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Linked bis(β-diketiminato) yttrium and lanthanum complexes as catalysts in asymmetric hydroamination/cyclization of aminoalkenes (AHA)

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Linked bis(β-diketiminato) rare-earth metal complexes based on the ethylene-bridged ligand $[C_2H_4(BDI^{DClP})_2]H_2$ [DClP = 2,6-$Cl_2C_6H_3$] and the cyclohexyl-bridged ligands $[Cy(BDI^{Ar})_2]H_2$ [Ar = PMP (= *p*-$MeOC_6H_4$), Mes (= 2,4,6-$Me_3C_6H_2$), DIPP (= 2,6-*i*$Pr_2C_6H_3$)] were prepared via amine elimination starting from $[Ln\{N(SiMe_3)_2\}_3]$ (Ln = La, Y). The three cyclohexyl-bridged complexes $[\{(R,R)\text{-}Cy(BDI^{Mes})_2\}YN(SiMe_3)_2]$ ((*R*,*R*)-**3**), $[\{(R,R)\text{-}Cy(BDI^{Mes})_2\}LaN(SiMe_3)_2]$ ((*R*,*R*)-**4**), and $[\{(R,R)\text{-}Cy(BDI^{DIPP})_2\}LaN(SiMe_3)_2]$ ((*R*,*R*)-**5**) were obtained enantiomerically pure. The X-ray crystal structure analysis of the racemic variants of **3** and **4** revealed a distorted square pyramidal coordination geometry around the rare-earth metal, in which the amido ligand occupies the apical position and the two linked β-diketiminato moieties form the basis. The two aromatic substituents adopt a *transoid* arrangement and both β-diketiminato moieties are bound in a η^5 coordination mode with close Ln···C contacts. Due to the smaller ionic radius of yttrium vs. lanthanum, the front side of the yttrium complex **3** is sterically more hindered than in the lanthanum complex **4**, but there is much more empty coordination space on the rear side, which may rationalize the observed differences in selectivity of **3** in comparison to **4**. The catalytic efficiency of the β-diketiminato complexes was strongly affected by steric factors such as ionic radius of the metal and the steric bulk of the aryl substituents, which is an indication for highly steric encumbered catalytic species. The complexes displayed good to moderate catalytic activity in the hydroamination/cyclization of aminoalkenes depending on the steric hindrance around the metal center. The sterically most demanding diisopropylphenyl-substituted complex (*R*,*R*)-**5** displayed significantly higher enantioselectivities (up to 76% ee), but lower catalytic activity in comparison to the sterically more open mesityl-substituted complex (*R*,*R*)-**4**. The smaller yttrium metal center in complex (*R*,*R*)-**3** led to reduced activity as well as a reversal in enantioselectivity, which may be rationalized by a change of the approach of the alkene moiety to the Ln-amido bond in the cyclization transition state.

1. Introduction

The hydroamination is a highly atom economical process in which an amine N–H bond is added to an unsaturated carbon–carbon bond. This reaction is of great potential interest for the waste-free synthesis of basic and fine chemicals, pharmaceuticals and other industrially relevant building blocks starting from inexpensive precursors [1,2].

Intensive research efforts from a growing number of research group has led to the development of a variety of catalytic systems based on alkali or alkaline-earth metals [2a,3], early (group 3–5, as well as lanthanides and actinides) [2c–f,h,j,l] and late (group 8–10) [2b,g,i,k] transition metals. Rare-earth metal-based catalysts [4], pioneered by Marks and co-workers [2f,5], are still among the most reactive and versatile systems.

The generation of new stereogenic centers during the hydroamination process is an attractive application of this reaction and the asymmetric hydroamination has found increased interest in recent years [6], in particular for catalyst systems facilitating the enantioselective cyclization of aminoalkenes [5b–e,7–9]. Most of these chiral catalyst systems have C_2-symmetry, while the number of catalysts with C_1-symmetry is rather limited [5b,e,8e,9e].

We have previously investigated various C_1 symmetric linked bis(β-diketiminato) rare-earth metal complexes [10–12] as catalysts in the epoxide/CO_2-copolymerization and the catalytic activity of related group IV metal complexes in ethylene polymerization was recently reported [13,14]. Herein we want to disclose the catalytic activity of these linked bis(β-diketiminato) rare-earth

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metal complexes in hydroamination/cyclization reactions and their effectiveness to perform enantioselective reactions.

2. Results and discussion

2.1. Synthesis of linked bis(β-diketiminato) lanthanum and yttrium complexes

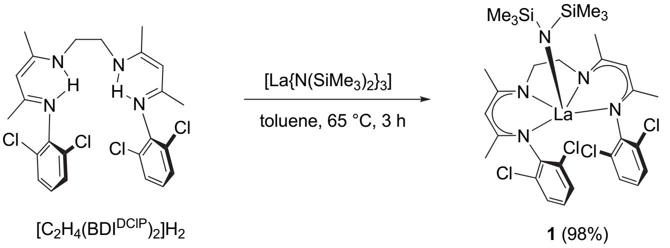
2.1.1. Synthesis of linked bis(β-diketiminato) ligands

As reported previously [10], various linked bis(β-diketiminato) ligands can be prepared through a two-step standard condensation route (Scheme 1). Reaction of 2,4-pentadione and an aniline derivative yields a β-enaminoketone. The carbonyl function of this intermediate was activated using Meerwein's salt, $[Et_3O]^+[BF_4]^-$, in order to introduce the ethylenediamine or *trans*-cyclohexane-1,2-diamine linkers. Thus, utilization of resolved *trans*-(*R*,*R*)-1,2-diaminocyclohexane provides access to the enantiomerically pure ligands $[(R,R)\text{-Cy}(BDI^{Mes})_2]H_2$ and $[(R,R)\text{-Cy}(BDI^{DIPP})_2]H_2$. The two new ligands $[C_2H_4(BDI^{DClP})_2]H_2$ (DClP = 2,6-$Cl_2C_6H_3$) and $[Cy(BDI^{PMP})_2]H_2$ (PMP = *p*-$MeOC_6H_4$) were prepared to probe the electronic influence of the aromatic substituent on catalytic activity.

2.1.2. Complex synthesis and structural characterization

The rare-earth metal complexes are most conveniently prepared via amine elimination starting from the homoleptic trisamide $[Ln\{N(SiMe_3)_2\}_3]$ (Ln = La, Y). While the reaction of the sterically less hindered trisamide $[Ln\{N(SiHMe_2)_2\}_3(THF)_2]$ proceed generally under milder reaction conditions [10b], the resulting bis(dimethylsilyl)amido complexes were considered less suitable for catalytic hydroamination. Previous studies [7b,15] have shown that bis(dimethylsilyl)amido complexes require higher reaction temperatures and only a fraction of the complex is catalytically active during the reaction. This hampered catalyst activation is a result of the lower basicity of the bis(dimethylsilyl)amido ligand (pK_a $[HN(SiHMe_2)_2] = 22.8$ [16a]) compared to the bis(trimethylsilyl)amido ligand (pK_a $[HN(SiMe_3)_2] = 25.8$ [16b]).

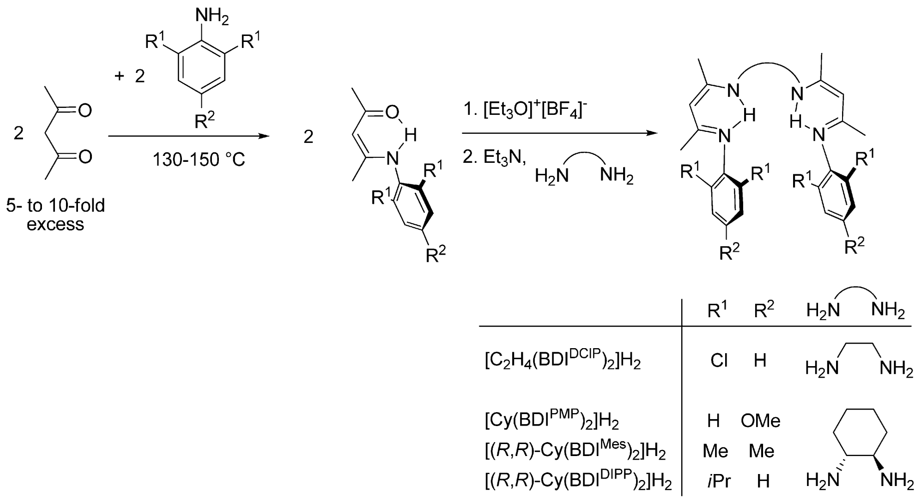
The reaction of the 2,6-dichlorophenyl-substituted ethylene-linked bis(β-diketiminato) ligand $[C_2H_4(BDI^{DClP})_2]H_2$ with $[La\{N(SiMe_3)_2\}_3]$ proceeded cleanly at 65 °C in toluene within 3 h to produce **1** in high yield (Scheme 2). In agreement to previously characterized ethylene-linked bis(β-diketiminato) rare-earth metal complexes [10], the ^1H and ^{13}C NMR spectra of complex **1** are in accordance with a C_s symmetric structure in solution on the NMR time scale. The $SiCH_3$ groups and the methine proton of the β-diketiminato ligand each give rise to one signal and the ethylene protons are split into two AA′BB′ doublets of triplets in the ^1H NMR spectrum.



Scheme 2.

As noted previously [10], the reactions of the more rigid cyclohexyl-bridged ligands require commonly harsher reaction conditions than the corresponding ethylene-bridged ligands. The reaction conditions also depend significantly on the steric demand of the aromatic substituent and the size of the rare-earth metal. The reaction of the sterically least hindered *p*-methoxyphenyl-substituted racemic ligand $[Cy(BDI^{PMP})_2]H_2$ with $[La\{N(SiMe_3)_2\}_3]$ proceeded readily in refluxing hexanes within 2 h to form *rac*-**2** in 68% yield (Scheme 3). The sterically more congested mesityl- and 2,6-diisopropylphenyl-substituted ligands required increasingly higher reaction temperatures to form the corresponding lanthanum complexes. The enantiopure complexes (*R*,*R*)-**4** (toluene, 100 °C, 6 h) and (*R*,*R*)-**5** (toluene, 110 °C, 9 d) were prepared using slightly higher reaction temperatures in comparison to the synthesis of their racemic counterparts [10] in order to improve the yield. The smaller yttrium was less reactive than lanthanum and the reaction of $[(R,R)\text{-Cy}(BDI^{Mes})_2]H_2$ with $[Y\{N(SiMe_3)_2\}_3]$ required significant harsher reaction conditions and longer reaction times to generate (*R*,*R*)-**3** (toluene, 120 °C, 8 d). The complexation of yttrium was also aided by the addition of two equiv of THF, although the product was isolated as a THF-free complex.

The ^1H and ^{13}C NMR spectra of the cyclohexyl-bridged complexes (*R*,*R*)-**4** and (*R*,*R*)-**5** are identical to their racemic counterparts [10]. The spectra of the yttrium complex (*R*,*R*)-**3** are in accordance with a C_1 symmetric structure in solution at room temperature based on the observation of two different β-diketiminato groups and two diastereotopic aromatic rings. However, the



Scheme 1.