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Enantiopure amidinate complexes of lutetium☆

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ABSTRACT

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

1. Introduction

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

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

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

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

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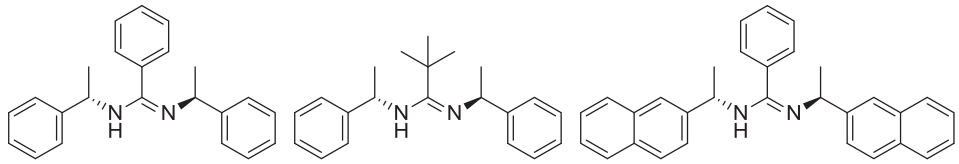


Scheme 1. Chiral amidines which were recently used by us (*S*)-HPEBA, (*S*)-HPETA, and (*S*)-HNEBA for the synthesis of enantiomerically pure rare earth metal complexes [1–3], [40,41].

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

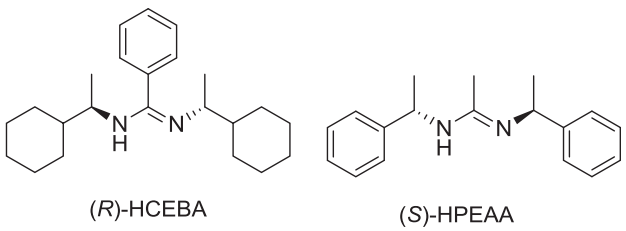
2. Results and discussion [42]

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

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

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

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



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

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

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

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

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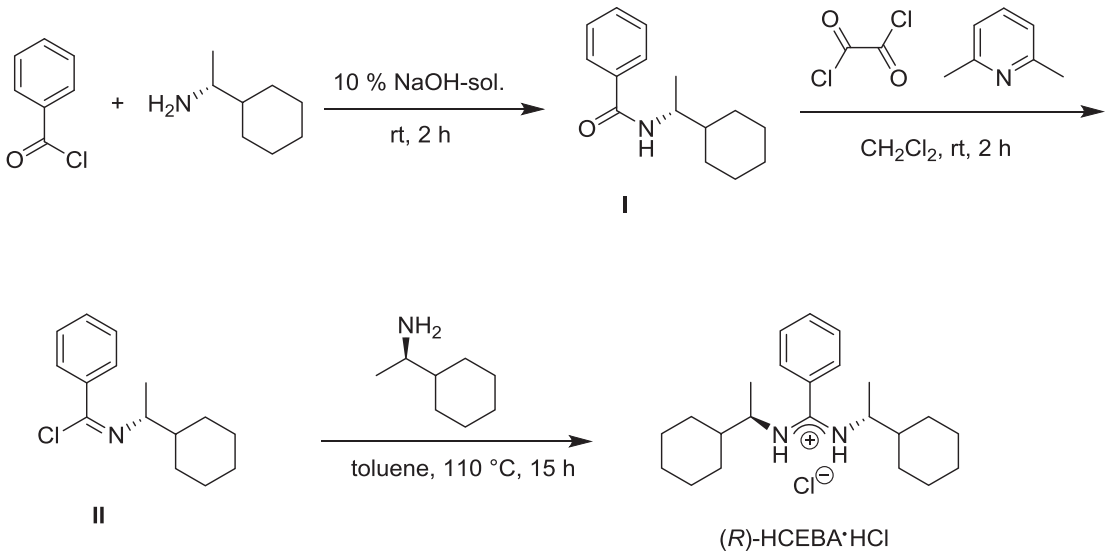
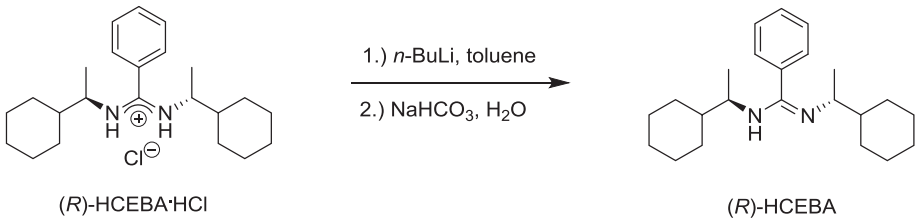
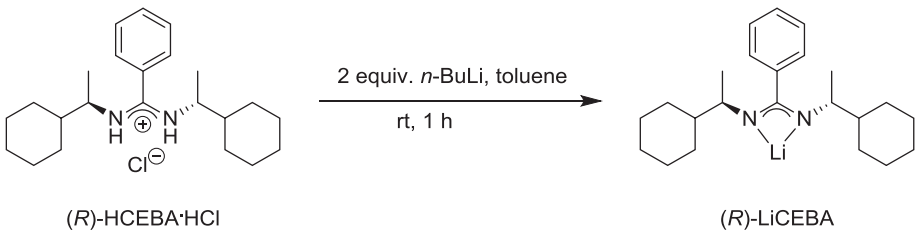


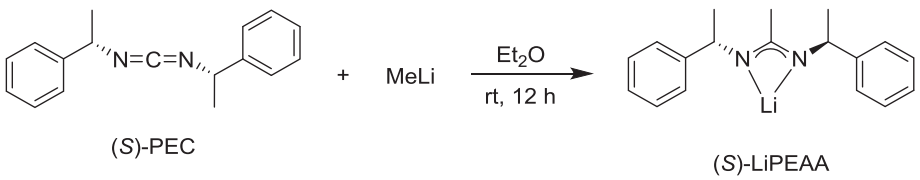
Scheme 3. Synthesis of amidine hydrochloride ((*R*)-HCEBA·HCl).



Scheme 4. Synthesis of amidine (*R*)-HCEBA.



Scheme 5. Synthesis of (*R*)-LiCEBA.



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

170.5 ppm.

Next, we reacted both lithium salts with $LuCl_3$ to generate the corresponding chiral lutetium complexes. First, (*R*)-LiCEBA was reacted with $LuCl_3$ at room temperature in a 2:1 stoichiometric ratio. This results in the double substituted chloride complex [{(*R*)-CEBA}$_2$Lu-μ-Cl]$_2$ (**1**) (Scheme 7). Alternatively, the easy accessible hydrochloride (*R*)-HCEBA·HCl can be deprotonated twice with $KN(SiMe_3)_2$. The resulting potassium salt was not isolated. Instead (*R*)-HCEBA·HCl, $KN(SiMe_3)_2$ and $LuCl_3$ were heated in a one pot reaction for two days in THF to give **1** (Scheme 7). Attempts to generate the corresponding amido complex [{(*R*)-CEBA}$_2$Lu{$N(SiMe_3)_2$}] by using an excess of $KN(SiMe_3)_2$ were not successful. Compound **1** was fully characterized by standard analytic/spectroscopic techniques and the solid state structure was established by single crystal X-ray diffraction.

Single crystals of **1** were obtained from a hot and saturated toluene solution. Compound **1** crystallizes in the tetragonal Sohncke space group $I4_122$ with eight molecules of **1** and toluene in

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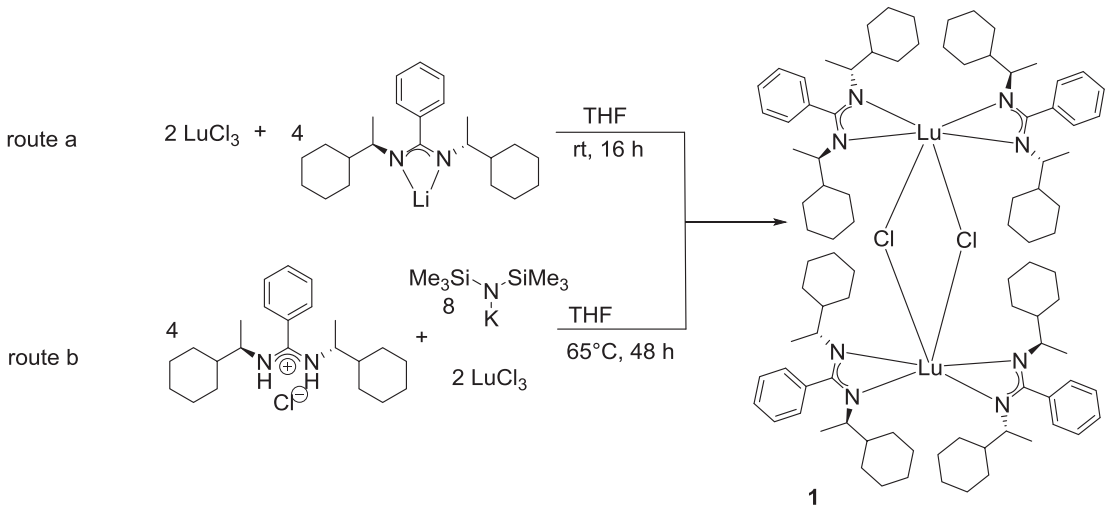

Scheme 7. Two pathways for the synthesis of **1**.

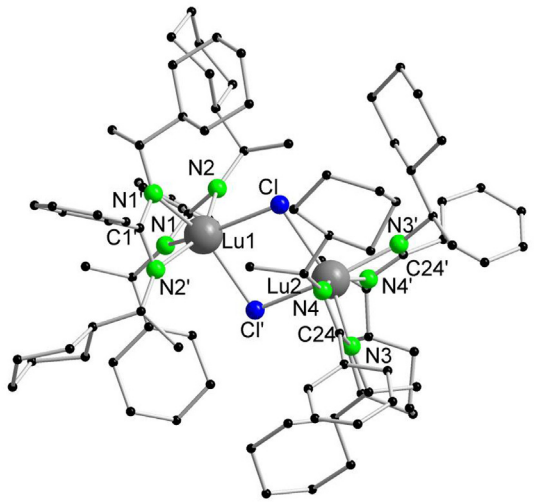

Fig. 1. Molecular structure of **1** in the solid-state. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Lu1-Cl 2.6405(13), Lu1-N1 2.267(5), Lu1-N2 2.351(5), Lu2-Cl 2.6640(13), Lu2-N3 2.255(5), Lu2-N4 2.359(5), N1-C1 1.337(6), N2-C1 1.321(7),N3-C24 1.322(7), N4-C24 1.341(7); N1-Lu1-N2 58.2(2), N3-Lu2-N4 58.1(2), Cl-Lu1-Cl' 80.38(5), Cl-Lu2-Cl' 79.52(5), Lu1-Cl-Lu2 100.05(4), N1-C1-N2 115.3(5), N3-C24-N4 114.8(5).

the unit cell (Fig. 1). Only half of a molecule is localized in the asymmetric unit. A crystallographic C2 axis is observed along Lu1 and Lu2. Compound **1** is a di-μ-chloro bridged dimeric compound. The central Lu-Cl-Lu-Cl four-membered ring is symmetrical with angles of Cl-Lu1-Cl' 80.38(5)°, Cl-Lu2-Cl' 79.52(5)°, and Lu1-Cl-Lu2 100.05(4)°. The Lu-N-C-N planes formed by the amidinate ligands are twisted to each other by about 99.8° (Lu1) and 104.8 (Lu2). The amidinate ligands coordinate asymmetrically to the lutetium atoms (Lu1-N1 2.267(5) Å, Lu1-N2 2.351(5) Å, Lu2-N3 2.255(5) Å, and Lu2-N4 2.359(5) Å). The deviation of the Lu-N bond distances of each amidinate ligand is about 0.1 Å. The phenyl rings are almost rectangular localized to these planes. The bite angles in **1** (N1-Lu1-N2 58.2(2)°, N3-Lu2-N4 58.1(2)°) are very similar to $[Lu(PEBA)_2(\mu\text{-}Cl)]_2$ (58.51(9)°) [1] but as expected larger than in the crowded PETA compound $[\{(S)\text{-PETA}\}_2LnCl]_2$ (av. 57.6°) [40].

The ^1H and $^{13}C\{^1H\}$ NMR spectra of **1** show the expected signals. However, as a result of the flexible cyclohexyl rings overlaid broad signals are seen in the aliphatic region. The ^1H NMR spectrum is thus not very conclusive. The $^{13}C\{^1H\}$ NMR spectrum points to an asymmetric coordination of the amidinate ligands. Thus, two sets of signals were observed for the amidinate ligands, e.g. the methyl and methine group each shows two resonances at 59.5 ppm, 59.0 ppm, 22.3 ppm, 21.3 ppm. Since the amidinate ligands are relatively large, we suggest steric reasons hamper a symmetric coordination in solution. Unfortunately, the by-product LiCl from salt metathesis could not be completely removed from the bulk material.

In similar manner as for the synthesis of **1**, we reacted (*S*)-LiPEAA with $LuCl_3$ in a 2:1 stoichiometric ratio in THF at room temperature to obtain $[\{(S)\text{-PEAA}\}_2LuCl(thf)]$ (**2**) as product Scheme 8. Single crystals of **2** were grown from THF/n-pentane.

Compound **2** crystallizes in the orthorhombic Sohncke space group $P2_12_12_1$ with four molecules in the unit cell (Fig. 2). The lutetium atom is six-fold coordinated by two amidinate ligands, one chlorine atom, and one additional molecule of THF. Compound **2** is the first monomeric lutetium bis amidinate chloro compound with a chiral ligand. All other related lutetium complexes form chloride bridged dimers e.g. **1**, $[\{(S)\text{-PETA}\}_2LuCl]_2$ [40] and $[\{(S)\text{-PEBA}\}_2LnCl]_2$ [1]. Obviously, in comparison to the other chiral amidinates, the reduced steric demand of $\{(S)\text{-PEAA}\}^-$ has a significant influence on the complex geometry. The Lu-N (av. 2.291 Å) bond distances in **2** are very similar to those observed in **1** (av. 2.308 Å). On the other hand, the ligand is more symmetrically coordinated to the metal atom as observed in **1**. Unfortunately, the bite angles of the ligands (N1-Lu-N2 57.66(14)° and N3-Lu-N4 59.18(15)°) differ significantly, precluding a detailed interpretation.

In contrast to **1**, the ^1H NMR spectrum of **2** shows sharp peaks and a symmetrical pattern. The characteristic signals of the methyl groups are observed at 1.52 and 1.64 ppm. In the $^{13}C\{^1H\}$ NMR spectrum, the signals of these groups were detected at 14.8 and 27.6 ppm. The characteristic signal of the NCN unit is seen at 178.8 ppm.

3. Summary

In summary, we prepared two new chiral amidinates $((R)\text{-CEBA})^-$ and $((S)\text{-PEAA})^-$ by two different synthetic pathways. The corresponding lithium salts (*R*)-LiCEBA and (*S*)-LiPEAA were obtained by deprotonation of the amidine or by direct reaction of a lithium alkyl reagent with the carbodiimide precursor. Further

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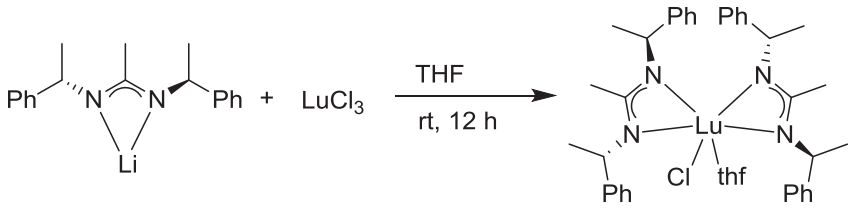

2

Scheme 8. Synthesis of **2**.

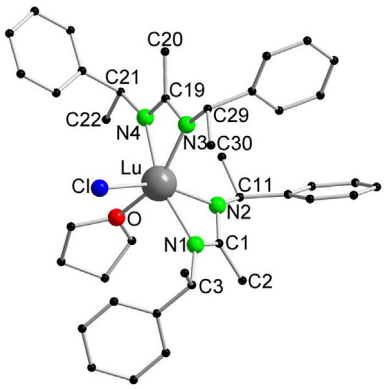

Fig. 2. Molecular structure of **2** in the solid-state. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Lu1-Cl 2.5590(11), Lu1-O1 2.311(4), Lu1-N1 2.311(4), Lu1-N2 2.295(4), Lu1-N3 2.254(4), Lu1-N4 2.304(4), N1-C1 1.340(6), N2-C1 1.339(7), N3-C19 1.342(6), N4-C19 1.332(7); N1-Lu-N2 57.66(14), N1-Lu-N3 114.0(2), N1-Lu-N4 159.6(2), N1-Lu-Cl 99.26(10), N1-Lu-O1 92.86(15), N2-Lu-N3 98.9(2), N2-Lu-N4 103(2), N2-Lu-Cl 156.80(11), N2-Lu-O1 88.80(15), N3-Lu-N4 59.18(15), N3-Lu-Cl 92.72(11), N3-Lu-O1 152.11(14), N4-Lu-Cl 100.21(12), N4-Lu-O1 93.01(14), Cl1-Lu-O1 90.24(10), N1-C1-N2 112.0(5), N3-C19-N4 114.7(4).

reactions of these lithium salts with $LuCl_3$ resulted in the bisamidinate complexes $[\{(R)\text{-CEBA}\}_2Lu\text{-}\mu\text{-}Cl]_2$ and $[\{(S)\text{-PEAA}\}_2LuCl(thf)]$, which are either dimeric or monomeric in the solid state. Further reactions to amido or alkyl derivatives suitable for σ-bond metathesis failed, unfortunately.

4. Experimental [42]

General procedures: All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in Schlenk-type glassware, either on a dual-manifold Schlenk line interfaced to a high-vacuum (10^{-3} mbar) line or in an argon-filled MBraun glove box. THF was distilled under a nitrogen atmosphere from potassium benzophenone ketyl prior to use. Hydrocarbon solvents (toluene, *n*-pentane and *n*-heptane) 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 GmbH (99 atom% D) and were degassed, dried, and stored *in vacuo* over Na/K alloy in resealable flasks. NMR spectra were recorded on Bruker Avance II 300 MHz or Avance III 400 MHz NMR spectrometers. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane. IR spectra were obtained on a Bruker Tensor 37. Mass spectra were recorded at 70 eV on a Finnigan MAT 8200. Elemental analysis was performed on an Elementar vario EL or microcube. $LnCl_3$ [52] and (*S*)-PEC [40] were prepared according to literature procedures. $KN(SiMe_3)_2$ was sublimed before use.

4.1. (R)-N-(1-cyclohexylethyl)benzamide (I)

To a reaction mixture of 10.00 mL (8.66 g, 68.1 mmol) (*R*)-1-cyclohexylethylamine in 55 mL of an aqueous sodium hydroxide solution (10%), 8.30 mL (10.05 g, 71.5 mmol) benzoylchloride was added dropwise under vigorous stirring. After 2 h of stirring at r.t. the colorless precipitate formed was filtered off, washed several times with water and then dried *in vacuo*. Yield: 14.0 g (60.5 mmol, 89%) of **I** as colorless solid. - ^{1}H NMR (400 MHz, DMSO-d_6, 298 K): δ (ppm) = 8.10 (d, ^3J = 8.4 Hz, 1 H, N*H*), 7.83 (d, ^3J = 7.2 Hz, 2 H, *m*-Ph), 7.50 (t, ^3J = 7.2 Hz, 1 H, *p*-Ph), 7.44 (t, ^3J = 7.2 Hz, 2 H, *o*-Ph), 3.84 (m, ^3J = 7.2 Hz, 1 H, NC*H*), 1.76–1.69 (m, 4 H, cyclohexyl-*H*), 1.61–1.59 (m, 1 H, cyclohexyl-*H*), 1.45–1.37 (m, 1 H, cyclohexyl-*H*), 1.20–1.09 (m, 6 H, cyclohexyl-*H* und C*H*$_3$), 0.99–0.90 (m, 2 H, cyclohexyl-*H*). - ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6, 298 K): δ (ppm) = 165.6 (*C*O), 135.0 (*i*-Ph), 130.9 (Ph), 128.1 (Ph), 127.3 (Ph), 49.2 (NCH), 42.4 (cyclohexyl-*C*H), 29.3 (*C*H$_2$), 29.0 (*C*H$_2$), 26.1 (*C*H$_2$), 25.8 (*C*H$_2$), 17.7 (*C*H$_3$).

4.2. (R)-N-(1-cyclohexylethyl)benzimidoylchloride (II)

A mixture of **I** 14.0 g (60.5 mmol) and 7.75 mL (7.13 g, 66.6 mmol) of 2,6-lutidine was dissolved in 150 mL of dry CH_2Cl_2 and cooled in a water bath. 5.20 mL (7.68 g, 60.5 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 and the mixture was stirred at r.t. for 2 h. The volatile components were removed *in vacuo*. Two times 100 mL of dry *n*-pentane were added to the dark brown residue and stirred for 1 h. The suspension was filtered and the volatile components of the combined filtrates were removed under vacuum. The resulting brown oil was distilled *in vacuo* at 125 °C ($3.4\cdot10^{-2}$ mbar) to obtain 12.04 g (48.2 mmol, 80%) of light yellow **II**.

4.3. (R)-1-Cyclohexylethyl-benzimidamide-hydrochloride (R)-HCEBA·HCl

The imidoylchloride **II** 12.04 g (48.2 mmol) was dissolved in 50 ml of dry toluene and 7.08 ml (6.13 g, 48.2 mmol) of (*R*)-1-cyclohexylethylamine was added dropwise. The reaction mixture was refluxed for 12 h. Upon cooling to room temperature, the desired product precipitates as a colorless solid. The solid was filtered off and recrystallized from hot toluene to obtain 16.23 g (43.0 mmol, 89%) of colorless (*R*)-HCEBA·HCl. - ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) = 10.46 (d, ^3J = 9.6 Hz, 2 H, N*H*), 7.64–7.56 (m, 3 H, Ph), 7.25 (s, 2 H, Ph), 2.86–2.77 (m, 2 H, NC*H*), 1.77–1.59 (m, 10 H, cyclohexyl-*H*), 1.39–1.34 (m, 2 H, cyclohexyl-*H*), 1.24–1.07 (m, 12 H, cyclohexyl-*H* and C*H*$_3$), 0.99–0.84 (m, 4 H, cyclohexyl-*H*). - ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ (ppm) = 166.1 (NCN), 131.8 (*i*-Ph), 129.8 (Ph), 127.1 (Ph), 126.9 (Ph), 56.7 (NCH), 43.4 (cyclohexyl-*C*H), 29.4 (*C*H$_2$), 29.0 (*C*H$_2$), 26.1 (*C*H$_2$), 26.1 (*C*H$_2$), 19.1 (*C*H$_3$). - HR

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ESI-MS (toluene): m/z = 717.57 ([(HCEBA)$_2$·HCl]$^+$), calc. for $C_{46}H_{74}N_4Cl$: 717.56. - IR (ATR): ν (cm^{-1}) = 3249 (w), 3154 (w), 3096 (w), 3032 (m), 2969 (m), 2928 (vs), 2852 (vs), 2669 (w), 2019 (w), 1939 (w), 1627 (vs), 1611 (w), 1572 (s), 1468 (w), 1448 (s), 1380 (m), 1323 (w), 1315 (m), 1288 (w), 1265 (w), 1240 (w), 1191 (w), 1174 (w), 1140 (m), 1080 (w), 1044 (w), 1015 (w), 1000 (w), 951 (w), 890 (w), 864 (w), 854 (w), 792 (s), 742 (m), 720 (s), 687 (w), 668 (w), 494 (w), 443 (w), 429 (w), 410 (w), 384 (w), 362 (w). - elemental analysis calc. (%) for $C_{23}H_{37}N_2Cl$ (377.006 g/mol): C 73.27; H 9.89, N 7.43; found: C 72.19, H 8.71, N 7.42.

4.4. (R,R)-N,N'-bis-(1-cyclohexylethyl)benzamidine ((R)-HCEBA)

1.0 ml (2.5 M in *n*-hexane, 2.50 mmol) *n*-butyl lithium was added dropwise to a suspension of 0.80 g (2.12 mmol) (*R*)-HCEBA·HCl in 20 ml toluene. Upon reaction the suspension clears up and was stirred at r.t. for 30 min. The clear solution is quenched with 30 ml of a saturated sodium bicarbonate solution. After vigorous stirring for 30 min, the phases were separated and the organic layer was dried over magnesium sulfate. The solvent was removed *in vacuo* to obtain (*R*)-HCEBA as colorless oil. Yield: 0.70 g (2.06 mmol, 97%). - ^{1}H NMR (300 MHz, DMSO-d_6, 298 K): δ (ppm) = 7.42–7.32 (m, 3 H, Ph), 7.14–7.11 (m, 2 H, Ph), 5.48 (d, ^3J = 6.9 Hz, 1 H, N*H*), 3.85 (br, 1 H, NC*H*), 2.67 (m, ^3J = 5.4 Hz, 1 H, NHC*H*), 1.71–1.62 (m, 10 H, cyclohexyl-*H*), 1.14–0.77 (m, 18 H, cyclohexyl-*H* and C*H*$_3$). - ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6, 298 K): δ (ppm) = 155.9 (N*C*N), 136.9 (*i*-Ph), 128.1 (Ph), 127.9 (Ph), 127.4 (Ph), 57.89 (NH*C*H), 48.9 (N*C*H), 45.1 (NHCH-cyclohexyl-*C*H), 41.4 (NCH-cyclohexyl-*C*H), 30.0 (*C*H$_2$), 29.7 (*C*H$_2$), 28.4 (*C*H$_2$), 28.0 (*C*H$_2$), 26.4 (*C*H$_2$), 26.1 (*C*H$_2$), 21.2 (NCH*C*H$_3$) 16.7 (NHCH*C*H$_3$).

4.5. Lithium-N,N'-bis-((R)-1-cyclohexylethyl)benzamidinate ((R)-LiCEBA)

3.42 mL (2.5 M in n-hexane, 8.55 mmol) *n*-butyl lithium was added dropwise to a solution of 1.50 g (3.98 mmol) (*R*)-HCEBA·HCl in 50 mL toluene. The light yellow mixture was stirred for 3 h at r.t. and the volatile components were removed *in vacuo*. The residue was washed with 30 mL of *n*-pentane. After drying under vacuum, the desired product is obtained as a colorless solid that includes one equivalent of lithium chloride, which was not separated. Yield: 1.14 g (2.93 mmol, 74%) - ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ (ppm) = 7.26–7.20 (m, 4 H, Ph), 7.12–7.08 (m, 1 H, Ph), 2.91 (m, ^3J = 4.5 Hz, 2 H, NC*H*), 1.95–1.70 (m, 11 H, cyclohexyl-*H*), 1.37–1.21 (m, 11 H, cyclohexyl-*H*), 1.06 (d, ^3J = 4.5 Hz, 6 H, C*H*$_3$). - ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 298 K): δ (ppm) = 176.8 (N*C*N), 139.2 (*i*-Ph), 128.3 (Ph), 127.9 (Ph), 127.1 (Ph), 56.8 (N*C*H), 47.1 (cyclohexyl-*C*H), 30.8 (*C*H$_2$), 30.5 (*C*H$_2$), 27.5 (*C*H$_2$), 27.3 (*C*H$_2$), 27.2 (*C*H$_2$), 22.4 (*C*H$_3$). - IR (ATR): ν (cm^{-1}) = 3442 (w), 3080 (w), 3058 (w), 3025 (w), 2921 (vs), 2850 (vs), 2665 (w), 1637 (vs), 1600 (m), 1578 (w), 1559 (w), 1480 (s), 1447 (s), 1366 (m), 1333 (m), 1292 (m), 1260 (m), 1189 (w), 1157 (w), 1123 (w), 1071 (w), 1026 (s), 915 (w), 890 (m), 861 (w), 841 (w), 798 (m), 768 (m), 701 (vs), 669 (w), 556 (w), 505 (w), 446 (m), 391 (w). - elemental analysis calc. (%) for $C_{23}H_{35}N_2Li$·LiCl (388.872 g/mol): C 71.04; H 9.07, N 7.20; found: C 72.05, H 9.18, N 6.89.

4.6. Lithium-N,N'-bis-((S)-1-phenylethyl)acetamidinate ((S)-LiPEAA)

2.3 ml (1.6 M in diethyl ether, 3.68 mmol) of methyl lithium was added dropwise to a solution of 0.92 g (3.68 mmol) (*S*)-PEC [40] in 20 ml of dry diethyl ether at −40 °C. The mixture was stirred at r.t. over night. All volatiles were removed *in vacuo* and the residue was washed with 25 ml of *n*-pentane to obtain (*S*)-LiPEAA as orange powder. Yield: 0.85 g (3.12 mmol, 85%). - ^{1}H NMR (400 MHz, d$_8$-THF, 298 K): δ (ppm) = 7.30 (d, ^3J = 7.2 Hz, 4 H, Ph), 7.14 (t, ^3J = 7.2 Hz, 4 H, Ph), 7.00 (t, ^3J = 7.2 Hz, 2 H, Ph), 4.41 (q, ^3J = 6.6 Hz, 4 H, C*H*), 1.58 (s, 3 H, CC*H*$_3$), 1.21 (d, ^3J = 6.6 Hz, 6 H, CHC*H*$_3$). - ^{13}C{^{1}H} NMR (75 MHz, d$_8$-THF, 298 K): δ (ppm) = 170.5 (N*C*N), 153.8 (*i*-Ph), 128.3 (Ph), 127.5 (Ph), 125.6 (Ph), 57.5 (*C*H), 29.1 (CH*C*H$_3$), 12.1 (*C*CH$_3$). - IR (ATR): ν (cm^{-1}) = 3428 (w), 3058 (w), 3023 (w), 2963 (m), 2922 (w), 2861 (w), 1947 (w), 1871 (w), 1808 (w), 1646 (m), 1621 (m), 1601 (w), 1583 (w), 1488 (s), 1446 (s), 1405 (w), 1363 (w), 1342 (w), 1321 (m), 1299 (w), 1269 (w), 1206 (w), 1173 (w), 1152 (w), 1091 (m), 1068 (w), 1024 (m), 1001 (w), 909 (w), 844 (w), 816 (w), 758 (s), 698 (vs), 614 (w), 585 (w), 496 (w), 439 (m), 356 (w).

4.7. [{(R)-CEBA}$_2$LuCl]$_2$ (**1**)

4.7.1. Route a

THF (ca. 10 ml) was condensed at −78 °C onto a mixture of 228 mg (0.810 mmol) $LuCl_3$ and 630 mg (1.620 mmol) (*R*)-LiCEBA and the reaction mixture was stirred overnight at r.t. The solvent was removed *in vacuo* and the residue was washed with 10 ml of *n*-pentane and then extracted with 10 ml of hot toluene. The solvent was removed *in vacuo* and the residue was washed with 10 ml *n*-pentane. The product was crystallized from hot toluene to yield 375 mg (0.422 mmol, 52%) of **1**.

4.7.2. Route b

THF (ca. 10 ml) was condensed at −78 °C onto a mixture of 95 mg (0.337 mmol) $LuCl_3$, 254 mg (0.675 mmol) (*R*)-HCEBA·HCl and 269 mg (1.349 mmol) KN(SiMe$_3$)$_2$ and the reaction mixture was refluxed for two days. The reaction mixture was filtered and the solvent was removed *in vacuo* from the clear pale yellow solution. The residue was washed with 10 ml of *n*-pentane and the product was crystallized from hot toluene to yield 85 mg (0.096 mmol, 28%) of **1**. ^{1}H NMR (400 MHz, d$_8$-THF, 298 K): δ (ppm) = 7.42–7.06 (m, 10 H, Ph), 2.86 (m, ^3J = 5.9 Hz, 1 H, NC*H*), 2.61 (m, ^3J = 7.0 Hz, 3 H, NC*H*), 2.21 (br, 1 H, cyclohexyl-*H*), 1.99 (br, 1 H, cyclohexyl-*H*), 1.73–1.52 (m, 18 H, cyclohexyl-*H*), 1.44–1.33 (m, 4 H, cyclohexyl-*H*), 1.27–1.21 (m, 8 H, cyclohexyl-*H*), 1.17–1.13 (m, 12 H, C*H*$_3$), 1.08–0.97 (m, 4 H, cyclohexyl-*H*), 0.92–0.85 (m, 2 H, cyclohexyl-*H*), 0.73–0.49 (m, 6 H, cyclohexyl-*H*). (The region between 2.9 and 0.49 shows broad peaks, which overlap and shows small solvent signals. Perfect integration of these signals is not possible. Intensities are thus partly estimated.) - ^{13}C{^{1}H} NMR (101 MHz, d$_8$-THF, 298 K): δ (ppm) = 180.9 (N*C*N), 177.7 (N*C*N), 138.2 (*i*-Ph), 137.8 (*i*-Ph), 129.8 (Ph), 128.9 (Ph), 128.5 (Ph), 128.3 (Ph), 128.0 (Ph), 127.9 (Ph), 59.5 (N*C*H), 59.0 (N*C*H), 45.6 (cyclohexyl-*C*H), 45.1 (cyclohexyl-*C*H), 33.1 (*C*H$_2$), 32.8 (*C*H$_2$), 31.2 (*C*H$_2$), 29.6 (*C*H$_2$), 28.1 (*C*H$_2$), 27.8 (*C*H$_2$), 27.4 (*C*H$_2$), 27.3 (*C*H$_2$), 22.3 (*C*H$_3$), 21.3 (*C*H$_3$). - IR (ATR): ν (cm^{-1}) = 3442 (w), 3058 (w), 3024 (w), 2921 (vs), 2850 (s), 2665 (w), 1637 (vs), 1600 (w), 1577 (w), 1559 (w), 1540 (w), 1447 (vs), 1367 (m), 1339 (m), 1294 (w), 1262 (w), 1240 (w), 1190 (w), 1153 (w), 1129 (w), 1104 (w), 1070 (w), 1028 (w), 988 (w), 968 (w), 915 (w), 890 (m), 841 (w), 773 (s), 740 (w), 726 (w), 701 (vs), 668 (w), 629 (w), 557 (w), 511 (w), 468 (w), 383 (w). - elemental analysis calc. (%) for $C_{46}H_{70}N_4ClLu$•LiCl (931.889 g/mol): C 59.29; H 7.57, N 6.01; found: C 58.86, H 7.14, N 5.60.

4.8. [{(S)-PEAA}$_2$LuCl(thf)] (**2**)

THF (ca. 10 ml) was condensed at −78 °C onto a mixture of 152 mg (0.540 mmol) $LuCl_3$ and 294 mg (1.081 mmol) (*S*)-LiPEAA and the reaction mixture was stirred overnight at r.t. The solvent was removed *in vacuo* and the residue was washed with 10 ml *n*-pentane and then extracted with 10 ml of *n*-pentane. The solvent was removed *in vacuo* and the product was crystallized from

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saturated *n*-pentane/THF solution to yield 160 mg (0.197 mmol, 36%) of **2**. - ^{1}H NMR (300 MHz, d$_8$-THF, 298 K): δ (ppm) = 7.39–7.36 (m, 8 H, Ph), 7.11–7.01 (m, 12 H, Ph), 4.48 (q, ^3J = 6.0 Hz, 4 H, C*H*), 3.64–3.59 (m, 4 H, OCH_2), 1.79–1.75 (m, 4 H, OCH$_2$CH_2), 1.64 (br, 6 H, CCH_3), 1.52 (d, ^3J = 6.9 Hz, 12 H, CHCH_3). - ^{13}C{^{1}H} NMR (75 MHz, d$_8$-THF, 298 K): δ (ppm) = 178.8 (NCN), 150.2 (*i*-Ph), 128.9 (Ph), 127.7 (Ph), 126.5 (Ph), 68.4 (OCH$_2$), 57.8 (*C*H), 27.6 (CHCH$_3$), 26.5 (OCH$_2$CH$_2$), 14.8 (CCH$_3$). - IR (ATR): ν (cm^{-1}) = 3429 (w), 3058 (w), 3025 (w), 2966 (m), 2926 (w), 2867 (w), 1950 (w), 1884 (w), 1811 (w), 1643 (s), 1601 (w), 1583 (w), 1489 (s), 1447 (s), 1406 (w), 1372 (w), 1317 (w), 1274 (w), 1214 (m), 1177 (w), 1148 (w), 1099 (m), 1068 (w), 1024 (m), 987 (w), 910 (w), 864 (w), 820 (w), 761 (s), 699 (vs), 653 (w), 615 (w), 605 (w), 585 (w), 533 (m), 404 (w), 382 (w).

X-ray crystallographic studies of 1 and 2: Suitable crystals **1** and **2** were covered in mineral oil (Aldrich) and mounted onto a glass fiber. The crystals were transferred directly into the cold stream of a Stoe IPDS 2 or StadiVari diffractometer.

All structures were solved by using the program SHELXS/T [53]. 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 by using the program SHELXL [53]. The hydrogen atom contributions of all of the compounds were calculated, but not refined. In each case, the locations of the largest peaks in the final difference Fourier map calculations, as well as the magnitude of the residual electron densities, were of no chemical significance.

Crystal data for **1**: $C_{92}H_{140}Cl_2Lu_2N_8 \cdot C_7H_8$, M = 1871.09, a = 19.8151(5) Å, c = 49.3993(15) Å, V = 19396.0(11) Å^3, T = 190 K, space group $I4_122$, Z = 8, μ(MoKα) = 2.126 mm^{-1}, 371232 reflections measured, 13638 independent reflections (R_{int} = 0.0820). The final R_1 values were 0.0305 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0671 ($I > 2\sigma(I)$). The final R_1 values were 0.0537 (all data). The final $wR(F^2)$ values were 0.0813 (all data). The goodness of fit on F^2 was 1.091. Flack parameter = −0.043(3).

Crystal data for **2**: $C_{40}H_{50}ClLuN_4O$, M = 813.26, a = 13.7119(2) Å, b = 14.2659(3) Å, c = 19.2517(3) Å, V = 3765.88(11) Å^3, T = 100 K, space group $P2_12_12_1$, Z = 4, μ(MoKα) = 2.728 mm^{-1}, 32388 reflections measured, 9075 independent reflections (R_{int} = 0.0358). The final R_1 values were 0.0247 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0504 ($I > 2\sigma(I)$). The final R_1 values were 0.0277 (all data). The final $wR(F^2)$ values were 0.0508 (all data). The goodness of fit on F^2 was 0.950. Flack parameter = −0.011(5).

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. 1529650–1529651. 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).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2017.03.041.

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