 3.555(8) Å, which is not shown in Fig. 3, indicates a η^1-coordination of the phenyl rings.

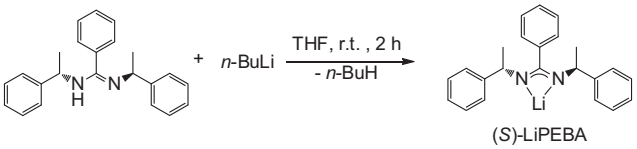
3. Summary

In summary we have developed a new synthesis, which gave the chiral amidines (*S*,*S*)- and (*R*,*R*)-*N*,*N*-bis-(1-phenylethyl)benzamidine ((*S*)- and (*R*)-HPEBA) in good yields. 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 (*rac*)-KPEBA forms a dimer, in which all four nitrogen atoms are in a plane. To each potassium atom a toluene molecule is η^6-coordinated.

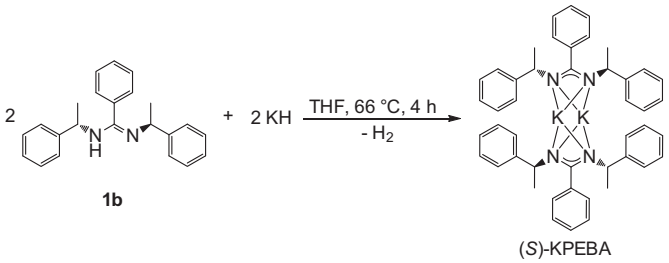
4. Experimental section

4.1. General

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried



Scheme 5. Synthesis of (*S*)-LiPEBA.



Scheme 6. Synthesis of (*S*)-KPEBA.

Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high vacuum (10^{-3} torr) line, or in an argon-filled MBraun glove box. THF was distilled under nitrogen from potassium benzophenone ketyl prior to use. Hydrocarbon solvents (toluene and *n*-pentane) were dried using an MBraun solvent purification system (SPS-800). All solvents for vacuum line manipulations were stored *in vacuo* over $LiAlH_4$ in resealable flasks. Deuterated solvents were obtained from Aldrich (99 atom % D). NMR spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane. IR spectra were obtained on a Bruker Tensor 34. Mass spectra were recorded at 70 eV on a Finnigan MAT 8200. Elemental analyses were carried out with an Elementar vario EL. Optical rotation was measured on a Jasco P2000.

4.2. (*R*)- and (*S*)-*N*-(1-Phenylethyl)benzamide (**3**)

To a reaction mixture of 10.00 mL (9.40 g, 78 mmol) (*R*)- respectively (*S*)-1- phenylethylamine in 80 mL of an aqueous sodium hydroxide solution (10%), 9.46 mL (11.45 g, 81 mmol) benzoylchloride was added dropwise under vigorous stirring. After 1 h of stirring at r.t. the colorless precipitate formed was filtered off, washed several times with water and then dried *in vacuo*. 13.57 g (60 mmol, 78%) of (*R*)- respectively (*S*)-*N*-(1-phenylethyl)benzamide (**3**) were obtained as colorless solid. – ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ (ppm) = 7.69–7.17 (m, 10 H, Ph), 6.47 (br s, 1 H, N*H*), 4.06 (q, ^3J = 6.8 Hz, 1H, C*H*), 1.49 (d, ^3J = 6.8 Hz, 3H, CH_3). – ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 23 °C): δ (ppm) = 166.6 (*C*O), 143.1 (*i*-Ph), 134.5 (*i*-Ph), 131.4 (Ph), 128.7 (Ph), 128.5 (Ph), 127.3 (Ph), 126.9 (Ph), 126.2 (Ph), 49.2 (*C*H), 21.7 (*C*H$_3$).

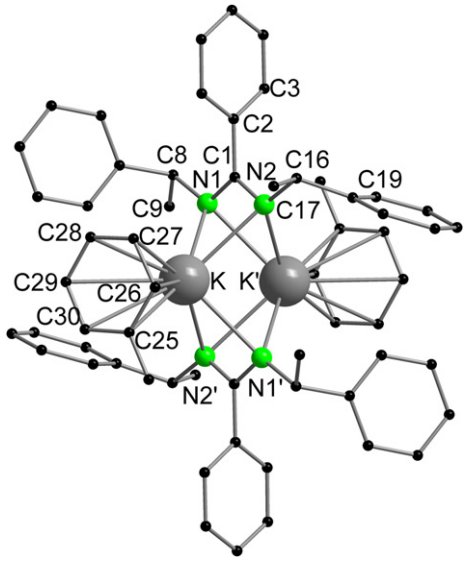


Fig. 3. Solid state structure of (*rac*)-KPEBA, omitting the hydrogen atoms. Selected bond lengths [Å] or angles [°]: C1–N1 1.334(5), C1–N2 1.336(5), C8–N1 1.481(5), C8–C9 1.527(7), C16–N2 1.465(5), C16–C17 1.516(7), K–N1 2.831(4), K–N2 2.830(4), C19–K 3.555(8), C25–K 3.451(7), C26–K 3.349(8), C27–K 3.381(10), C28–K 3.436(10), C29–K 3.530(9), C30–K 3.554(7), K–K′ 3.352(2); N1–C1–N2 117.2(4), N1–C1–C2 121.7(4), N2–C1–C2 121.1(4), N1–C1–K 63.0(2), N2–C1–K 62.8(2), N1–C8–C9 107.8 (4), C10–C8–C9 110.9(4), N2–C16–C17 109.6(4), C1–N1–C8 119.4(4), C1–N1–K 90.0 (2), C8–N1–K 131.0(3), C1–N2–C16 120.1(4), C1–N2–K 92.4(2), C16–N2–K 133.4(3), N2–K–N2 107.30(9), N1–K–N1 107.41(9).

4.3. (*R*)- and (*S*)-*N*-(1-Phenylethyl) benzimidoylchloride (**4**)

A mixture of **3** and 11.65 mL (10.71 g, 100 mmol) of 2,6-lutidine was dissolved in 150 mL of dry CH_2Cl_2 and cooled to 0 °C. 5.17 mL (7.65 g, 60 mmol) oxalylchloride, dissolved in 50 mL dry CH_2Cl_2, was slowly added dropwise to the reaction mixture within an hour. The color of the reaction mixture turned to reddish-brown. The mixture was stirred for 30 min at 0 °C and after warming up to r.t. stirred for another 30 min. The volatile components were removed *in vacuo*. 150 mL dry *n*-pentane was added to the dark brown residue and stirred for 1 h. The suspension was filtered and the volatile components of the filtrate were removed under vacuum. The resulting brown oil was distilled *in vacuo* at 130–140 °C ($2.1\cdot10^{-1}$ mbar) to obtain 9.55 g (39 mmol, 65%) of light yellow (*R*)- respectively (*S*)-*N*-(1-phenylethyl) benzimidoylchloride (**4**). – ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ (ppm) = 7.94–7.10 (m, 10 H, Ph), 6.99 (br s, 1 H, N*H*), 5.05 (q, ^3J = 6.6 Hz, 1 H, C*H*), 1.44 (d, ^3J = 6.6 Hz, 3 H, CH_3). – ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 23 °C): δ (ppm) = 144.1 (*C*Cl), 142.9 (*i*-Ph), 136.0 (*i*-Ph), 131.5 (Ph), 129.3 (Ph), 128.6 (Ph), 128.3 (Ph), 127.2 (Ph), 126.8 (Ph), 63.2 (*C*H), 23.8 (*C*H$_3$).

5. (*R*,*R*)- and (*S*,*S*)-*N*,*N*′-bis-(1-Phenylethyl)benzamidine ((*R*)- and (*S*)-HPEBA) (1a,b)

The imidoylchloride (**4**) was dissolved in 40 mL dry toluene and 5.05 ml (4.75 g, 39 mmol) of (*R*)- respectively (*S*)-1-phenylethylamine was added dropwise. The reaction mixture was refluxed for 12 h. After cooling to −30 °C the solvent was decanted from the highly viscous oil. The oily residue is dried *in vacuo*, dissolved in 100 mL of CH_2Cl_2 and treated with 100 mL of a saturated sodium bicarbonate solution. After 1 h of vigorous stirring, the phases were separated and the water layer was extracted twice with CH_2Cl_2. The combined organic layers were dried over magnesium sulfate, filtered, and then the solvent was removed *in vacuo*. After recrystallization from hot ethanol (*R*)- respectively (*S*)-HPEBA **(1a,b)** were obtained as colorless crystals. – Yield: 7.18 g, 22 mmol, 56% (overall yield: 28%). – ^{1}H NMR (300 MHz, d_6-DMSO, 17 °C): δ (ppm) = 7.42–6.67 (m, 15 H, Ph), 5.16 (br s, 1 H, NC*H*), 4.06 (br s, 1 H, NHC*H*), 1.40 (s, 3 H, NHCH_3), 1.20 (s, 3 H, NHCHCH_3). – ^{13}C{^{1}H} NMR (75 MHz, d_6-DMSO, 17 °C): δ (ppm) = 156.4 (*N*CN), 148.7 (*i*-Ph), 147.5 (*i*-Ph), 136.2 (*i*-Ph), 128.9–126.4 (m, Ph), 57.2 (*N*CH), 50.1 (NH*C*H), 27.3 (NCH*C*H$_3$), 23.6 (NHCH*C*H$_3$). – MS (EI, 70 eV): *m*/*z* (%) = 328 ([M]$^+$, 87), 313 ([M − CH_3]$^+$, 15), 223 ([M − PhEt]$^+$, 94), 209 (M − PhEtN]$^+$, 27), 180 (42), 120 (PhEtN]$^+$, 100), 105 ([PhEt]$^+$, 100), 91 ([Bz]$^+$, 37), 77 ([Ph]$^+$, 92), 56 (68), 41 ([C_2H_3N]$^+$, 64). – IR (ATR): ν (cm^{-1}) = 3405 (w), 3058 (w), 2954 (w), 2917 (w), 1635 (m), 1484 (m), 1447 (m), 1303 (w), 1265 (w), 1141 (w), 1071 (m), 1027 (w), 762 (s), 699 (s), 543 (s). – $C_{23}H_{23}N_2$ (328.45): Calc.: C, 84.11; H, 7.37; N, 8.53; Found: C, 84.33; H, 7.40; N, 8.47. – $[\alpha]_D^{28}$ 58.9° (*c* 0.14, THF) for (*S*)-HPEBA; $[\alpha]_D^{27}$ −53.2° (*c* 0.17, THF) for (*R*)-HPEBA. The data is in agreement with the literature [22]. Mp: 98 °C.

6. Lithium-*N,N′*-bis-((*S*)-1-phenylethyl)benzamidinate ((*S*)-LiPEBA)

3.14 mL (1.6 M in *n*-hexane, 5.02 mmol) *n*-butyl lithium was added dropwise to a solution of 1.50 g (4.57 mmol) (*S*)-HPEBA in 20 mL THF. The mixture was stirred overnight at r.t. The solution turns dark red. The volatile components were removed *in vacuo*. After washing with 20 mL *n*-pentane and drying under vacuum, the product is obtained as an orange solid. – Yield: 1.32 g, 3.96 mmol, 87%. – ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ (ppm) = 7.59–7.37 (m, 4 H, Ph), 7.34–6.98 (m, 11 H, Ph), 4.43–4.21 (m, 2 H, C*H*), 1.41 (d, J = 6.5 Hz, 6 H, CH_3). – ^{13}C{^{1}H}-NMR (101 MHz, C_6D_6, 25 °C): δ (ppm) = 176.2 (NCN), 151.4 (*i*-Ph), 139.6 (*i-Ph*), 129.5 (Ph), 128.7 (Ph), 128.3 (Ph), 128.1 (Ph), 127.6 (Ph), 126.8 (Ph), 57.7 (*C*H), 28.0 (*C*H$_3$). – MS (EI, 70 eV): m/z (%) = 341 ([M]$^+$, 100), 328 ([M – Li]$^+$, 95), 223 ([M-LiPhEt]$^+$, 86), 180 ([M-2Ph]$^+$, 35), 120 ([PhEtN]$^+$, 100), 105 ([PhEt]$^+$, 99), 77 ([Ph]$^+$, 86), 42 ([C_2H_4N]$^+$, 28), 27 ([CHN]$^+$, 9). – IR (ATR): ν (cm^{-1}) = 3058 (w), 2953 (w), 2919 (w), 2875 (w), 1635 (m), 1598 (w), 1484 (m), 1447 (m), 1355 (w), 1303 (w), 1265 (w), 1211 (w), 1141 (w), 1070 (w), 1025 (w), 1006 (w), 907 (w), 762 (m), 699 (s), 599 (w), 571 (w), 542 (w). – $C_{23}H_{23}N_2Li\cdot 2C_4H_8O$ (478.59): Calc.: C, 77.80; H, 8.21; N, 5.85; Found: C, 78.12; H, 7.37; N, 5.93.

6.1. Potassium-N,N′-bis-((S)-1-phenylethyl)benzamidinate ((S)-KPEBA)

1.36 g (4.13 mmol) of (*S*)-HPEBA and 0.20 g (4.95 mmol) of KH were suspended in 20 mL dry THF and refluxed for 3 h. The color of the solution turned to pink. After cooling to r.t. the excess KH was filtered off and the solvent was evaporated under vacuum. Washing with 20 mL of *n*-pentane gave the orange product. The racemic product was synthesized by carrying out the reaction in toluene. Crystals were obtained by layering a toluene solution with *n*-pentane. – Yield: 1.40 g, 3.82 mmol, 93%. – ^{1}H NMR (300 MHz, C_6D_6, 17 °C): δ (ppm) = 7.51–6.82 (m, 15 H, Ph), 4.22 (br s, 2H, C*H*), 1.30 (d, ^3J = 6.3 Hz, 4 H, CH_3). – ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 17 °C): δ (ppm) = 171.8 (NCN), 152.0 (*i*-Ph), 141.7 (*i*-Ph), 128.2 (Ph), 127.8 (Ph), 127.6 (Ph), 126.6 (Ph), 126.1 (Ph), 125.1 (Ph), 57.2 (*C*H), 26.3 (*C*H$_3$). – IR (ATR): ν (cm^{-1}) = 3057 (w), 3024 (w), 2974 (w), 2954 (w), 2918 (w), 2877 (w), 1635 (m), 1598 (w), 1482 (m), 1446 (m), 1364 (w), 1304 (w), 1266 (w), 1211 (w), 1141 (w), 1071 (w), 1027 (w), 1005 (w), 883 (w), 762 (m), 698 (s), 600 (w), 571 (w), 543 (m). – $C_{23}H_{23}N_2K\cdot C_7H_8$ (458.68): Calc.: C, 78.56; H, 6.81; N, 6.11; Found: C, 78.26; H, 6.68; N, 6.21.

6.2. X-ray crystallographic studies of **1a** and (rac)-KPEBA

Crystals of **1a** were grown from ethanol. Crystals of (*rac*)-KPEBA were obtained from toluene/*n*-pentane. A suitable crystal of compounds **1a** and (*rac*)-KPEBA was covered in mineral oil (Aldrich) and mounted onto a glass fiber. The crystal was transferred directly to the −73 °C or −123 °C N_2 cold stream of a Stoe IPDS II diffractometer. Subsequent computations were carried out on a Pentium Core2Duo.

All structures were solved by direct methods (SHELXS-97 [38]). The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F^2, minimizing the function $(F_o-F_c)^2$, where the weight is defined as $4F_o^2/2(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes using the program SHELXL-97 [38]. Carbon-bound hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded. The hydrogen atom contributions of all compounds were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance.

Crystal data for **1b**: $C_{23}H_{24}N_2$, M = 328.44, orthorhombic, a = 8.2244(9) Å, b = 12.3838(11) Å, c = 18.916(3) Å, α = 90.00°, β = 90.00°, γ = 90.00°, V = 1926.6(4) Å^3, T = 200(2) K, space group $P2_12_12_1$, Z = 4, μ(MoKα) = 0.066 mm^{-1}, 5355 reflections measured, 3384 independent reflections (R_{int} = 0.0298). The final R_1 values were 0.0387 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0825 (all data). The goodness of fit on F^2 was 0.918. Flack parameter = 0(3).

Crystal data for (*rac*)-KPEBA: $C_{46}H_{46}K_2N_4\cdot 2(C_7H_8)$, M = 917.34, monoclinic, a = 12.786(3) Å, b = 13.424(3) Å, c = 15.821(3) Å, α = 90.00°, β = 105.36(3)°, γ = 90.00°, V = 2618.5(9) Å^3, T = 200(2) K, space group $P2_1/n$, Z = 2, μ(MoKα) = 0.222 mm^{-1}, 76916 reflections measured, 7100 independent reflections ($R_{\rm int}$ = 0.2436). The final R_1 values were 0.1304 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.2366 (all data). The goodness of fit on F^2 was 1.215.

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Appendix. Supplementary material

Positional parameters, hydrogen atom parameters, thermal parameters, bond distances and angles have been deposited as supporting information. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. CCDC-779939 and CCDC-779940. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +(44)1223-336-033; email: deposit@ccdc.cam.ac.uk; website: www.ccdc.cam.ac.uk/data_request/cif).

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