

Rare earth metal complexes based on β -diketiminato and novel linked bis(β -diketiminato) ligands: Synthesis, structural characterization and catalytic application in epoxide/ CO_2 -copolymerization

Daniela V. Vitanova, Frank Hampel, Kai C. Hultzsch *

Institut für Organische Chemie, Friedrich-Alexander Universität Erlangen-Nürnberg, Henkestr. 42, D-91054 Erlangen, Germany

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Abstract

Mesityl substituted β -diketiminato lanthanum and yttrium complexes $[(\text{BDI})\text{Ln}\{\text{N}(\text{SiRMe}_2)\}_2]$ ($\text{BDI} = \text{ArNC}(\text{Me})\text{CHC}(\text{Me})\text{-NAr}$, $\text{Ar} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$, $\text{Ln} = \text{La}$, $\text{R} = \text{Me}$ (**1**), H (**2a**); $\text{Ln} = \text{Y}$, $\text{R} = \text{H}$ (**2b**)) can be prepared via facile amine elimination starting from $[\text{La}\{\text{N}(\text{SiMe}_3)_2\}_3]$ and $[\text{Ln}\{\text{N}(\text{SiHMe}_2)_2\}_3(\text{THF})_2]$ ($\text{Ln} = \text{Y}$, La), respectively. The X-ray crystal structure analysis of **1** revealed a distorted tetrahedral geometry around lanthanum with a η^2 -bound β -diketiminato ligand. A series of novel ethylene- and cyclohexyl-linked bis(β -diketiminato) ligands $[\text{C}_2\text{H}_4(\text{BDI}^{\text{Ar}})_2]\text{H}_2$ and $[\text{Cy}(\text{BDI}^{\text{Ar}})_2]\text{H}_2$ [$\text{Ar} = \text{Mes}$ ($=2,4,6\text{-Me}_3\text{C}_6\text{H}_2$), DEP ($=2,6\text{-Et}_2\text{C}_6\text{H}_3$), DIPP ($=2,6\text{-i-Pr}_2\text{C}_6\text{H}_3$)] were synthesized in a two step condensation procedure. The corresponding bis(β -diketiminato) yttrium and lanthanum complexes were obtained via amine elimination. The X-ray crystal structure analysis of the ethylene-bridged bis(β -diketiminato) complex $[\{\text{C}_2\text{H}_4(\text{BDI}^{\text{Mes}})_2\}\text{YN}(\text{SiMe}_3)_2]$ (**3b**) and cyclohexyl-bridged complexes $[\{\text{Cy}(\text{BDI}^{\text{Mes}})_2\}\text{LaN}(\text{SiHMe}_2)_2]$ (**7**) and $[\{\text{Cy}(\text{BDI}^{\text{DEP}})_2\}\text{LaN}(\text{SiMe}_3)_2]$ (**8**) 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 geometry of the bis(β -diketiminato) ligands depends significantly on the linker unit. While complexes with an ethylene-linked ligand adopt a *cisoid* arrangement of the two aromatic substituents, complexes with cyclohexyl linker adopt a *transoid* arrangement. Either one (**3b**) or both (**7**, **8**) of the β -diketiminato moieties are tilted out of the η^2 coordination mode, resulting in close $\text{Ln} \cdots \text{C}$ contacts. The β -diketiminato and linked bis(β -diketiminato) complexes were moderately active in the copolymerization of cyclohexene oxide with CO_2 . A maximum of 92% carbonate linkages were obtained using the ethylene-bridged bis(β -diketiminato) complex $[\{\text{C}_2\text{H}_4(\text{BDI}^{\text{Mes}})_2\}\text{LaN}(\text{SiHMe}_2)_2]$ (**4**).

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1. Introduction

The organometallic chemistry of the rare earth elements has attracted significant attention in particular due to their high catalytic activity for a wide range of organic transformations [1] and polymerizations [2]. An increasingly important field of research focuses on the

development of non-metallocene catalyst systems [3]. Non-cyclopentadienyl ligands can be easily modified in their electronic and steric properties, allowing facile catalyst tuning.

The utilization of CO_2 as a C1 feedstock is an appealing goal in contemporary catalysis research, because CO_2 is naturally abundant, inexpensive, nontoxic and non-flammable [4]. In particular, the metal-catalyzed copolymerization of CO_2 and epoxides has been studied extensively, because the resulting polycarbonates are biodegradable polymers with attractive material properties

* Corresponding author. Fax: +49 9131 8526865.

E-mail address: hultzsch@chemie.uni-erlangen.de (K.C. Hultzsch).

[5]. Homogeneous catalyst systems based on β -diketiminato zinc [5d,6] and salen chromium [5b,7] complexes are most prominent examples of recent developments.

Despite their wide application in polymerization catalysis, there has been no example of a well-defined homogeneous rare earth metal based catalyst system for the epoxide/ CO_2 copolymerization. Only some ill-defined ternary catalyst systems, consisting of a rare earth metal carboxylate, a zinc or aluminum alkyl and glycerol, have been reported [8]. The role of the rare earth metal in these systems is not clear at present, because most of these systems are also active in the absence of the rare earth metal. Furthermore, it was reported that ytterbium naphthalide, an insoluble compound, produces a small amount of polycarbonate besides the cyclic carbonate main product [9]. Interestingly, rare metal complexes are well known to activate epoxides [10] and CO_2 [11,12], therefore the lack of a well-defined homogeneous rare earth metal based epoxide/ CO_2 copolymerization catalyst system seemed rather astonishing to us.

We came to the conclusion that the most promising candidates for homogeneous rare earth metal based epoxide/ CO_2 copolymerization catalyst systems would utilize β -diketiminato ligands [13], in analogy to highly active β -diketiminato zinc complexes. β -Diketiminato rare earth metal complexes have been prepared via salt metathesis [14]. However, for practical synthetic reasons we decided to utilize the more convenient single-step amine elimination route [15].

In this paper, we report the synthesis and structural characterization of β -diketiminato and novel linked bis(β -diketiminato) rare earth metal complexes [16,17] as well as their application in the copolymerization of CO_2 and cyclohexene oxide.

2. Results and discussion

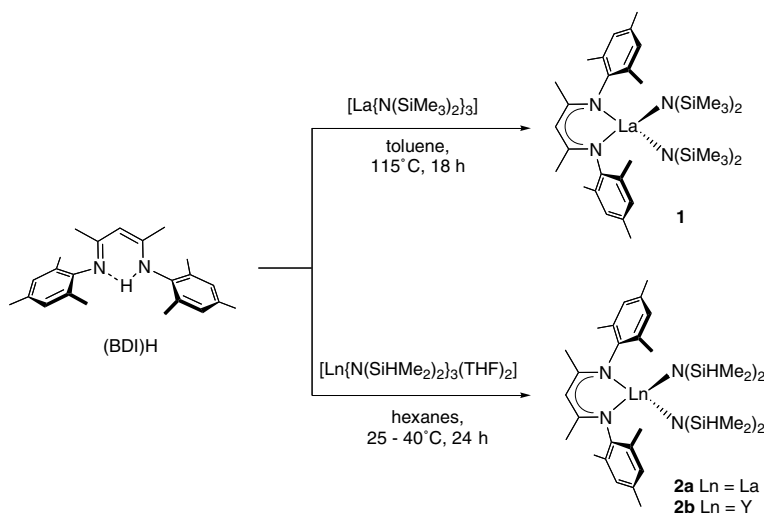
2.1. Synthesis of β -diketiminato complexes

The mesityl substituted β -diketiminato ligand (BDI)H reacted selectively with $[\text{La}\{\text{N}(\text{SiMe}_3)_2\}_3]$ [18] at 115°C within 18 h to yield the mono β -diketiminato complex **1** in 98% yield (Scheme 1). Reactions with the sterically less hindered and more reactive $[\text{Ln}\{\text{N}(\text{SiHMe}_2)_2\}_3(\text{THF})_2]$ ($\text{Ln} = \text{Y}, \text{La}$) [19] could be performed under significant milder conditions (25°C for La, 40°C for Y). The bis(dimethylsilyl)amido complexes **2a** and **2b** were obtained free of coordinated THF.

Attempts to synthesize analogous 2,6-diisopropylphenyl substituted β -diketiminato complexes were plagued by very slow reactions at high temperatures (65 – 95°C) and incomplete conversion, even when the more reactive trisamido complexes $[\text{Ln}\{\text{Ni-Pr}_2\}_3(\text{THF})_2]$ ($\text{Ln} = \text{Y}, \text{La}$) [20] were employed. Furthermore, in the reaction of $[\text{La}\{\text{Ni-Pr}_2\}_3(\text{THF})_2]$ with either β -diketiminato ligand an inseparable mixture of products was formed, most likely mono and bis(β -diketiminato) complexes. The yttrium aryl complex $[\text{Y}(o\text{-C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_3]$ was also unsuccessfully applied in complex synthesis, no β -diketiminato complexes were formed and only decomposition of the yttrium aryl starting material was observed.

The ^1H and ^{13}C NMR spectra of complexes **1**, **2a** and **2b** are in agreement with a C_{2v} symmetric structure, giving rise to a single signal for the SiCH_3 groups and one signal for the *ortho* methyl groups on the mesityl substituents.

The high solubility of complexes **1**, **2a** and **2b** in aromatic and aliphatic solvents suggested a monomeric structure, which was confirmed for complex **1** via X-ray diffraction analysis. Suitable pale yellow crystals of



Scheme 1.

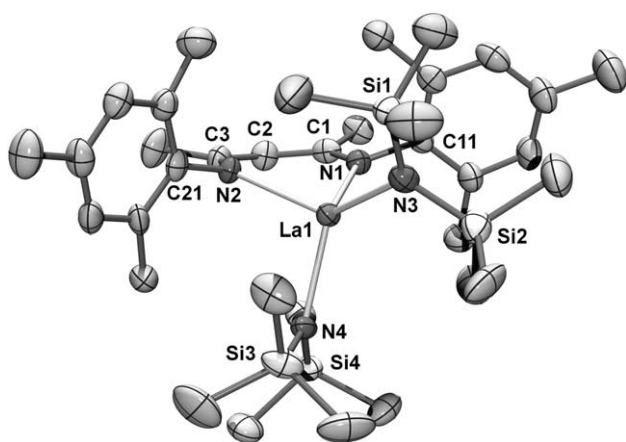


Fig. 1. ORTEP diagram of the molecular structure of one of the two independent molecules of **1**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for the sake of clarity.

1 were obtained by cooling of a concentrated pentane solution to $-20\text{ }^{\circ}\text{C}$. An ORTEP diagram of one of the two independent molecules of compound **1** is shown in Fig. 1, crystallographic data are compiled in Table 4, selected bond lengths and angles are summarized in Table 1.

The lanthanum atom is coordinated in a distorted tetrahedral fashion by the β -diketiminato and two amido ligands. The β -diketiminato ligand is coordinated in a η^2 -fashion, as indicated by long lanthanum–carbon distances (3.48–3.86 Å for both independent molecules). The lanthanum atom is situated slightly out of the plane of the β -diketiminato ligand (0.758 Å for molecule a,

0.88 Å for molecule b). The β -diketiminato ligand is essentially planar, with the largest deviation being C2 for molecule a (0.059 Å), respectively C1' for molecule b (0.078 Å). The La–N bond lengths for the β -diketiminato ligand (2.511(4) and 2.521(4) Å for molecule a, 2.538(4) and 2.493(4) Å for molecule b) are at the upper limit of typical La–N bonds (2.30–2.49 Å [21]), but comparable to other β -diketiminato rare earth metal complexes [14], when considering the larger ionic radius of lanthanum. The La–N bonds to the bis(trimethylsilyl)amido ligands on the other hand are significant shorter (2.387(4)–2.415(4) Å), well within the typical range of La–N bonds. The aromatic substituents are oriented perpendicular to the plane of the β -diketiminato moiety, with a slight tilt towards the *exo*-amido ligand [14g]. The amido ligands show only weak monoagostic interactions [19,21,22]. One of the two silicon atoms on each amido ligand gets slightly closer to lanthanum (La \cdots Si = 3.4948(18) vs. 3.655(2) Å and 3.448(2) vs. 3.611(2) Å for molecule a; 3.3842(16) vs. 3.677(2) Å and 3.5259(18) vs. 3.565(2) Å for molecule b), concomitant with a decrease in the La–N–Si angle ($114.7(2)^{\circ}$ vs. $124.2(2)^{\circ}$ and $113.0(2)^{\circ}$ vs. $123.2(2)^{\circ}$ for molecule a; $110.1(2)^{\circ}$ vs. $126.8(2)^{\circ}$ and $116.7(2)^{\circ}$ vs. $119.2(2)^{\circ}$ for molecule b), while the Si–N–Si angle remains normal (close to 120°). Finally, in molecule b one of the SiMe₃ methyl groups is in close contact with lanthanum (3.117(6) Å).

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

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

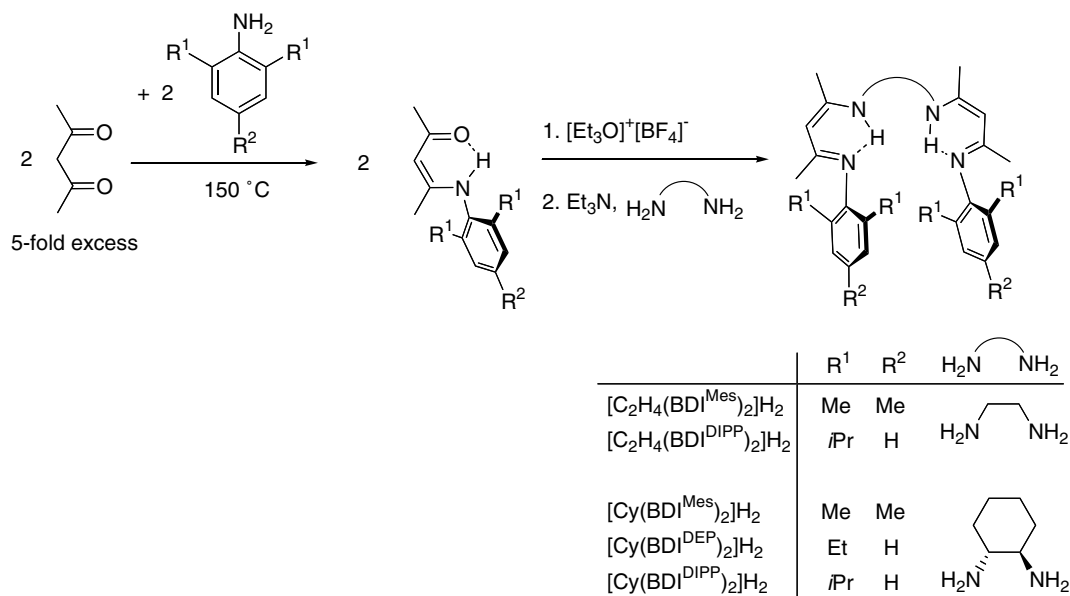
The linked bis(β -diketiminato) ligands were prepared through a two-step standard condensation route (Scheme 2). Reaction of 2,4-pentadione and an aniline derivative yields a β -enaminoketone. The carbonyl function of this intermediate was activated using Meerwein's salt, [Et₃O]⁺[BF₄][−], in order to introduce the ethylene diamine or *trans*-cyclohexane-1,2-diamine linkers. Overall the ligand synthesis is highly modular and allows easy modification of either the linker unit or the aromatic substituents.

2.2.2. Complex synthesis and structural characterization

Reaction of the mesityl substituted linked bis(β -diketiminato) ligand [C₂H₄(BDI^{Mes})₂]H₂ with [Ln{N(SiMe₃)₂}₃] (Ln = La, Y) proceeded at 60–70 °C in hexanes or toluene, under significantly milder conditions than for the mono(β -diketiminato) ligand (BDI)H; generating the desired linked bis(β -diketiminato) complexes **3a** and **3b** in high yield (Scheme 3). The more reactive [La{N(SiHMe₂)₂}₃(THF)₂] formed the THF-free bis(dimethylsilyl)amido complex **4** at room temperature. The increased steric hindrance of the aromatic substituents in [C₂H₄(BDI^{DIPP})₂]H₂ required higher reaction

Table 1
Selected bond lengths (Å), atomic distances (Å) and angles ($^{\circ}$) for **1**

	1	
	Molecule a	Molecule b
La–N1	2.511(4)	2.538(4)
La–N2	2.521(4)	2.493(4)
La–N3	2.415(4)	2.388(4)
La–N4	2.387(4)	2.401(4)
La \cdots Si2	3.4948(18)	3.3842(16)
La \cdots Si3	3.448(2)	3.5259(18)
La \cdots C43	–	3.117(6)
N1–La–N2	72.43(13)	73.44(13)
N1–La–N3	108.70(14)	108.05(14)
N1–La–N4	119.79(14)	121.72(14)
N2–La–N3	134.31(15)	126.58(14)
N2–La–N4	100.87(14)	107.43(14)
N3–La–N4	115.30(14)	114.50(14)
La–N3–Si1	124.2(2)	126.8(2)
La–N3–Si2	114.7(2)	110.1(2)
La–N4–Si3	113.0(2)	116.7(2)
La–N4–Si4	123.2(2)	119.2(2)
Si1–N3–Si2	121.1(3)	123.0(2)
Si3–N4–Si4	123.8(3)	124.1(3)
Distance of La from N ₂ C ₃	0.758	0.88



Scheme 2.

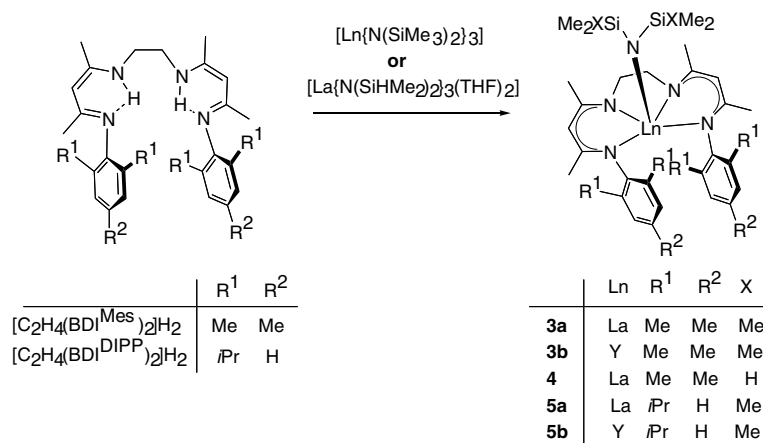
temperatures (70–95 °C) and longer reaction times to form complexes **5a** and **5b**. In general, all amine elimination reactions with linked bis(β-diketiminato) ligands reported herein proceeded cleanly to the desired product and no byproducts were observed. However, in some cases the prolonged heating at high temperatures led to some thermal decomposition.

The ¹H and ¹³C NMR spectra of ethylene-bridged complexes **3a**, **3b** and **4** are in accordance with a C_s symmetric structure in solution on the NMR time scale, giving rise to one signal for the SiCH₃ groups and the methyne proton of the β-diketiminato ligand. The ethylene protons of **3a**, **3b** and **4** are split into two AA'BB' multiplets in the ¹H NMR spectra. The aromatic mesityl substituents give rise of two aromatic proton singlets and two signals for the *ortho* mesityl methyl groups.

Coincidentally, the ¹³C NMR spectra show six aromatic carbon signals.

The sterically more demanding 2,6-diisopropylphenyl substituents in **5a** and **5b** show hindered rotation in their ¹H NMR spectra (Fig. 2). At elevated temperatures (60 °C, toluene-*d*₈) the spectra display the same C_s symmetry as observed for complexes **3a**, **3b** and **4** at room temperature. The NMR spectra of **5b** at –20 °C indicate a C₁ symmetric structure similar to that observed for the cyclohexyl-linked complexes **6–10** (vide infra). The larger ionic radius in **5a** reduces the barrier of rotation and decoalescence to the C₁ symmetric structure was only observed at –60 °C.

The cyclohexyl-bridged ligands [Cy(BDI^{Mes})₂]₂H₂, [Cy(BDI^{DEP})₂]₂H₂ and [Cy(BDI^{DIPP})₂]₂H₂ required higher reaction temperatures and longer reaction times than the



Scheme 3.

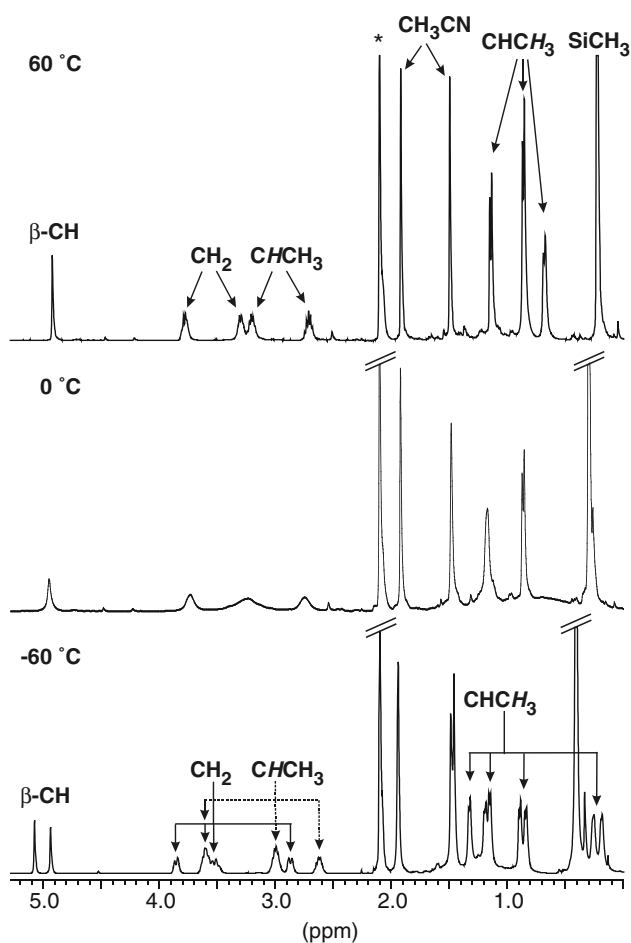


Fig. 2. Temperature dependence of the ^1H NMR spectrum of **5a** in toluene- d_3 (*toluene- d_0 impurity).

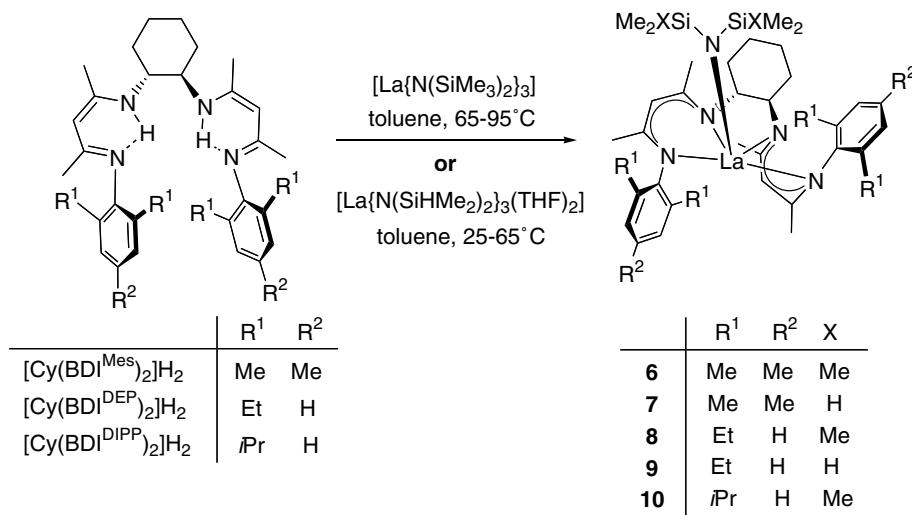
corresponding ethylene-bridged ligands, reflecting the higher rigidity of the cyclohexyl linker in comparison to the ethylene linker (Scheme 4). Whereas ethylene-bridged complexes **3–5** are only slightly soluble in ali-

phatic solvents, the cyclohexyl-bridged complexes **6–10** are generally better soluble.

The ^1H and ^{13}C NMR spectra of cyclohexyl-bridged complexes **6–9** show significant line broadening at room temperature. At $-20\text{ }^\circ\text{C}$ the spectra are in accordance with a C_1 symmetric structure in solution, similar to that observed for the sterically more hindered diisopropylphenyl substituted complex **10** at room temperature. The spectra show two diastereomeric SiCH_3 groups and two different β -diketiminato groups. Both aromatic rings are diastereotopic, giving rise of 12 signals in the ^{13}C NMR spectra. Complexes **6** and **7** display six signals for the mesityl methyl groups at low temperature, whereas in the sterically more demanding diisopropylphenyl substituted complex **10** all eight isopropyl methyl groups are already at room temperature well separated in the ^1H and ^{13}C NMR spectra.

X-ray crystallographic analyses of **3b**, **7** and **8** confirmed their monomeric structure (Figs. 3–5). For better comparison selected metrical parameters of **3b**, **7** and **8** together with parameters of complex **5a** and **10** [16] are tabulated in Table 2.

In complex **3b**, yttrium is coordinated in a distorted square pyramidal fashion, in which the amido ligand occupies the apical position and the two linked β -diketiminato moieties form the basis. Similar to the lanthanum complex **5a** [16] both aromatic substituents have a *cisoid* arrangement in **3b**, pointing away from the apical amido group, but the difference in the binding modes of the two β -diketiminato moieties is significantly less pronounced. The first β -diketiminato fragment comprising of N1, N2 and C11–C13 is bonded in a η^2 fashion, analogous to the binding mode found in complex **1** and other previously characterized mono(β -diketiminato) complexes [14]. The yttrium atom is placed only 0.707 Å out of the N_2C_3 plane and both Y–N bonds are very similar (2.3522(17) and 2.3632(18) Å). The other β -dike-



Scheme 4.

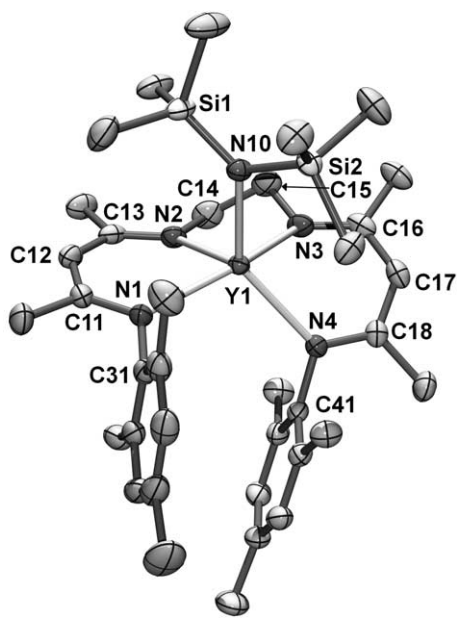


Fig. 3. ORTEP diagram of the molecular structure of **3b**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for the sake of clarity.

timinato moiety, comprising of N3, N4 and C16–C18, is bound unsymmetrically with Y1–N3 (2.3065(17) Å) being 0.1 Å shorter than Y1–N4 (2.4098(17) Å). Here the yttrium is displaced by 1.163 Å from the N₂C₃ plane. The slightly different binding of the β-diketiminato moieties is also reflected in the decreased yttrium to carbon distances (3.34–3.66 Å for β-diketiminato group 1 vs. 3.23–3.56 Å for β-diketiminato group 2). Note that the

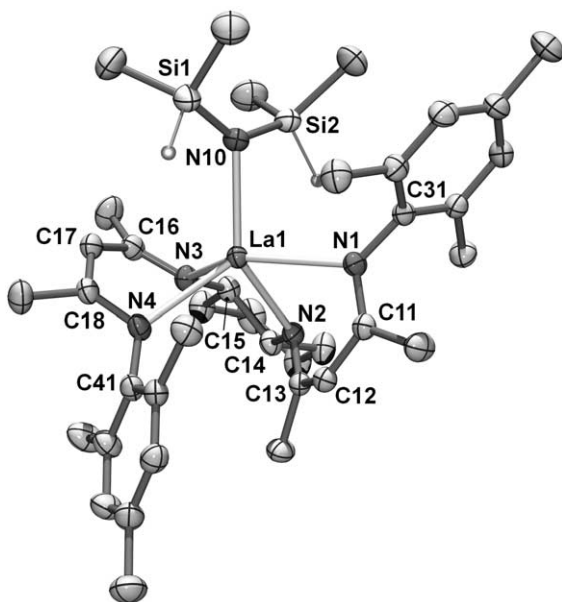


Fig. 4. ORTEP diagram of the molecular structure of **7**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms except for those attached to silicon have been omitted for the sake of clarity.

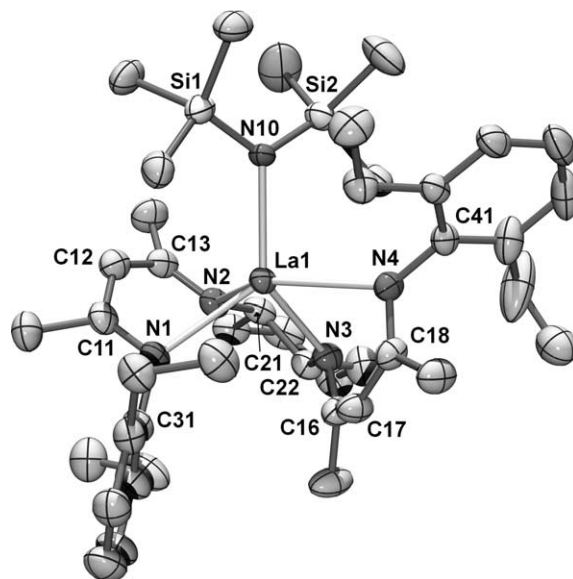


Fig. 5. ORTEP diagram of the molecular structure of **8**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for the sake of clarity. For the disordered carbon atoms C36B and C42B only one of the two independent positions is shown.

metal carbon distances in the lanthanum complex **5a** deviate much more dramatically (two independent molecules: 3.45–3.72 Å vs. 3.01–3.18 Å for molecule a, 3.54–3.84 Å vs. 3.20–3.43 for molecule b). While the first β-diketiminato moiety is virtually planar, with C13 deviating the most from the N₂C₃ plane (0.06 Å), the second β-diketiminato moiety is slightly more puckered (0.113 Å deviation for C18 from the N₂C₃ plane).

The mesityl substituents in **3b** are π-stacked with a ring distance of 3.06–3.63 Å and a dihedral angle between the planes of the aromatic rings of 12.9°. The yttrium amido bond (2.2843(17) Å) is within the typical range of Y–N bond lengths (2.18–2.32 Å [23]), and the amido ligand adopts a similar monoagostic interaction as observed for **1**.

The geometry of the linked bis(β-diketiminato) ligand in **7**, **8**, as well as **10** [16], differs significantly from that observed for **3b** and **5a** [16]. The two aromatic substituents are oriented in a *transoid* fashion in the cyclohexyl-linked complexes, with one aromatic substituent pointing away from the amido group and the other aromatic substituent pointing towards the amido group. This significant change in ligand geometry is inflicted by a slight decrease of the dihedral angle of the linker unit (N2–C–C–N3) from 51.4(3) in **3b** (respectively 49.3(4)° and –53.1(5)° for the two independent molecules in **5a** [16]) to –44.1(3) in **7**, –41.5(2) in **8** and 42.25(19) in **10** [16].

Contrary to the findings for complex **3b** and **5a**, both β-diketiminato moieties in complexes **7**, **8** and **10** are bound in the η⁵ bonding mode with the lanthanum atom being displaced by 1.74–1.97 Å out of the N₂C₃

Table 2
Selected bond lengths (Å), atomic distances (Å) and angles (°) for **3b**, **5a**, **7**, **8** and **10**^a

	3b (Ln = Y)	5a (Ln = La)		7 (Ln = La)	8 (Ln = La)	10 (Ln = La)
		Molecule a	Molecule b			
Ln–N1	2.3522(17)	2.557(3)	2.540(3)	2.5154(16)	2.5514(19)	2.4977(15)
Ln–N2	2.3632(18)	2.536(3)	2.425(3)	2.4554(16)	2.4318(18)	2.4340(14)
Ln–N3	2.3065(17)	2.394(3)	2.573(3)	2.4574(16)	2.481(2)	2.5063(15)
Ln–N4	2.4098(17)	2.559(3)	2.554(3)	2.4729(16)	2.5518(18)	2.5939(15)
Ln–N10	2.2843(17)	2.425(3)	2.426(3)	2.4128(17)	2.4310(18)	2.4543(15)
Ln···Si1	3.6176(6)	3.6808(13)	3.6819(12)	3.4643(6)	3.545(1)	3.5756(5)
Ln···Si2	3.3156(6)	3.5401(16)	3.5818(13)	3.3574(6)	3.615(1)	3.6631(6)
Ln···C11	3.337(2)	3.483(3)	3.321(3)	3.146(2)	3.166(2)	3.0554(18)
Ln···C12	3.655(2)	3.725(3)	3.429(3)	3.110(2)	3.122(2)	3.0469(18)
Ln···C13	3.351(2)	3.446(3)	3.197(3)	2.9781(19)	2.978(2)	2.9690(17)
Ln···C16	3.231(2)	3.014(3)	3.538(3)	3.0885(19)	3.022(3)	3.036(2)
Ln···C17	3.560(2)	3.162(3)	3.844(3)	3.184(2)	3.065(3)	3.153(2)
Ln···C18	3.340(2)	3.180(3)	3.547(3)	3.1170(19)	3.078(2)	3.193(2)
N1–Ln–N2	78.18(6)	72.33(9)	73.34(10)	74.13(5)	71.75(6)	72.15(5)
N1–Ln–N3	147.55(7)	137.01(9)	114.97(9)	135.70(5)	98.50(7)	98.27(5)
N1–Ln–N4	107.90(6)	119.95(9)	119.32(9)	130.28(5)	132.77(6)	132.85(5)
N1–Ln–N10	103.92(6)	105.01(10)	114.96(9)	95.42(6)	125.06(6)	118.20(5)
N2–Ln–N3	72.23(7)	65.47(9)	66.65(10)	64.94(5)	64.09(6)	63.72(5)
N2–Ln–N4	116.76(6)	112.93(9)	136.97(10)	96.67(5)	134.01(7)	133.85(5)
N2–Ln–N10	101.27(6)	112.22(10)	95.21(10)	127.89(6)	97.35(6)	100.05(5)
N3–Ln–N4	75.03(6)	72.06(9)	71.17(9)	72.71(5)	73.04(6)	73.45(5)
N3–Ln–N10	94.76(6)	98.16(10)	117.69(10)	96.50(6)	125.44(7)	133.96(5)
N4–Ln–N10	134.19(6)	123.36(9)	111.81(9)	125.07(6)	94.06(6)	97.34(5)
Ln–N10–Si1	128.62(9)	124.61(15)	124.52(13)	114.75(9)	116.57(9)	117.31(8)
Ln–N10–Si2	111.31(8)	116.90(15)	118.55(14)	108.79(8)	120.53(9)	122.13(8)
Si1–N10–Si2	120.04(10)	118.50(18)	116.69(15)	136.33(11)	122.85(10)	120.47(9)
N2–C–C–N3	51.4(3)	49.3(4)	–53.1(5)	–44.1(3)	–41.5(2)	42.25(19)
Distance of Ln from N ₂ C ₃						
Ring 1	0.707	1.235	1.626	1.890	1.934	1.941
Ring 2	1.163	1.883	1.029	1.740	1.969	1.940

^a Structures **5a** and **10** were reported in [16].

planes and short La···C contacts (2.97–3.19 Å). The La–N bonds within the β-diketiminato moieties vary less dramatically (0.02 and 0.06 Å for **7**, 0.07 and 0.12 Å for **8**, 0.06 and 0.09 Å for **10**) than the 0.17 Å observed in **5a** [16].

The bis(dimethylsilyl)amido complex **7** displays a weak β-SiH monoagostic interaction [19,21,24], as indicated by one shorter La···Si distance (3.3574(6) vs. 3.4643(6) Å), a decreased La–N–Si angle (108.79(8)° vs. 114.75(9)°) and a widened Si–N–Si angle

Table 3
Rare earth metal catalyzed copolymerization of CO₂ and cyclohexene oxide

Cat.	[M]/[cat.]	<i>p</i> (CO ₂) (atm)	<i>T</i> (°C)	<i>t</i> (h)	TON	TOF (h ^{–1})	% Cyclic carbonate ^a	% Carbonate linkages ^a	<i>M_n</i> ^b	<i>M_w</i> ^a	<i>M_w</i> / <i>M_n</i> ^a
3a	500	41	55	24	13	0.55	0	60	56700	301000	5.3
5a	500	41	55	18	23	1.3	0	40	72100	197000	2.7
6	1000	41	60	18	90	5	0	87	3940	28800	7.3
[Y{N(SiMe ₃) ₂ }] ₃	900	41	55	18	160	8.9	0	14	6770	97700	14.4
1	500	1	75	90	89	1.0	10	82	2240	4730	2.1
2b	600	1	75	88	204	2.3	5	68	3810	10700	2.8
3b	500	1	75	90	86	0.96	6	41	2540	8520	3.4
4	500	1	75	24	173	7.2	4	92	7120	10500	1.5
5a	500	1	75	24	251	10.5	6	82	12000	17200	1.4
6	500	1	75	24	159	6.6	5	80	8430	15100	1.8
8	500	1	75	24	304	12.7	5	88	13500	21800	1.6
10	500	1	75	48	292	6.1	8	83	11200	18000	1.6
[La{N(SiMe ₃) ₂ }] ₃	1000	1	70	72	62	0.86	17	66	600	4420	7.4

^a Determined by ¹H NMR spectroscopy.

^b Determined by gel permeation chromatography relative to polystyrene standards.

Table 4
Summary of crystallographic data of complexes **1** and **3b**, **7** and **8**

Complex	1	3b	7	8
<i>Crystal data</i>				
Empirical formula	C ₃₅ H ₆₅ LaN ₄ Si ₄	C ₃₆ H ₅₈ N ₅ Si ₂ Y	C ₃₈ H ₆₂ LaN ₅ Si ₂	C ₄₂ H ₆₈ LaN ₅ Si ₂
Formula weight	793.18	705.96	784.02	838.10
Crystal color, habit	Yellow plate	Colorless block	Colorless block	Colorless block
Crystal dimensions (mm)	0.15 × 0.10 × 0.10	0.35 × 0.30 × 0.20	0.15 × 0.15 × 0.15	0.30 × 0.25 × 0.20
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
<i>a</i> (Å)	31.222(6)	13.4080(2)	10.9150(2)	12.076(2)
<i>b</i> (Å)	12.426(3)	17.4103(2)	12.6095(2)	12.243(2)
<i>c</i> (Å)	22.968(5)	16.9623(3)	14.9986(2)	16.157(3)
α (°)	90	90	84.631(1)	80.89(3)
β (°)	107.02(3)	103.3060(10)	84.263(1)	73.68(3)
γ (°)	90	90	83.927(1)	74.64(3)
<i>V</i> (Å ³)	8520(3)	3853.34(10)	2035.23(6)	2201.7(8)
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>Z</i>	8	4	2	2
<i>D</i> _{calc} (Mg/m ³)	1.237	1.217	1.279	1.264
<i>F</i> (000)	3328	1504	820	880
μ (Mo K α) (mm ⁻¹)	1.142	1.606	1.139	1.058
<i>Data collection</i>				
λ (Mo K α radiation) (Å)	0.71073	0.71073	0.71073	0.71073
Temperature (K)	173(2)	173(2)	173(2)	173(2)
θ Range for data collection (°)	1.8–27.5	2.8–27.5	2.2–27.5	1.3–27.5
Number of total reflections	36 515	16 629	17 476	19 749
Number of unique reflections (<i>R</i> _{int})	19 500 (0.0805)	8817 (0.0252)	9293 (0.0153)	10 082 (0.0145)
<i>Structure solution and refinement</i>				
Number of observations (<i>I</i> > 2 σ (<i>I</i>))	10 840	7090	8528	9251
Data/restraints/parameters	19 500/0/793	8817/0/413	9293/0/429	10 082/2/471
Final <i>R</i> indices (<i>I</i> > 2 σ (<i>I</i>)); <i>R</i> ₁ , <i>wR</i> ₂	0.0530, 0.1111	0.0331, 0.0825	0.0246, 0.0638	0.0273, 0.0766
Final <i>R</i> indices (all data); <i>R</i> ₁ , <i>wR</i> ₂	0.1202, 0.1407	0.0494, 0.0925	0.0281, 0.0664	0.0309, 0.0797
Goodness-of-fit	0.956	0.837	0.935	1.022
Maximum peak in final difference map (e/Å ³)	0.816	0.361	0.843	0.949
Minimum peak in final difference map (e/Å ³)	−0.699	−0.384	−0.850	−0.726

(136.33(11)°). The geometry of the bis(trimethylsilyl)amido ligand in lanthanum complexes **5a**, **8** and **10** is less distorted than in the yttrium complex **3b** with La···Si distances greater than 3.54 Å and La–N–Si angles close to 120°.

2.3. Copolymerization of CO₂ and cyclohexene oxide

Initial experiments indicate that the mono(β -diketiminato) complex as well as the bis(β -diketiminato) complexes catalyze the copolymerization of cyclohexene oxide and CO₂ (Eq. (1)) at elevated temperatures with moderate activity (Table 3). The highest carbonate linkage contents of 92% was obtained with the ethylene-bridged lanthanum complex **4**. The mono(β -diketiminato) complex **1** produced polycarbonate with up to 82% carbonate-linkages, but catalytic activity was lower. No cyclic carbonates were formed at 41 atm CO₂ and 55–60 °C, but at lower CO₂ pressure (1 atm) and higher temperatures (70–75 °C) all catalysts produced small amounts (5–10%) of the cyclic carbonate byproduct. The highest turnover frequency was observed for the cyclohexyl-bridged complex **8** containing 2,6-diethylphenyl substituents.

Homoleptic trisamido complexes [Ln{N(SiMe₃)₂}₃] on the other hand produced either polymer with low contents in carbonate linkages (Ln = Y) or significant larger amount of cyclic carbonates (Ln = La).

3. Conclusion

β -Diketiminato and novel linked bis(β -diketiminato) rare earth metal complexes are accessible via a facile amine elimination procedure. The complexes presented here are the first homogeneous rare earth metal based catalysts for epoxide/CO₂ copolymerization with carbonate contents of up to 92%. Although catalyst activity seems to be rather low in comparison to the most active zinc or chromium based catalyst systems, we are hopeful that tuning of the electronic and steric properties of the highly modular linked bis(β -diketiminato) ligands will lead to more active catalysts. We are exploring other linker units in order to better understand the factors governing the binding mode of the β -diketiminato ligands in these systems. Furthermore, rare earth metal complexes have proven to be very versatile polymerization catalysts for a wide variety of non-polar and polar

monomers. Therefore, (block) copolymerization of such non-polar or polar monomers in combination with epoxide/CO₂ copolymerization will give access to new materials with highly attractive properties.

4. Experimental

4.1. General procedures

All operations were performed under an inert atmosphere of nitrogen or argon using standard Schlenk-line or glovebox techniques. After drying over KOH, THF was distilled from sodium benzophenone ketyl. Hexanes, pentane and toluene were purified by distillation from sodium/triglyme benzophenone ketyl. Anhydrous YCl₃ (Aldrich) and LaCl₃ (Strem) were used as received. [Ln{N(SiMe₃)₂}₃] (Ln = Y, La) [18], [Ln{N(SiHMe₂)₂}₃(THF)₂] (Ln = Y, La) [19], 4-((2,6-diethylphenyl)amino)pent-3-en-2-one [6d] and (BDI)H [25] were synthesized as described in the literature. Cyclohexene oxide was dried by distillation from CaH₂. All other chemicals were commercially available and used as received. ¹H and ¹³C NMR spectra were recorded on Bruker Avance 300 or Avance 400 spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of this department. Although metal complexes were combusted with V₂O₅ as burning aid, some analyses gave low carbon content repeatedly, presumably due to carbide formation. Molecular weights of the polycarbonates were determined by GPC (Agilent 1100 Series using RI detector, 3 SDV Linear M 5μm columns with 8 × 50 mm, 8 × 300 mm and 8 × 600 mm dimensions) versus polystyrene standards using THF at 35 °C as eluent.

4.2. Preparation of 4-((2,4,6-trimethylphenyl)amino)-pent-3-en-2-one

Following the procedure reported for 4-((2,6-diethylphenyl)amino)pent-3-en-2-one in [6d], 2,4,6-trimethylaniline (13.17 g, 97.4 mmol) and excess of 2,4-pentadione (68.0 g, 679 mmol) were added to a 250 mL round-bottom flask equipped with a stirring bar. A distillation apparatus was attached to collect water and the neat solution was heated to 150 °C for 24 h. Excess 2,4-pentadione was removed in vacuo, and the residue was distilled under vacuum at 0.02 mmHg and 100–110 °C to give the desired compound. The obtained pale yellow solid product was recrystallized from hexanes to give 18.30 g (86%). ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ = 11.82 (br s, 1H, NH), 6.87 (s, 2H, C₆H₂), 5.17 (s, 1H, β-CH), 2.25 (s, 3H, 4-C₆H₂CH₃), 2.13 (s, 6H, 2-C₆H₂CH₃), 2.07 (s, 3H, CH₃CO), 1.60 (s, 3H, CH₃CN); ¹³C{¹H} NMR (CDCl₃, 100.6 MHz, 25 °C): δ = 195.8 (CO), 163.0 (CH₃CN), 137.0, 135.7, 133.8, 128.8 (aryl),

95.6 (β-CH), 29.0 (CH₃CO), 20.9 (4-C₆H₂CH₃), 18.8 (CH₃CN), 18.1 (2-C₆H₂CH₃).

4.3. Preparation of 4-((2,6-diisopropylphenyl)amino)-pent-3-en-2-one [14m,26]

Following the procedure reported for 4-((2,6-diethylphenyl)amino)pent-3-en-2-one in [6d], 2,6-diisopropylaniline (15.94 g, 90.1 mmol) and excess of 2,4-pentadione (56.9 g, 568 mmol) were added to a round-bottom flask equipped with a stirring bar. A distillation apparatus was attached to collect water and the neat solution was heated to 150 °C for 24 h. Excess 2,4-pentadione was removed in vacuo, and the residue was distilled under vacuum to give a reddish solid, which was crystallized from hexanes to give 12.57 g (54%) of the aimed compound. ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ = 12.04 (br s, 1H, NH), 7.27 (t, ³J = 7.7 Hz, 1H, 4-C₆H₃), 7.15 (d, ³J = 7.7 Hz, 1H, 3-C₆H₃), 5.19 (s, 1H, β-CH), 3.00 (sept, ³J = 6.9 Hz, 2H, CHCH₃), 2.10 (s, 3H, CH₃CO), 1.61 (s, 3H, CH₃CN), 1.19 (d, ³J = 6.9 Hz, 6H, CHCH₃), 1.12 (d, ³J = 6.8 Hz, 6H, CHCH₃); ¹³C{¹H} NMR (CDCl₃, 100.6 MHz, 25 °C): δ = 195.9 (CO), 163.2 (CH₃CN), 146.2, 133.5, 128.2, 123.5 (aryl), 95.5 (β-CH), 29.0 (CH₃CO), 28.4 (CHCH₃), 24.5 (CHCH₃), 22.6 (CHCH₃), 19.1 (CH₃CN).

4.4. Preparation of [C₂H₄(BDI^{Mes})₂]H₂

A solution of [Et₃O]⁺[BF₄]⁻ (2.106 g, 11.09 mmol) in CH₂Cl₂ (10 mL) was slowly added to a solution of 4-((2,4,6-trimethylphenyl)amino)pent-3-en-2-one (2.354 g, 10.83 mmol) in CH₂Cl₂ (15 mL) under a nitrogen atmosphere. The mixture was stirred for 2.5 h at room temperature. Et₃N (1.5 mL) was added and the mixture was stirred for another 5 min. A solution of ethylene diamine (326 mg, 5.42 mmol) in Et₃N (6 mL) was added to the mixture and the stirring was continued overnight. The solvent was removed in vacuo and the product was extracted with toluene. [Et₃NH]⁺[BF₄]⁻ was separated as an oily precipitate. Toluene was removed in vacuo and the residue was taken up in hexanes and cooled to -20 °C. The solid was separated by filtration and was washed with ethanol to remove remaining starting material. Yield 1.32 g (52%) of [C₂H₄(BDI^{Mes})₂]H₂. ¹H NMR (C₆D₆, 400 MHz, 25 °C): δ = 10.90 (NH), 6.91 (s, 4H, C₆H₂), 4.60 (s, 2H, β-CH), 2.72 (s, 4H, CH₂), 2.23 (s, 6H, 4-C₆H₂CH₃), 2.15 (s, 12H, 2-C₆H₂CH₃), 1.62 (s, 6H, CH₃), 1.60 (s, 6H, CH₃); ¹³C{¹H} NMR (C₆D₆, 100.6 MHz, 25 °C): δ = 166.5, 155.2 (CH₃CN), 147.5, 131.2, 128.9, 127.7 (aryl), 94.3 (β-CH), 44.5 (CH₂), 21.2 (CH₃CNAr), 20.9 (4-C₆H₂CH₃), 19.1 (CH₃CNHCH₂), 18.6 (2-C₆H₂CH₃). Anal. Calc. for C₃₀H₄₂N₄ (458.68): C, 78.56; H, 9.23; N, 12.21. Found: C, 78.39; H, 9.35; N, 12.27%.

4.5. Preparation of $[C_2H_4(BDI^{DIPP})_2]H_2$

A solution of $[Et_3O]^+[BF_4]^-$ (3.836 g, 20.2 mmol) in CH_2Cl_2 (10 mL) was added slowly to a solution of 4-((2,6-diisopropylphenyl)amino)-pent-3-en-2-one (5.22 g, 20.1 mmol) in CH_2Cl_2 (15 mL). The reaction mixture was stirred for 3 h and then Et_3N (2.8 mL) was added. After 5 min a solution of ethylene diamine (0.736 g, 12.2 mmol) in Et_3N (15 mL) was added to the mixture. After stirring at room temperature for 16 h all volatiles were removed in vacuo. Toluene was added to extract the product from the oily precipitate of $[Et_3NH]^+[BF_4]^-$. Toluene was removed and the crude product was dissolved in ethanol. Pale yellow crystals were obtained after 12 h at $-20^\circ C$. Drying in vacuo gave 4.192 g (77%) of $[C_2H_4(BDI^{DIPP})_2]H_2$. 1H NMR ($CDCl_3$, 400 MHz, $25^\circ C$): δ = 10.93 (br s, 2H, NH), 7.09 (d, 3J = 7.2 Hz, 4H, 3- C_6H_2), 7.01 (m, 2H, 4- C_6H_2), 4.64 (s, 2H, β -CH), 3.29 (s, 4H, CH_2), 2.82 (sept, 3J = 6.8 Hz, 4H, $CHCH_3$), 1.95 (s, 6H, CH_3CNAr), 1.61 (s, 6H, CH_3CNHCH_2), 1.13 (d, 12H, 3J = 6.8 Hz, $CHCH_3$), 1.10 (d, 12H, 3J = 6.8 Hz, $CHCH_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz, $25^\circ C$): δ = 166.2, 155.3 (CH_3CN), 146.6, 138.1, 122.7, 122.6 (aryl), 93.8 (β -CH), 44.5 (CH_2), 28.0 ($CHCH_3$), 23.8 ($CHCH_3$), 22.8 ($CHCH_3$), 21.6 (CH_3CNAr), 19.1 (CH_3CNHCH_2). Anal. calc. for $C_{36}H_{54}N_4$ (542.84): C, 79.65; H, 10.03; N, 10.32. Found: C, 79.63; H, 9.99; N, 10.38%.

4.6. Preparation of $[Cy(BDI^{Mes})_2]H_2$

A solution of $[Et_3O]^+[BF_4]^-$ (4.179 g, 22.00 mmol) in CH_2Cl_2 (20 mL) was slowly added to a solution of 4-(2,4,6-trimethylphenyl)-aminopent-3-en-4-one (5.222 g, 24.03 mmol) in CH_2Cl_2 (10 mL) under a nitrogen atmosphere. The mixture was stirred for 2.5 h at room temperature. Et_3N (3.1 mL) was added to the clear pale solution and the mixture was stirred for another 5 min. A solution of *trans*-cyclohexane-1,2-diamine (1.256 g, 11.01 mmol) in Et_3N (15 mL) was added to the reaction mixture and the stirring was continued overnight. All volatiles were removed in vacuo and the residue was extracted with pentane (2 \times 20 mL) and toluene (20 mL). The $[Et_3NH]^+[BF_4]^-$ byproduct was separated from the organic solution as an oily precipitate via decantation. The solvent was removed in vacuo and the residue was taken up in pentane. Crystallization at $-20^\circ C$ afforded 3.39 g (60%) of $[Cy(BDI^{Mes})_2]H_2$. 1H NMR ($CDCl_3$, 300 MHz, $25^\circ C$): δ = 11.03 (br s, 1H, NH), 6.86 (s, 4H, C_6H_2), 4.56 (s, 2H, β -CH), 3.13 (br s, 2H, ring-CH), 2.27 (s, 6H, 4- $C_6H_2CH_3$), 2.01 (s, 6H, 2- $C_6H_2CH_3$), 2.00 (s, 6H, 2- $C_6H_2CH_3$), 1.90–1.98 (br m, 2H, ring- CH_2), 1.94 (s, 6H, CH_3), 1.68 (m, 2H, ring- CH_2), 1.60 (s, 6H, CH_3), 1.15–1.35 (m, 4H, ring- CH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz, $25^\circ C$): δ = 166.2, 155.2 (CH_3CN), 147.2, 130.9, 128.3, 128.2,

128.0, 127.6 (aryl), 92.6 (β -CH), 58.0 (ring-CH), 33.4 (ring- CH_2), 24.7 (ring- CH_2), 21.2 (CH_3CNAr), 20.7, 19.6, 18.5, 18.2 (CH_3). Anal. calc. for $C_{34}H_{48}N_4$ (512.77): C, 79.64; H, 9.44; N, 10.93. Found: C, 79.54; H, 9.54; N, 11.03%.

4.7. Preparation of $[Cy(BDI^{DEP})_2]H_2$

A solution of $[Et_3O]^+[BF_4]^-$ (4.910 g, 25.8 mmol) in CH_2Cl_2 (20 mL) was added to a solution of 4-((2,6-diethylphenyl)amino)-pent-3-en-2-one (5.693 g, 24.6 mmol) in CH_2Cl_2 (10 mL) under a nitrogen atmosphere. After stirring for 3 h at room temperature Et_3N (3.4 mL) was added to the solution. The mixture was stirred for another 15 min and *trans*-cyclohexane-1,2-diamine (1.405 g, 12.3 mmol) in Et_3N (15 mL) was added. After stirring 16 h at room temperature all volatiles were removed in vacuo. The residue was extracted with pentane (3 \times 50 mL) and the extracts were concentrated in vacuo. Addition of MeOH to the solution resulted in precipitation of the product. The product was filtered, washed with MeOH and dried in vacuo to give 4.138 g (62%) of $[Cy(BDI^{DEP})_2]H_2$. 1H NMR ($CDCl_3$, 400 MHz, $25^\circ C$): δ = 10.93 (br s, 2H, NH), 7.07 (pt, 4H, 3- C_6H_3), 6.96 (pt, 2H, 4- C_6H_3), 4.58 (s, 2H, β -CH), 3.14 (br s, 2H, ring-CH), 2.30–2.50 (m, 8H, CH_2CH_3), 1.95 (br s, 8H, CH_3 and ring- CH_2), 1.66 (br m, 2H, ring- CH_2), 1.60 (s, 6H, CH_3), 1.19–1.35 (br m, 4H, ring- CH_2), 1.15 (t, 3J = 7.6 Hz, 6H, CH_2CH_3), 1.13 (t, 3J = 7.6 Hz, 12H, CH_2CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz, $25^\circ C$): δ = 166.2, 155.1 (CH_3CN), 148.6, 133.8, 133.6, 125.7, 125.5, 122.1 (aryl), 92.8 (β -CH), 57.8 (ring-CH), 33.4 (ring- CH_2), 24.9 (CH_2CH_3), 24.5 (ring- CH_2), 24.2 (CH_2CH_3), 21.5 (CH_3CNAr), 19.5 (CH_3CNHCH_2), 14.29 (CH_2CH_3), 14.26 (CH_2CH_3). Anal. calc. for $C_{36}H_{52}N_4$ (540.83): C, 79.95; H, 9.69; N, 10.36. Found: C, 79.90; H, 9.75; N, 10.47%.

4.8. Preparation of $[Cy(BDI^{DIPP})_2]H_2$

A 100 mL Schlenk flask was charged with 4-((2,6-diisopropylphenyl)amino)-pent-3-en-2-one (5.46 g, 21.1 mmol). This was dissolved in CH_2Cl_2 (10 mL) and a solution of $[Et_3O]^+[BF_4]^-$ (3.80 g, 20.0 mmol) in CH_2Cl_2 (20 mL) was slowly added under nitrogen atmosphere. After stirring for 3 h at room temperature, Et_3N (2.02 g) was added slowly. The mixture was stirred for another 15 min and then a solution of *trans*-cyclohexane-1,2-diamine (1.142 g, 10.0 mmol) in Et_3N (15 mL) was added to the mixture. After stirring for 18 h at room temperature all volatiles were removed in vacuo. The product was extracted with hexanes and crystallized at $-20^\circ C$ to afford 3.586 g (57%) of $[Cy(BDI^{DIPP})_2]H_2$. 1H NMR ($CDCl_3$, 400 MHz, $25^\circ C$): δ = 11.02 (br s, 2H, NH), 7.10 (m, 4H, 3- C_6H_3), 7.02 (pt, 2H, 4- C_6H_3),

4.61 (s, 2H, β -CH), 3.17 (br s, 2H, ring-CH), 2.90 (m, 4H, CHCH₃), 1.98 (s, 6H, CH₃), 1.90 (m, 2H, ring-CH₂), 1.61 (br s, 8H, CH₃ and ring-CH₂), 1.18–1.35 (m, 4H, ring-CH₂), 1.16 (d, 6H, $^3J = 6.8$ Hz, CHCH₃), 1.14 (d, 6H, $^3J = 6.6$ Hz, CHCH₃), 1.10 (d, 6H, $^3J = 6.6$ Hz, CHCH₃), 1.09 (d, 6H, $^3J = 6.8$ Hz, CHCH₃); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃, 100.6 MHz, 25 °C) $\delta = 166.6$, 155.0 (CH₃CN), 146.8, 138.3, 138.2, 122.7, 122.6, 122.5 (aryl), 92.9 (β -CH), 57.2 (ring-CH), 32.4 (ring-CH₂), 28.0 (CHCH₃), 27.8 (CHCH₃), 24.3 (ring-CH₂), 24.0 (2 C, CHCH₃), 23.1, 22.8 (CHCH₃), 21.7 (CH₃CNAr), 19.4 (CH₃CNHCH₂). Anal. calc. for C₄₀H₆₀N₄ (596.93): C, 80.48; H, 10.13; N, 9.39. Found: C, 80.43; H, 10.26; N, 9.38%.

4.9. Preparation of [(BDI)La{N(SiMe₃)₂}₂] (1)

A Schlenk flask was charged with (BDI)H (35 mg, 0.105 mmol) and [La{N(SiMe₃)₂}₃] (65 mg, 0.105 mmol). Toluene (0.5 mL) was added and the solution was stirred at 115 °C for 18 h. The solvent was removed in vacuo to yield 82 mg (98%) of **1** as a pale yellow solid, which was pure according to NMR spectroscopy. Crystals suitable for X-ray analysis were grown from pentane solution at –20 °C. ^1H NMR (C₆D₆, 400 MHz, 25 °C): $\delta = 6.81$ (s, 4H, C₆H₂), 5.03 (s, 1H, β -CH), 2.28 (s, 12H, 2-C₆H₂CH₃), 2.15 (s, 6H, 4-C₆H₂CH₃), 1.56 (s, 6H, CH₃CN), 0.23 (s, 36H, SiCH₃); $^{13}\text{C}\{^1\text{H}\}$ NMR (C₆D₆, 100.6 MHz, 25 °C): $\delta = 164.6$ (CH₃CN), 144.3 (aryl-C_{ipso}), 134.6, 132.0, 130.1 (aryl), 96.8 (β -CH), 24.4 (CH₃CN), 20.8 (4-C₆H₂CH₃), 20.6 (2-C₆H₂CH₃), 4.4 (SiCH₃). Anal. calc. for C₃₅H₆₅LaN₄Si₄ (793.18): C, 53.00; H, 8.26; N, 7.06. Found: C, 52.82; H, 8.04; N, 6.79%.

4.10. Preparation of [(BDI)La{N(SiHMe₂)₂}₂] (2a)

A Schlenk flask was charged with (BDI)H (336 mg, 1.00 mmol) and [La{N(SiHMe₂)₂}₃(THF)₂] (680 mg, 1.00 mmol). Hexanes (10 mL) was added and the reaction mixture was stirred for 24 h at 25 °C. The mixture was filtered and the clear solution was concentrated in vacuo to give **2a** as a pale yellow powder (634 mg, 86%), which was clean according to NMR spectroscopy. ^1H NMR (C₆D₆, 400 MHz, 25 °C): $\delta = 6.82$ (s, 4H, C₆H₂), 5.11 (s, 1H, β -CH), 4.74 (sept, $^3J = 3.0$ Hz, 4H, SiH), 2.29 (s, 12H, 2-C₆H₂CH₃), 2.20 (s, 6H, 4-C₆H₂CH₃), 1.60 (s, 6H, CH₃CN), 0.18 (d, $^3J = 3.1$ Hz, 24H, SiCH₃); $^{13}\text{C}\{^1\text{H}\}$ NMR (C₆D₆, 100.6 MHz, 25 °C): $\delta = 164.6$ (CH₃CN), 142.9 (aryl-C_{ipso}), 134.5, 131.9, 130.1 (aryl), 97.6 (β -CH), 23.5 (CH₃CN), 20.8 (4-C₆H₂CH₃), 19.6 (2-C₆H₂CH₃), 2.7 (SiCH₃). Anal. calc. for C₃₁H₅₇LaN₄Si₄ (737.07): C, 50.52; H, 7.79; N, 7.60. Found: C, 49.85; H, 7.82; N, 7.16%.

4.11. Preparation of [(BDI)Y{N(SiHMe₂)₂}₂] (2b)

A 50 mL Schlenk flask was charged with (BDI)H (250 mg, 0.75 mmol) and [Y{N(SiHMe₂)₂}₃(THF)₂] (446 mg, 0.71 mmol). Hexanes (15 mL) was added and the reaction mixture was stirred for 18 h at 40 °C. The mixture was filtered and the clear solution was concentrated and cooled to –30 °C. Compound **2b** was obtained as colorless crystals in 289 mg (59%) yield. ^1H NMR (C₆D₆, 400 MHz, 25 °C): $\delta = 6.81$ (s, 4H, C₆H₂), 5.21 (s, 1H, β -CH), 4.75 (sept, $^3J = 3.0$ Hz, 4H, SiH), 2.30 (s, 12H, 2-C₆H₂CH₃), 2.16 (s, 6H, 4-C₆H₂CH₃), 1.58 (s, 6H, CH₃CN), 0.16 (d, $^3J = 3.0$ Hz, 24H, SiCH₃); $^{13}\text{C}\{^1\text{H}\}$ NMR (C₆D₆, 100.6 MHz, 25 °C): $\delta = 167.3$ (CH₃CN), 144.1 (aryl-C_{ipso}), 134.6, 131.9, 129.9 (aryl), 98.7 (β -CH), 23.8 (CH₃CN), 20.8 (4-C₆H₂CH₃), 19.8 (2-C₆H₂CH₃), 2.9 (SiCH₃). Anal. calc. for C₃₁H₅₇N₄Si₄Y (688.07): C, 54.11; H, 8.35; N, 8.14. Found: C, 53.71; H, 8.38; N, 7.88%.

4.12. Preparation of [{C₂H₄(BDI^{Mes})₂}LaN(SiMe₃)₂] (3a)

A Schlenk flask was charged with [C₂H₄(BDI^{Mes})₂]H₂ (459 mg, 1.00 mmol) and [La{N(SiMe₃)₂}₃] (619 mg, 1.00 mmol). Hexanes (20 mL) was added and the mixture was stirred at 60 °C for 30 min. All volatiles were removed in vacuo to give 642 mg (85%) of **3a** in form of a pale yellow powder, which was clean according to NMR spectroscopy. ^1H NMR (C₆D₆, 400 MHz, 25 °C): $\delta = 6.76$ (s, 2H, C₆H₂), 6.66 (s, 2H, C₆H₂), 4.94 (s, 2H, β -CH), 3.82 (m, 2H, CH₂), 3.35 (m, 2H, CH₂), 2.18 (s, 6H, 4-C₆H₂CH₃), 2.05 (s, 6H, 2-C₆H₂CH₃), 1.93 (s, 6H, CH₃CN), 1.52 (s, 6H, 2-C₆H₂CH₃), 1.47 (s, 6H, CH₃CN), 0.33 (s, 18H, SiCH₃); $^{13}\text{C}\{^1\text{H}\}$ NMR (C₆D₆, 100.6 MHz, 25 °C): $\delta = 163.3$, 162.0 (CH₃CN), 143.1 (aryl-C_{ipso}), 133.8, 133.5, 133.3, 130.2, 129.8 (aryl), 97.3 (β -CH), 52.3 (CH₂), 23.3, 23.0 (CH₃CN), 20.9 (4-C₆H₂CH₃), 20.3, 17.8 (2-C₆H₂CH₃), 5.0 (SiCH₃). Anal. calc. for C₃₆H₅₈LaN₅Si₂ (755.97): C, 57.20; H, 7.73; N, 9.26. Found: C, 57.28; H, 7.75; N, 8.97%.

4.13. Preparation of [{C₂H₄(BDI^{Mes})₂}YN(SiMe₃)₂] (3b)

A Schlenk flask was charged with [C₂H₄(BDI^{Mes})₂]H₂ (459 mg, 1.00 mmol) and [Y{N(SiMe₃)₂}₃] (599 mg, 1.05 mmol). Toluene (10 mL) was added and the mixture was stirred at 70 °C for 24 h. All volatiles were removed in vacuo to give 697 mg (98%) of **3b** in form of a pale yellow powder, which was clean according to NMR spectroscopy. Crystals suitable for X-ray analysis were grown from hexanes solution at –35 °C. ^1H NMR (C₆D₆, 400 MHz, 25 °C): $\delta = 6.67$ (s, 4H, C₆H₂), 6.59 (s, 2H,

C₆H₂), 4.97 (s, 2H, β-CH), 3.73 (m, 2H, CH₂), 3.30 (m, 2H, CH₂), 2.19 (s, 6H, 4-C₆H₂CH₃), 2.07 (s, 6H, 2-C₆H₂CH₃), 1.86 (s, 6H, CH₃CN), 1.50 (s, 6H, CH₃), 1.39 (s, 6H, CH₃), 0.37 (s, 18H, SiCH₃); ¹³C{¹H} NMR (C₆D₆, 100.6 MHz, 25 °C): δ = 165.1, 165.0 (CH₃CN), 144.7 (aryl-C_{ipso}), 133.8 (2 C), 129.94, 129.87 (aryl), 99.6 (β-CH), 51.7 (CH₂), 23.5, 22.9 (CH₃CN), 20.9 (4-C₆H₂CH₃), 20.8, 18.0 (2-C₆H₂CH₃), 5.7 (SiCH₃). Anal. calc. for C₃₆H₅₈N₅Si₂Y (705.97): C, 61.25; H, 8.28; N, 9.92. Found: C, 61.08; H, 8.50; N, 9.70%.

4.14. Preparation of [$\{C_2H_4(BDI^{Mes})_2\}La-N(SiHMe_2)_2$] (**4**)

A Schlenk flask was charged with [C₂H₄(BDI^{Mes})₂]₂H₂ (460 mg, 1.00 mmol) and [La{N(SiMe₂H)₂]₃(THF)₂] (682 mg, 1.00 mmol). Toluene (5 mL) was added and the mixture was stirred at room temperature for 16 h. All volatiles were removed in vacuo to give a pale yellow powder. Crystallization from pentane at –35 °C yielded 601 mg (82%) of **4** as pale yellow crystals. ¹H NMR (C₆D₆, 400 MHz, 25 °C): δ = 6.67 (s, 2H, C₆H₂), 6.56 (s, 2H, C₆H₂), 4.94 (s, 2H, β-CH), 4.88 (sept, ³J = 3.0 Hz, 2H, SiH), 3.79 (m, 2H, CH₂), 3.43 (m, 2H, CH₂), 2.18 (s, 3H, 4-C₆H₂CH₃), 2.05 (s, 3H, 2-C₆H₂CH₃), 1.92 (s, 3H, CH₃CN), 1.66 (s, 3H, 2-C₆H₂CH₃), 1.48 (s, 3H, CH₃CN), 0.35 (d, ³J = 3.0 Hz, 12H, SiCH₃); ¹³C{¹H} NMR (C₆D₆, 100.6 MHz, 25 °C): δ = 163.4, 161.6 (CH₃CN), 142.6 (aryl-C_{ipso}), 133.3, 132.9, 132.5, 130.0, 129.8 (aryl), 97.2 (β-CH), 53.0 (CH₂), 23.1, 22.8 (CH₃CN), 21.0 (4-C₆H₂CH₃), 19.4, 18.0 (2-C₆H₂CH₃), 3.5 (SiCH₃). Anal. calc. for C₃₄H₅₄LaN₅Si₂ (727.92): C, 56.10; H, 7.48; N, 9.62. Found: C, 55.70; H, 7.71; N, 9.32%.

4.15. Preparation of [$\{C_2H_4(BDI^{DIPP})_2\}LaN(SiMe_3)_2$] (**5a**)

A Schlenk flask was charged with [C₂H₄(BDI^{DIPP})₂]₂H₂ (544 mg, 1.00 mmol) and [La{N(SiMe₃)₂]₃] (621 mg, 1.00 mmol). Toluene (10 mL) was added and the mixture was stirred at 72 °C for 110 h. All volatiles were removed in vacuo to give 718 mg (80%) of **5a** in form of a pale yellow powder, which was clean according to NMR spectroscopy. Crystals suitable for X-ray analysis [16] could be grown from hexanes solution at –35 °C. ¹H NMR (toluene-*d*₈, 400 MHz, 25 °C): δ = 7.00 (m, 4H, 3-C₆H₃), 6.91 (m, 2H, 4-C₆H₃), 4.95 (s, 2H, β-CH), 3.76 (m, 2H, CH₂), 3.26 (br m, 4H, CH₂ and CHCH₃), 2.71 (m, 2H, CHCH₃), 1.92 (s, 6H, CH₃), 1.50 (s, 6H, CH₃), 1.14 (br d, 6H, CHCH₃), 0.87 (br d, 12H, CHCH₃), 0.70 (br d, 6H, CHCH₃), 0.21 (s, 18H, SiCH₃); ¹H NMR (toluene-*d*₈, 400 MHz, 80 °C): δ = 6.84–7.08 (m, 6H, C₆H₃), 4.92 (s, 2H, β-CH), 3.81 (br m, 2H, CH₂), 3.33 (br m, 2H, CH₂), 3.20 (m, 2H, CHCH₃), 2.70 (m, 2H, CHCH₃), 1.93 (s,

6H, CH₃), 1.51 (s, 6H, CH₃), 1.14 (br d, 6H, CHCH₃), 0.87 (br d, 12H, CHCH₃), 0.70 (br d, 6H, CHCH₃), 0.21 (s, 18H, SiCH₃); ¹³C{¹H} NMR (toluene-*d*₈, 100.6 MHz, 80 °C): δ = 164.5, 161.6 (CH₃CN), 146.8 (aryl-C_{ipso}), 143.3, 143.0, 125.4, 124.2, 124.0 (aryl), 96.9 (β-CH), 52.1 (CH₂), 28.8, 28.1 (CHCH₃), 25.4 (CHCH₃), 24.9 (CH₃CN), 24.6, 24.5, 24.0 (CHCH₃), 21.8 (CH₃CN), 5.4 (SiCH₃). Anal. calc. for C₄₂H₇₀LaN₅Si₂ (840.13): C, 60.05; H, 8.40; N, 8.34. Found: C, 59.48; H, 8.32; N, 7.98%.

4.16. Preparation of [$\{C_2H_4(BDI^{DIPP})_2\}YN(SiMe_3)_2$] (**5b**)

A Schlenk flask was charged with [C₂H₄(BDI^{DIPP})₂]₂H₂ (543 mg, 1.00 mmol) and [Y{N(SiMe₃)₂]₃] (570 mg, 1.00 mmol). Toluene (10 mL) was added and the mixture was stirred at 95 °C for 5 days. All volatiles were removed in vacuo to give a reddish solid. Washing with hexanes (2 × 3 mL) gave 377 mg of complex **5b** as a white powder. The hexanes washing solution was cooled to –35 °C for a few days, after which further 218 mg of **2b** were isolated. Total yield: 595 mg (77%). ¹H NMR (toluene-*d*₈, 400 MHz, –20 °C): δ = 7.11 (m, 1H, C₆H₃), 7.03 (m, 1H, C₆H₃), 6.92 (m, 1H, C₆H₃), 6.86 (dd, ³J = 7.3 Hz, ⁴J = 1.8 Hz, 1H, C₆H₃), 6.82 (dd, ³J = 6.3 Hz, ⁴J = 1.0 Hz, 1H, C₆H₃), 5.05 (s, 1H, β-CH), 4.89 (s, 1H, β-CH), 3.65–3.73 (m, 3H, CH₂ and CHCH₃), 3.49 (m, 1H, CHCH₃), 2.92 (m, 3H, CH₂ and CHCH₃), 2.46 (m, 1H, CHCH₃), 1.88 (s, 3H, CH₃), 1.86 (s, 3H, CH₃), 1.45 (d, ³J = 6.6 Hz, CHCH₃), 1.39 (s, 3H, CH₃CN), 1.35 (m, 6H, CH₃CN and CHCH₃), 1.11 (d, ³J = 6.1 Hz, 3H, CHCH₃), 1.10 (d, ³J = 6.3 Hz, 3H, CHCH₃), 0.91 (d, ³J = 6.8 Hz, 3H, CHCH₃), 0.89 (d, ³J = 6.8 Hz, 3H, CHCH₃), 0.38 (s, 18H, SiCH₃), 0.32 (d, ³J = 6.6 Hz, 3H, CHCH₃), 0.25 (d, ³J = 6.6 Hz, 3H, CHCH₃); ¹³C{¹H} NMR (toluene-*d*₈, 100.6 MHz, –20 °C): δ = 167.5, 167.3, 164.0, 162.8 (CH₃CN), 148.2, 147.7 (aryl-C_{ipso}), 143.8, 143.6, 143.3, 142.5, 126.1, 125.7, 125.0, 124.5, 124.4, 124.0 (aryl), 100.4, 99.1 (β-CH), 53.8, 49.0 (CH₂), 29.7, 29.3, 28.1, 27.4 (CHCH₃), 26.2, 26.1, 25.9, 25.4, 25.1, 24.8, 24.5 (2 C), 24.3, 24.2, 23.9, 21.3 (CH₃), 6.4 (SiCH₃). Anal. calc. for C₄₂H₇₀N₅Si₂Y (790.13): C, 63.85; H, 8.93; N, 8.86. Found: C, 62.75; H, 8.57; N, 8.42%.

4.17. Preparation of [$\{Cy(BDI^{Mes})_2\}LaN(SiMe_3)_2$] (**6**)

A Schlenk flask was charged with [Cy(BDI^{Mes})₂]₂H₂ (513 mg, 1.00 mmol) and [La{N(SiMe₃)₂]₃] (622 mg, 1.00 mmol). Toluene (10 mL) was added and the mixture was stirred for 24 h at 65 °C. All volatiles were removed in vacuo to give a pale yellow powder. A small amount of impurities was removed by washing with hexanes (5 mL) to yield 667 mg (82%) of clean **6**. ¹H NMR

(toluene- d_8 , 400 MHz, $-20\text{ }^\circ\text{C}$): $\delta = 6.88$ (s, 1H, C_6H_2), 6.82 (s, 2H, C_6H_2), 6.74 (s, 1H, C_6H_2), 5.10 (s, 1H, $\beta\text{-CH}$), 4.25 (s, 1H, $\beta\text{-CH}$), 4.21 (m, 1H, ring-CH), 3.09 (m, 1H, ring-CH), 2.45 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 2.30 (m, 2H, ring- CH_2), 2.21 (s, 6H, CH_3), 2.10 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 1.73 (s, 3H, CH_3), 1.64 (s, 3H, CH_3), 1.58 (m, 2H, ring- CH_2), 1.54 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 1.05–1.30 (m, 4H, ring- CH_2), 0.23 (s, 18H, SiCH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (toluene- d_8 , 100.6 MHz, $-20\text{ }^\circ\text{C}$): $\delta = 162.6$, 161.12, 161.08, 159.7 (CH_3CN), 147.4, 147.0 (aryl- C_{ipso}), 132.5, 131.7, 130.5, 130.0, 129.9, 129.6, 129.4, 129.2, 129.1, 129.0 (aryl), 94.5, 88.2 ($\beta\text{-CH}$), 71.7, 64.7 (ring-CH), 33.3, 32.6, 25.8, 25.6 (ring- CH_2), 23.9, 23.8, 23.2, 21.2, 21.04, 20.99, 20.7, 18.5, 18.1 (CH_3), 4.6 (SiCH_3). Anal. calc. for $\text{C}_{40}\text{H}_{64}\text{LaN}_5\text{Si}_2$ (810.06): C, 59.31; H, 7.96; N, 8.65. Found: C, 59.12; H, 7.81; N, 8.48%.

4.18. Preparation of [$\{\text{Cy}(\text{BDI}^{\text{Mes}})_2\}\text{LaN}(\text{SiHMe}_2)_2$] (7)

A Schlenk flask was charged with [$\text{Cy}(\text{BDI}^{\text{Mes}})_2$] H_2 (256 mg, 0.500 mmol) and [$\text{La}\{\text{N}(\text{SiHMe}_2)_2\}_3(\text{THF})_2$] (340 mg, 0.500 mmol). Toluene (5 mL) was added and the mixture was stirred for 60 h at room temperature. All volatiles were removed in vacuo. The residue was treated with hexanes, which caused the product to precipitate. Filtration and drying in vacuo gave 370 mg (95%) of complex 7 as a pale yellow powder. Crystals suitable for X-ray analysis were grown from hexanes solution at $-35\text{ }^\circ\text{C}$. ^1H NMR (toluene- d_8 , 400 MHz, $-20\text{ }^\circ\text{C}$): $\delta = 6.84$ (s, 1H, C_6H_2), 6.81 (s, 1H, C_6H_2), 6.78 (s, 1H, C_6H_2), 6.76 (s, 1H, C_6H_2), 4.96 (s, 1H, $\beta\text{-CH}$), 4.81 (sept, $^3J = 2.8$ Hz, 2H, SiH), 4.41 (s, 1H, $\beta\text{-CH}$), 4.15 (m, 1H, ring-CH), 3.29 (m, 1H, ring-CH), 2.39 (s, 3H, Me), 2.33 (m, 1H, ring- CH_2), 2.21 (s, 6H, 2- $\text{C}_6\text{H}_2\text{CH}_3$), 2.18 (s, 6H, 2- $\text{C}_6\text{H}_2\text{CH}_3$), 2.04 (s, 3H, CH_3), 1.90 (s, 3H, CH_3), 1.72 (m, 1H, ring- CH_2), 1.66 (s, 3H, CH_3), 1.63 (s, 3H, CH_3), 1.62 (m, 3H, ring- CH_2 , obscured by other signal), 1.53 (s, 3H, CH_3), 1.15–1.35 (m, 4H, ring- CH_2), 0.26 (d, $^3J = 2.8$ Hz, 6H, SiCH_3), 0.04 (d, $^3J = 2.8$ Hz, 6H, SiCH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (toluene- d_8 , 100.6 MHz, $-20\text{ }^\circ\text{C}$): $\delta = 162.1$, 160.9, 160.7, 160.4 (CH_3CN), 147.0, 146.0 (aryl- C_{ipso}), 132.5, 132.1, 130.9, 130.6, 129.7, 129.6, 129.2 (br, 2 C), 129.00, 128.95 (aryl), 93.9, 89.3 ($\beta\text{-CH}$), 70.6, 64.4 (ring-CH), 33.6, 32.6, 25.9, 25.6, (ring- CH_2), 24.3, 23.4, 22.7, 21.3, 21.1 (2 C), 20.4, 20.2, 18.8, 18.4 (CH_3), 3.6, 3.1 (SiCH_3). Anal. calc. for $\text{C}_{38}\text{H}_{60}\text{LaN}_5\text{Si}_2$ (782.00): C, 58.37; H, 7.73; N, 8.96. Found: C, 57.97; H, 7.93; N, 8.60%.

4.19. Preparation of [$\{\text{Cy}(\text{BDI}^{\text{DEP}})_2\}\text{LaN}(\text{SiMe}_3)_2$] (8)

A Schlenk flask was charged with [$\text{Cy}(\text{BDI}^{\text{DEP}})_2$] H_2 (540 mg, 1.00 mmol) and [$\text{La}\{\text{N}(\text{SiMe}_3)_2\}_3$] (624 mg,

1.01 mmol). Toluene (10 mL) was added and the mixture was stirred for 40 h at $95\text{ }^\circ\text{C}$. All volatiles were removed in vacuo, the residue was dissolved in pentane (10 mL) and filtered. The filtrate was concentrated in vacuo to yield 793 mg (95%) of 8 as a pale yellow powder. Crystals suitable for X-ray analysis were grown from hexanes solution at $-35\text{ }^\circ\text{C}$. ^1H NMR (toluene- d_8 , 400 MHz, $-20\text{ }^\circ\text{C}$): $\delta = 6.98$ –7.15 (m, 6H, C_6H_3), 5.10 (s, 1H, $\beta\text{-CH}$), 4.17 (m, 1H, ring-CH), 4.14 (s, 1H, $\beta\text{-CH}$), 3.27 (m, 1H, CH_2CH_3), 3.08 (m, 1H, ring-CH), 2.78 (m, 1H, CH_2CH_3), 2.68 (m, 2H, CH_2CH_3), 2.58 (m, 1H, CH_2CH_3), 2.44 (m, 1H, CH_2CH_3), 2.31 (m, 1H, ring- CH_2), 2.12 (m, 1H, CH_2CH_3), 2.04 (s, 3H, CH_3CN), 2.01 (m, 1H, CH_2CH_3), 1.64 (s, 3H, CH_3CN), 1.56–1.65 (br m, 4H, ring- CH_2 , obscured by other signal), 1.51 (s, 3H, CH_3CN), 1.40 (t, $^3J = 7.4$ Hz, 3H, CH_2CH_3), 1.34 (s, 3H, CH_3CN), 1.28 (t, $^3J = 7.4$ Hz, 3H, CH_2CH_3), 1.20 (t, $^3J = 7.6$ Hz, 3H, CH_2CH_3), 1.1–1.3 (m, 3H, ring- CH_2 , obscured by other signals), 1.09 (t, $^3J = 7.5$ Hz, 3H, CH_2CH_3), 0.19 (br s, 18H, SiCH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (toluene- d_8 , 100.6 MHz, $-20\text{ }^\circ\text{C}$): $\delta = 162.5$, 161.3, 161.0, 160.0 (CH_3CN), 149.1, 148.5 (aryl- C_{ipso}), 136.0, 135.3, 134.9, 134.8, 126.2, 125.5, 124.8, 124.4, 124.3, 123.5 (aryl), 94.4, 87.8 ($\beta\text{-CH}$), 71.8, 64.6 (ring-CH), 33.1, 32.7 (ring- CH_2), 27.7 (CH_2CH_3), 25.73, 25.68 (ring- CH_2), 25.4 (CH_2CH_3), 23.9 (2 C, CH_2CH_3 and CH_3CN), 23.6, 23.4 (CH_3CN), 22.9 (CH_2CH_3), 21.1 (CH_3CN), 14.4, 14.3, 13.3, 12.9 (CH_2CH_3), 4.6 (SiCH_3). Anal. calc. for $\text{C}_{42}\text{H}_{68}\text{LaN}_5\text{Si}_2$ (838.11): C, 60.19; H, 8.18; N, 8.36. Found: C, 59.95; H, 8.25; N, 8.15%.

4.20. Preparation of [$\{\text{Cy}(\text{BDI}^{\text{DEP}})_2\}\text{LaN}(\text{SiHMe}_2)_2$] (9)

A Schlenk flask was charged with [$\text{Cy}(\text{BDI}^{\text{DEP}})_2$] H_2 (550 mg, 1.02 mmol) and [$\text{La}\{\text{N}(\text{SiHMe}_2)_2\}_3(\text{THF})_2$] (857 mg, 1.26 mmol). Toluene (10 mL) was added and the mixture was stirred for 51 h at $65\text{ }^\circ\text{C}$. All volatiles were removed in vacuo, the residue was dissolved in hexanes (2.5 mL). Crystallization at $-35\text{ }^\circ\text{C}$ produced 738 mg (90%) of 9 after a few days in form of pale yellow crystals. ^1H NMR (toluene- d_8 , 400 MHz, $-20\text{ }^\circ\text{C}$): $\delta = 6.96$ –7.13 (m, 6H, C_6H_3), 4.96 (s, 1H, $\beta\text{-CH}$), 4.75 (sept, $^3J = 2.8$ Hz, 2H, SiH), 4.31 (s, 1H, $\beta\text{-CH}$), 4.07 (m, 1H, ring-CH), 3.28 (m, 1H, ring-CH), 2.83 (m, 2H, CH_2CH_3), 2.67 (m, 2H, CH_2CH_3), 2.52 (m, 2H, CH_2CH_3), 2.32 (m, 2H, CH_2CH_3 and ring- CH_2), 2.17 (m, 1H, CH_2CH_3), 2.01 (s, 3H, CH_3CN), 1.67 (s, 3H, CH_3CN), 1.60 (s, 3H, CH_3CN), 1.57–1.74 (br m, 4H, ring- CH_2 , obscured by other signals), 1.49 (s, 3H, CH_3CN), 1.15–1.38 (br m, 3H, ring- CH_2 obscured by other signals), 1.35 (pt, $^3J = 7.3$ Hz, 3H, CH_2CH_3), 1.32 (pt, $^3J = 7.3$ Hz, 3H, CH_2CH_3), 1.27 (pt, $^3J = 7.6$ Hz, 3H, CH_2CH_3), 1.10 (pt, $^3J = 7.5$ Hz, 3H, CH_2CH_3), 0.22 (d, $^3J = 2.8$ Hz, 6H, SiCH_3), -0.03 (d, $^3J = 2.8$ Hz,

6H, SiCH₃); ¹³C{¹H} NMR (toluene-*d*₈, 100.6 MHz, –20 °C): δ = 162.2, 160.8 (CH₃CN), 160.7 (2 C, CH₃CN), 148.9, 148.0 (aryl-*C*_{ipso}), 136.5, 136.0, 134.8, 134.7 (aryl), 126.8, 126.4, 124.9, 124.3, 124.2, 123.8 (aryl), 93.2, 88.2 (β-CH), 71.0, 64.5 (ring-CH), 33.2, 32.7 (ring-CH₂), 26.6 (CH₂CH₃), 25.8, 25.7 (ring-CH₂), 25.2, 25.0, 24.4 (CH₂CH₃), 24.0, 23.6, 22.8, 21.5 (CH₃CN), 15.0, 14.2, 14.1, 13.2 (CH₂CH₃), 3.5, 3.2 (SiCH₃). Anal. calc. for C₄₀H₆₄LaN₅Si₂ (810.06): C, 59.31; H, 7.96; N, 8.65. Found: C, 58.23; H, 7.99; N, 8.27%.

4.21. Preparation of [*Cy*(BDI^{DIPP})₂]*La*N(SiMe₃)₂ (**10**)

A Schlenk flask was charged with [*Cy*(BDI^{DIPP})₂]*H*₂ (602 mg, 1.01 mmol) and [*La*(N(SiMe₃)₂)₃] (625 mg, 1.01 mmol). Toluene (10 mL) was added and the mixture was stirred for 4 days at 95 °C. All volatiles were removed in vacuo to give 707 mg (79%) of **10** as a pale yellow powder. Crystals suitable for X-ray analysis [16] could be grown from hexanes solution at –35 °C. ¹H NMR (C₆D₆, 400 MHz, 25 °C): δ = 7.02–7.18 (m, 6H, C₆H₃), 5.17 (s, 1H, β-CH), 4.22 (s, 1H, β-CH), 4.20 (m, 1H, ring-CH), 3.50 (sept., ³*J* = 6.8 Hz, 1H, CHCH₃), 3.16 (m, 1H, ring-CH), 3.14 (sept., ³*J* = 6.8 Hz, 1H, CHCH₃), 3.05 (sept., ³*J* = 6.8 Hz, 1H, CHCH₃), 2.54 (sept., ³*J* = 6.8 Hz, 1H, CHCH₃), 2.30 (m, 1H, ring-CH₂), 2.05 (s, 3H, CH₃CN), 1.75 (s, 3H, CH₃CN), 1.64 (s, 3H, CH₃CN), 1.50–1.70 (m, 6H, ring-CH₂, obscured by other signals), 1.54 (d, ³*J* = 6.8 Hz, 3H, CHCH₃), 1.47 (s, 3H, CH₃CN), 1.42 (d, ³*J* = 6.8 Hz, 3H, CHCH₃), 1.34 (d, ³*J* = 7.1 Hz, 3H, CHCH₃), 1.27 (d, ³*J* = 6.8 Hz, 3H, CHCH₃), 1.21 (d, ³*J* = 6.6 Hz, 3H, CHCH₃), 1.10–1.14 (m, 1H, ring-CH₂, obscured by other signal), 1.13 (d, ³*J* = 6.8 Hz, 3H, CHCH₃), 1.04 (d, ³*J* = 6.8 Hz, 3H, CHCH₃), 0.94 (d, ³*J* = 6.8 Hz, 3H, CHCH₃), 0.28 (s, 9H, SiCH₃), 0.03 (s, 9H, SiCH₃); ¹³C{¹H} NMR (C₆D₆, 100.6 MHz, 25 °C): δ = 164.9, 161.4, 160.4, 160.3 (CH₃CN), 148.0, 147.3 (aryl-*C*_{ipso}), 141.4, 141.1, 140.8, 140.6, 124.9, 124.1, 124.0, 123.9, 123.8, 123.0 (aryl), 95.3, 87.1 (β-CH), 71.5, 65.2 (ring-CH), 33.3, 32.7 (ring-CH₂), 31.4, 29.3, 27.9, 27.4 (CHCH₃), 27.0, 26.0 (CHCH₃), 25.8, 25.7 (ring-CH₂), 25.1, 25.0 (CHCH₃), 24.9 (2 C, CH₃CN), 24.49, 24.47 (ring-CH₂), 24.0, 23.5 (CHCH₃), 23.3, 21.4 (CH₃CN), 5.0, 2.6 (SiCH₃). Anal. calc. for C₄₆H₇₆LaN₅Si₂ (894.22): C, 61.79; H, 8.57; N, 7.83. Found: C, 60.77; H, 8.67; N, 7.43%.

4.22. X-ray crystal structure analysis of **1**, **3b**, **7** and **8**

Clear, colorless crystals suitable for X-ray diffraction analysis were obtained by cooling of a concentrated pentane solution to –20 °C (for **1**), respectively from hexanes at –35 °C (for **3b**, **7** and **8**). Data were collected

on a Nonius KappaCCD area detector. Cell parameters were obtained from 10 frames using a 10° scan and refined with 18958 reflections for **1**, 8799 reflections for **3b**, 8875 reflections for **7** and 10074 reflections for **8**. Lorentz, polarization, and empirical absorption corrections were applied [27a,27b]. The space groups were determined from systematic absences and subsequent least-squares refinement. The structures were solved by direct methods. The parameters were refined with all data by full-matrix least-squares on *F*² using SHELXL-97 [27c]. Hydrogen atoms were fixed in idealized positions using a riding model. Non-hydrogen atoms were refined anisotropically. The methyl groups attached to C36A and C42A in complex **8** are disordered and were refined with two independent positions (position occupation of 80:20 for C36B/C36C and 70:30 for C42B/C42C). Scattering factors and Δ*f*' and Δ*f*'' values were taken from the literature [27d].

4.23. Typical high pressure procedure for the copolymerization of cyclohexene oxide and CO₂

The steel autoclave was loaded in the glovebox with catalyst **6** (33.0 mg, 40.7 μmol), cyclohexene oxide (4.00 g, 40.8 mmol) and a stirring bar. The vessel was removed from the glovebox and pressurized to 41 atm CO₂. The reactor was then heated with stirring to 60 °C for 18 h. Excess cyclohexene oxide was then removed in vacuo. The polymer was redissolved in CH₂Cl₂ and dried in vacuo at 60 °C until constant weight. Yield: 507 mg. The carbonate linkage content was determined from the intensity of the cyclohexyl methyne proton signals (4.6 ppm for carbonate linkages, 3.3 ppm for ether linkages) in the ¹H NMR spectrum of the polymer.

4.24. Typical normal pressure procedure for the copolymerization of cyclohexene oxide and CO₂

A Schlenk flask was loaded with the catalyst **6** (32.6 mg, 40.2 μmol) and a stirring bar. Toluene (1 mL) was added to dissolve the catalyst and the nitrogen atmosphere was exchanged for 1 atm CO₂. After 5 min stirring, cyclohexene oxide (4.135 g, 42.1 mmol) was added via syringe. A CO₂-filled balloon was attached and the mixture was stirred at 75 °C for 24 h. The solvent and excess cyclohexene oxide was then removed in vacuo. The polymer was redissolved in CH₂Cl₂ and dried in vacuo at 60 °C until constant weight. Yield: 533 mg.

5. Supporting information

Crystallographic data (excluding structure factors) for the structure of complexes **1**, **3b**, **7** and **8** reported in this paper have been deposited with Cambridge

Crystallographic Data Centre as supplementary publication nos. CCDC-262007 for **1**, CCDC-262008 for **3b**, CCDC-266998 for **7** and CCDC-266997 for **8**. Copies of the data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (int code) +44 1223 336 033 or e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>.

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