ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

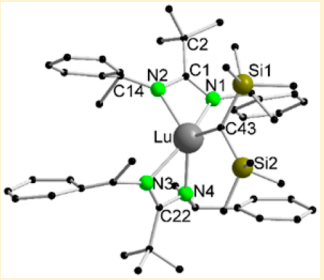
Enantiopure Amidinate Complexes of the Rare-Earth Elements

Tobias S. Brunner, Paul Benndorf, Michael T. Gamer, Nicolai Knöfel, Katharina Gugau, and Peter W. Roesky*

Institut für Anorganische Chemie, Karlsruher Institut für Technologie (KIT), Engesserstraße 15, 76131 Karlsruhe, Germany

Supporting Information

ABSTRACT: The synthesis of the new chiral amidine (*S,S*)-*N,N*′-bis(1-phenylethyl)-pivalamidine ((*S*)-HPETA) and its corresponding lithium salt (*S*)-LiPETA are reported, and their solid-state structures were investigated by single-crystal X-ray diffraction. Depending on the stoichiometric ratio and the ion radius of the rare-earth metal, the reaction of (*S*)-LiPETA with anhydrous lanthanide trihalides (Ln = Sc, Y, La, Nd, Sm, Lu) afforded mono-, bis-, and tris(amidinate) complexes. The mono(amidinate) compound [{(*S*)-PETA}$LaI_4Li_2(thf)_4$], the bis(amidinate) complexes [({(*S*)-PETA}$_2$Ln-μ-Cl)$_n$] (Ln = Sc, Y, Nd, Sm, Lu), and the tris(amidinate) compound [{(*S*)-PETA}$_3$Y] were isolated and structurally characterized by single-crystal X-ray diffraction. For the bis(amidinate) compounds, either monomeric or chloro-bridged dimeric structures were observed in the solid state. Furthermore, chiral bis(amidinate)-amido and -alkyl complexes [{(*S*)-PETA}$_2$Ln{E($SiMe_3$)$_2$}] (E = N, Ln = Y; E = CH, Ln = Sc, Y, Lu) were synthesized by salt metathesis and their catalytic activity and enantioselectivities were investigated in hydroamination/cyclization reactions. All of these compounds showed very good catalytic activity, and all of the investigated substrates were converted regiospecifically into their corresponding cyclic products under mild reaction conditions within good reaction times. The lutetium alkyl compound combined a high activity with good enantioselectivity.

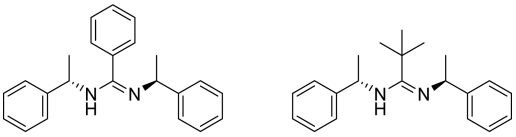


INTRODUCTION

Amidinate anions of the general formula [RC(NR′)$_2$]$^-$ are the nitrogen analogues of the carboxylate anions. Together with their closely related guanidinates, they represent a well-established class of N-chelating ligands that form complexes with almost all metals of the periodic table.[1−6] Amidinates have been widely employed as spectator ligands in main-group and transition-metal coordination chemistry. Furthermore, they were intensively used for the synthesis of lanthanide and actinide complexes.[2,7] The substituents R and R′ can easily be varied in numerous ways. This has a direct effect on the steric and electronic properties of these ligands, and also chiral side groups may be introduced.[7] In combination with their ease of accessibility, this high flexibility in ligand design is one factor which makes amidinates very popular as ligands in coordination chemistry. Their implementation as ligands in rare-earth-metal coordination chemistry was pioneered by Edelmann et al. in the 1990s[7,8] and later also established by Deacon and Junk et al.[9−14] Since then, the number of publications in this area has been rapidly expanding.[2,3,15−18] The most intensely studied amidinate ligand, *N,N*′-bis(trimethylsilyl)benzamidinate,[19,20] has been found to stabilize lanthanide complexes in all three accessible oxidation states (+II, +III, +IV).[7] Furthermore, this ligand was used for the synthesis of mono-, bis-, and tris(amidinate) complexes. Numerous applications of rare-earth-metal amidinate complexes have been reported in the literature,[15] especially as homogeneous catalysts in the polymerization of ethene[21] and isoprene,[22,23] ring-opening polymerization of polar monomers, e.g. ϵ-caprolactone and trimethylene carbonate, hydroboration, hydrosilylation, and intramolecular hydroamination/cyclization[24] reactions.[7,15,24]

In contrast to this great amount of research activity, only very few chiral amidinates are known and their coordination chemistry is limited to group 4 metals,[25−28] molybdenum,[29,30] rhodium,[31,32] and nickel.[33] We recently published an improved synthesis of the chiral amidine *N,N*′-bis(1-phenylethyl)-benzamidine (HPEBA; Scheme 1),[34] which was reported for

Scheme 1. Chiral Amidines (*S*)-HPEBA and (*S*)-HPETA



(*S*)-HPEBA (*S*)-HPETA

the first time about 35 years ago by Brunner et al.[29,32] In 2011, we presented the synthesis of the lithium and potassium derivatives[34] and also the first rare-earth-metal complexes with this chiral amidinate as a ligand. Within this series mono-, bis-, and tris(amidinate) complexes are accessible.[35,36] We also disclosed the synthesis of chiral mono(amidinate) bisborohydride complexes and their application as catalysts in the ring-opening polymerization of *rac*-lactide.[37] Furthermore, bis-(amidinate)-amido complexes with yttrium and lutetium [{(*S*)-PEBA}$_2$Ln{N($SiMe_3$)$_2$}] (Ln = Y, Lu) were synthesized and their catalytic activities and enantioselectivities in hydro-amination reactions were investigated.[35,36] In their application

Received: June 28, 2016

DOI: 10.1021/acs.organomet.6b00523
Organometallics XXXX, XXX, XXX−XXX

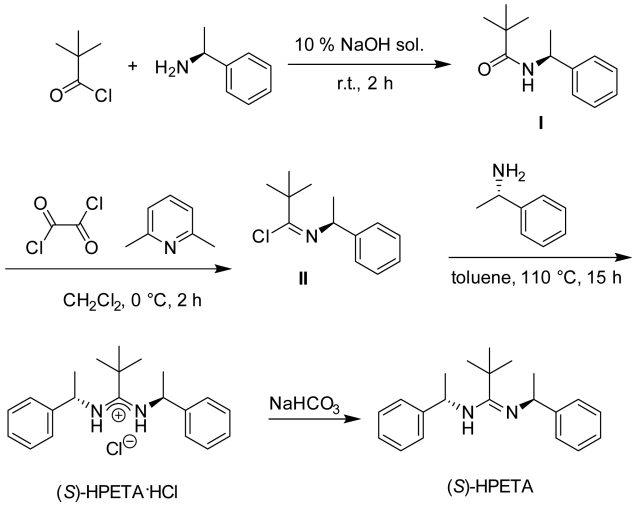
as homogeneous catalysts, rare-earth-metal alkyl complexes are even more reactive than amido complexes. In 1982, Watson et al. described the reaction of lutetium alkyl and hydride compounds $[(\eta^5\text{-}C_5Me_5)_2LuCH_3\cdot Et_2O]$ as analogues of Ziegler–Natta catalysts in the polymerization of ethene.[38,39] Furthermore, solvent-free rare-earth-metal alkyl compounds showed high reactivity not only toward relatively acidic compounds such as alkynes[40−42] but also toward very weakly acidic compounds such as methane.[38,43−45]

Since the coordination chemistry of the lanthanides is strongly influenced by the steric demand of the ligand, we intended to modify the bite angle of the PEBA ligand slightly. Therefore, we substituted the phenyl group in the ligand backbone by the bulkier *t*Bu group. Herein, we describe the synthesis and characterization of the new chiral amidine (*S,S*)-*N,N′*-bis(1-phenylethyl)pivalamidine ((*S*)-HPETA) (Scheme 1) and its corresponding lithium salt (*S*)-LiPETA. We also describe the reactivity of the PETA ligand in its coordination chemistry of rare-earth elements, including a structural investigation and synthesis of the first chiral amidinate rare-earth-metal alkyl compound. Moreover, the application of some selected compounds as catalysts in enantioselective intramolecular hydroamination reactions of nonactivated terminal amino olefins is shown.

RESULTS AND DISCUSSION

The synthesis of ligand (*S*)-HPETA is analogous to the synthesis of (*S*)-HPEBA via the so-called imidoyl chloride route (Scheme 2).[34] The amidine (*S*)-HPETA is a viscous colorless oil, making it challenging to work with in stoichiometric amounts.

Scheme 2. Synthesis of Amidine (*S*)-HPETA



In the three-step synthesis leading to (*S*)-HPETA (Scheme 2) pivalyl chloride was treated first with enantiomerically pure (*R*)- or (*S*)-1-phenylethylamine to give (*R*)- or (*S*)-*N*-(1-phenylethyl)pivalimidoyl chloride (**I**) in moderate yield. Further treatment of **I** with oxalyl chloride and lutidine in CH_2Cl_2 gave (*S*)-*N*-(1-phenylethyl)pivalimidoyl chloride (**II**).[46,47] In the final step **II** was heated in toluene with (*R*)- or (*S*)-1-phenylethylamine to give the hydrochlorides (*R*)- and (*S*)-HPETA·HCl. Pure (*S*)-HPETA can be obtained by recrystallization of the hydrochloric acid adduct (*S*)-HPETA·HCl from hot toluene followed by workup in aqueous alkaline solution. The NMR spectra show in different solvents only broad peaks, which are not conclusive.[34] However, full characterization by other methods was possible. The solid-state structure of (*S*)-HPETA·HCl was established by single-crystal X-ray diffraction. (*S*)-HPETA·HCl crystallizes in the monoclinic space group $P2_1$ having four molecules of (*S*)-HPETA·HCl and two molecules of toluene in the unit cell (Figure 1).

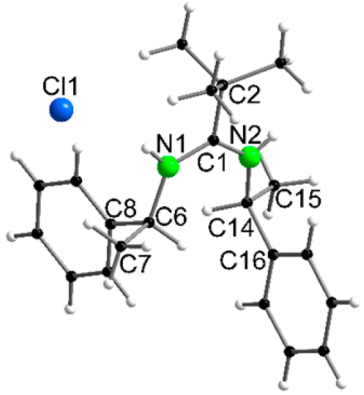
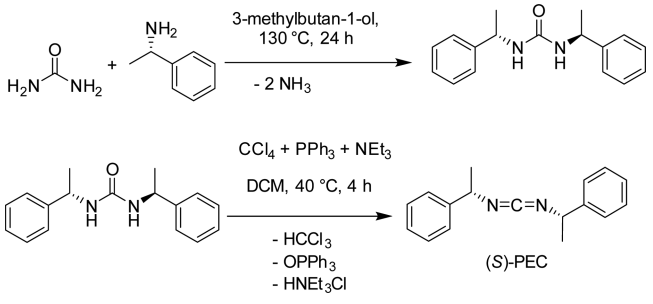


Figure 1. Solid-state structure of (*S*)-HPETA·HCl. One of two independent molecules is shown. Selected bond lengths (Å) and angles (deg): C1−N1 1.315(5), C1−N2 1.322(4), C1−C2 1.535(5), C6−N1 1.473(5), C6−C8 1.524(5), C6−C7 1.534(5), C14−N2 1.467(5), C14−C15 1.526(5), C14−C16 1.520(5); N1−C1−N2 125.2(2), N1−C1−C2 116.0(3), N2−C1−C2 118.8(3), N1−C6−C8 113.2(2), N1−C6−C7 107.9(3), C8−C6−C7 110.6(3), N2−C14−C15 109.0(3), N2−C14−C16 112.2(3), C16−C14−C15 110.8(3).

The lithium derivative, which is needed for salt metathesis reactions, was more conveniently obtained by reaction of the corresponding carbodiimide bis((*S*)-1-phenylethyl)-carbodiimide ((*S*)-PEC) with *tert*-butyllithium. The synthesis of (*S*)-PEC is known in the literature.[48−51] It was obtained, for example, via a thiourea derivative which was desulfinated with chemicals such as HgO.[48] We performed a more convenient synthesis, by the reaction of urea with 2 equiv of (*S*)-1-phenylethylamine followed by dehydration with a mixture of triphenylphosphine, carbon tetrachloride, and triethylamine, to give (*S*)-PEC as a colorless liquid (Scheme 3). (*S*)-PEC was purified by vacuum distillation and characterized by NMR, IR, and mass spectrometry. The data agree with those in the literature.[51]

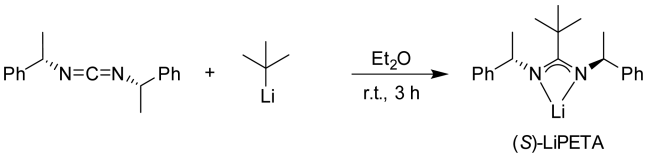
For synthesis of pure lithium *N,N′*-bis((*S*)-1-phenylethyl)-*tert*-butylamidinate ((*S*)-LiPETA), carbodiimide (*S*)-PEC was reacted with 1 equiv of *tert*-butyllithium (Scheme 4). (*S*)-

Scheme 3. Synthesis of Carbodiimide (*S*)-PEC



DOI: 10.1021/acs.organomet.6b00523
Organometallics XXXX, XXX, XXX−XXX

Scheme 4. Synthesis of Lithium Salt (*S*)-LiPETA



LiPETA was isolated as an orange powder, which was characterized by standard analytical/spectroscopic techniques. As a result of the deprotonation, the symmetry of (*S*)-LiPETA increases in comparison to the amidine (*S*)-HPETA in solution. Thus, only one set of signals is observed for the phenylethyl substituents in the ^{1}H and ^{13}C{^{1}H} NMR spectra. In (*S*)-LiPETA both methine protons are homotopic, giving only one quartet at δ 5.14 ppm ($^{3}J_{H,H}$ = 6.3 Hz) in the ^{1}H NMR spectrum. Consequently, only one doublet is seen for the methyl groups at δ 1.25 ppm ($^{3}J_{H,H}$ = 6.3 Hz).

Single crystals of the adduct (*S*)-LiPETA·LiCl were obtained as a side product in a salt metathesis reaction with $LnCl_3$ and crystallized from a hot heptane/THF mixture. Single crystals of pure (*S*)-LiPETA were not obtained. (*S*)-LiPETA·LiCl crystallizes in the orthorhombic space group $P2_12_12$ having four molecules of (*S*)-LiPETA·LiCl in the unit cell (Figure 2).

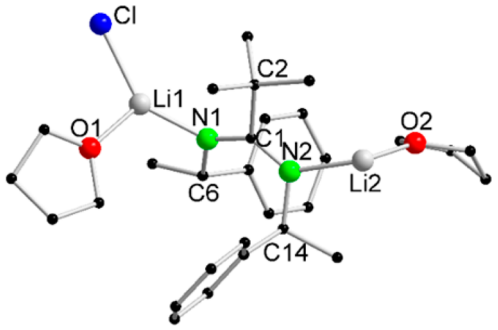


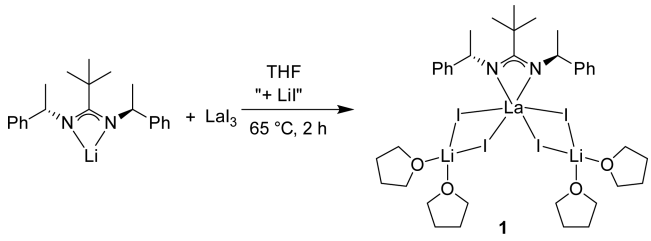
Figure 2. Solid-state structure of (*S*)-LiPETA·LiCl. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): N1−C1 1.34(2), N2−C1 1.311(15), N1−Li1 1.99(3), N2−Li2 1.97(2), C1−C2 1.579(12); N1−C1−N2 133.7(9).

In the solid state (*S*)-LiPETA forms a chainlike structure, in which the NCN units are bridged by lithium chloride and one THF molecule is coordinated to each lithium atom. The C1−N bond distances N1−C1 = 1.34(2) Å and N2−C1 = 1.311(15) Å are in a similar range, indicating the delocalized heteroallyl system.

In a systematic approach, (*S*)-LiPETA was used to access mono-, di-, and trisubstituted amidinate complexes of the rare-earth elements by salt metathesis.[52]

Synthesis of Mono(amidinate) Complex. Since initial attempts to synthesize mono(amidinate) lanthanide chlorides [{(*S*)-PETA}$LnCl_2$] did not result in defined products, LnI_3 was therefore employed as a starting material instead. For lanthanum the mono(amidinate) complex [{(*S*)-PETA}-$LaI_4Li_2(thf)_4$] (**1**) was obtained by the reaction of anhydrous lanthanide triiodide with (*S*)-LiPETA in an equimolar ratio in refluxing THF for 2 h (Scheme 5). Interestingly, 2 equiv of the byproduct lithium iodide are incorporated in the coordination sphere of the lanthanum atom, resulting in a trimetallic $LaLi_2$ complex. The coordination of 2 equiv of lithium iodide is unique in the coordination chemistry of the rare-earth

Scheme 5. Synthesis of Mono(amidinate) Complex



elements. In contrast, a few complexes are known in which 2 equiv of lithium chloride is in the coordination sphere: e.g. in the amidinate complex [(dimb)$YCl_4Li_2(tmeda)_2$] (dimb = *N*,*N*′-diisopropyl(2,6-dimesityl)benzamidinate).[53]

Single crystals of **1** were obtained from hot toluene. Compound **1** crystallizes in the orthorhombic space group $P2_12_12_1$ with one molecule in the unit cell (Figure 3). The

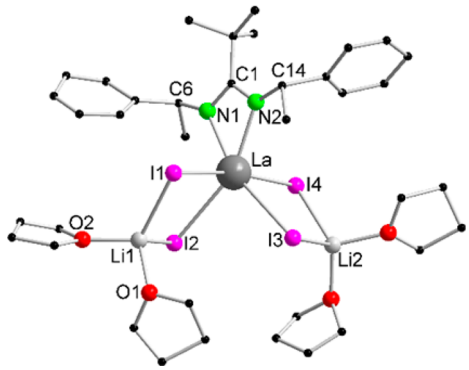


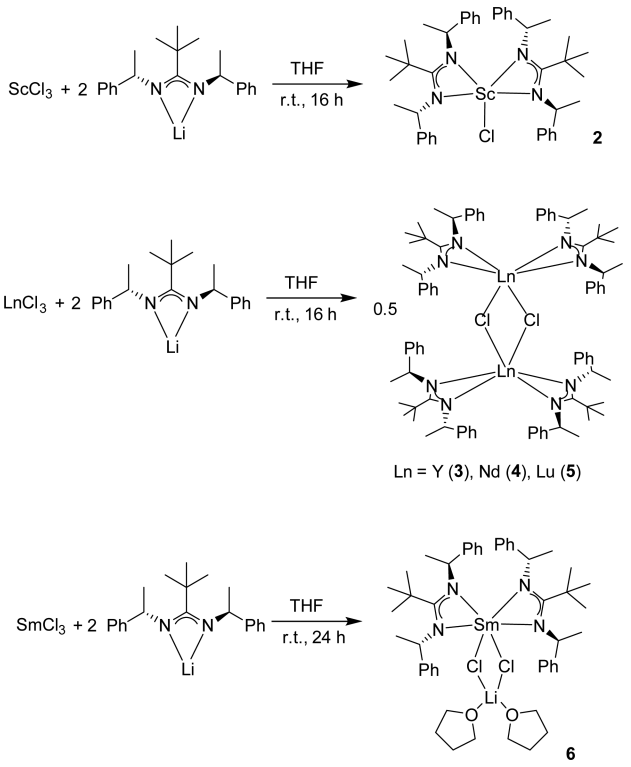
Figure 3. Solid-state structure of [{(*S*)-PETA}$LaI_4Li_2(thf)_4$] (**1**). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): La−N1 2.462(4), La−N2 2.43(2), La−I1 3.241(2), La−I2 3.205(2), La−I3 3.2298(15), La−I4 3.229(2), N1−C1 1.37(2), N2−C1 1.34(2), N1−C6 1.46(2), N2−C14 1.42(2), I1−Li1 2.75(4), I2−Li1 2.78(4), O1−Li1 1.94(4), O2−Li1 1.85(4); N1−La−N2 53.9(5), N1−C1−N2 109.6(14), C6−N1−La 135.1(12), C14−N2−La 131.1(12), I1−La−I2 83.68(4), I2−La−I3 92.18(5), I2−La−I4 92.12(5), I1−La−I3 90.19(4), I1−La−I4 171.89(5), I3−La−I4 83.03(4), I1−Li1−I2 102.0(11), I3−Li2−I4 102.0(10).

lanthanum atom is 6-fold coordinated by one (*S*)-PETA ligand and four iodine atoms in a distorted-octahedral fashion. For charge balance, two lithium atoms are in the complex structure, each coordinated in a tetrahedral fashion by two iodine atoms and two THF molecules. The (*S*)-PETA ligand coordinates symmetrically to the lanthanum atom. Thus, the La−N distances are similar (La−N1 = 2.462(4) Å and La−N2 = 2.43(2) Å). The N1−C1−N2 angle (109.6(14)°) is in the expected range.[35]

Synthesis of Bis(amidinate) Complexes. Treatment of (*S*)-LiPETA with various anhydrous rare-earth trichlorides resulted in salt metathesis reactions in bis(amidinate) chloro complexes with three slightly different structures (Scheme 6). For the smallest element scandium, the monomeric bis-(amidinate) chloro complex [{(*S*)-$PETA\}_2ScCl$] (**2**) was isolated. For the larger metals the dimeric species [{(*S*)-$PETA\}_2LnCl]_2$ (Ln = Y (**3**), Nd (**4**), Lu (**5**)) were obtained. In contrast, for samarium as the center metal the ate complex [{(*S*)-$PETA\}_2SmCl_2Li(THF)_2$] (**6**), in which 1 equiv of lithium chloride is in the coordination sphere, was isolated.

DOI: 10.1021/acs.organomet.6b00523
Organometallics XXXX, XXX, XXX−XXX

Scheme 6. Synthesis of Bis(amidinate) Complexes 2−6



Since neodymium is slightly larger than samarium, this observation is a bit surprising.

All complexes have been characterized by standard analytical/spectroscopic techniques, and their solid-state structures were investigated by single-crystal X-ray diffraction. Compound **2**, with the smallest investigated metal ion (scandium), forms a monomeric complex in the solid state (Figure 4). It crystallizes in the orthorhombic space group $P2_12_12_1$. The scandium atom is 5-fold coordinated by two (*S*)-PETA ligands and one chlorine atom. The plane of the two amidinate ligands is twisted by about 63°. Both (*S*)-PETA ligands are slightly asymmetrically bound to the metal atom with shorter Sc−N bond distances of Sc−N2 = 2.141(4) Å and Sc−N4 = 2.145(5) Å and slightly longer bond distances of Sc−N1 = 2.180(5) Å and Sc−N3 = 2.175(5) Å. The N1−C1−N2 angle is 110.4(5)°. The complexes of the larger elements Y (**3**), Nd (**4**), and Lu (**5**) crystallize in the triclinic space group *P*1. They are isostructural and form chloro-bridged dimers in the solid state, with 6-fold coordinated metal atoms (Figure 5 and

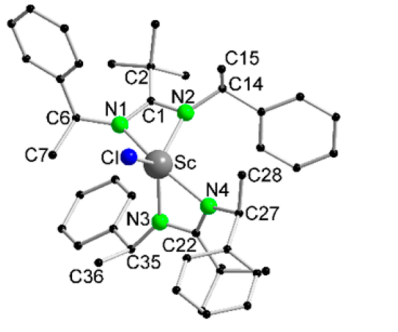


Figure 4. Solid-state structure of [{(*S*)-PETA}$_2$ScCl] (**2**). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sc−Cl 2.370(2), Sc−N1 2.180(5), Sc−N2 2.141(4), Sc−N3 2.175(5), Sc−N4 2.145(5), N1−C1 1.332(7), N1−C6 1.458(7), N2−C1 1.357(7), N2−C14 1.456(7), N3−C22 1.344(8), N3−C27 1.471(8), N4−C22 1.340(7), N4−C35 1.464(8), C1−C2 1.543(8), C22−C23 1.553(8); N1−Sc−N2 61.6(2), N1−C1−N2 110.4(5), N3−Sc−N4 61.3(2), N3−C22−N4 110.4(5).

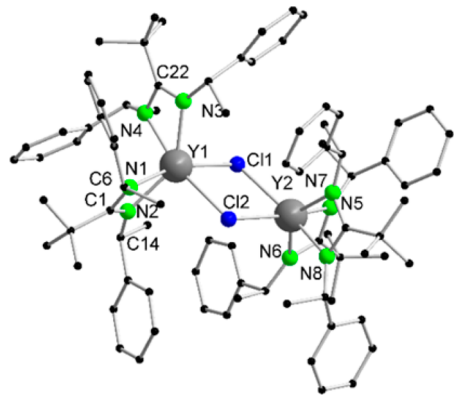


Figure 5. Solid-state structure of [{(*S*)-PETA}$_2$YCl]$_2$ (**3**). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): for **3** (data for the isostructural compounds **4** and **5** are also given), Y1−Cl1 2.7344(8), Y1−Cl2 2.7514(8), Y2−Cl1 2.7551(8), Y2−Cl2 2.7386(8), Y1−N1 2.351(3), Y1−N2 2.329(2), Y1−N3 2.332(2), Y1−N4 2.343(2), Y2−N5 2.348(2), Y2−N6 2.328(2), Y2−N7 2.338(2), Y2−N8 2.342(2), N1−C1 1.351(4), N2−C1 1.337(4), C1−C2 1.567(4), N1−C6 1.457(4), N2−C14 1.459(4), Cl1−Y1−Cl2 75.17(2), Cl1−Y2−Cl2 75.04(2), N1−C1−N2 111.1(2), N1−Y1−N2 56.53(8), N3−C22−N4 110.5(2), N3−Y1−N4 56.30(8), C6−N1−Y1 138.2(2), C14−N2−Y1 134.0(2), N1−C6−C7 108.7(2), N2−C14−C15 107.6(2), for **4**, Nd1−Cl1 2.8561(12), Nd1−Cl2 2.8407(11), Nd2−Cl1 2.8367(12), Nd2−Cl2 2.8485(11), Nd1−N1 2.450(3), Nd1−N2 2.411(3), Nd1−N3 2.453(3), Nd1−N4 2.402(3), Nd2−N5 2.406(3), Nd2−N6 2.452(3), Nd2−N7 2.454(3), Nd2−N8 2.402(3), N1−C1 1.346(4), N2−C1 1.340(4), C1−C2 1.559(4), N1−C6 1.457(4), N2−C14 1.465(4), Cl1−Nd1−Cl2 75.31(3), Cl1−Nd2−Cl2 75.49(3), N1−C1−N2 110.4(3), N1−Nd1−N2 53.94(9), N3−C22−N4 111.1(3), N3−Nd1−N4 53.89(9), C6−N1−Nd1 136.6(2), C14−N2−Nd1 131.3(2), N1−C6−C7 109.4(2), N2−C14−C15 106.3(3); for **5**, Lu1−Cl1 2.698(2), Lu1−Cl2 2.719(2), Lu2−Cl1 2.713(2), Lu2−Cl2 2.692(2), Lu1−N1 2.300(4), Lu1−N2 2.302(5), Lu1−N3 2.311(5), Lu1−N4 2.294(4), Lu2−N5 2.304(6), Lu2−N6 2.289(4), Lu2−N7 2.301(5), Lu2−N8 2.306(4), N1−C1 1.343(6), N2−C1 1.363(7), C1−C2 1.555(7), N1−C6 1.462(7), N2−C14 1.458(7), Cl1−Lu1−Cl2 74.49(5), Cl1−Lu2−Cl2 74.76(5), N1−C1−N2 110.4(4), N1−Lu1−N2 57.60(2), N3−C22−N4 110.8(4), N3−Lu1−N4 57.6(2), C6−N1−Lu1 135.3(3), C14−N2−Lu1 138.3(4), N1−C6−C7 106.3(4), N2−C14−C15 110.4(5).

Figures S6 and S7 in the Supporting Information). A distorted coordination polyhedron is formed by two (*S*)-PETA ligands and two bridged chlorine atoms. This structural motif is quite common in amidinate chemistry.[3,7] In contrast to the scandium complex, the amidinate ligands are rather symmetrically coordinated in **3**−**5**: e.g., Y1−N1 = 2.351(3) Å and Y1−N2 = 2.329(2) Å in **3**. The N−C−N (110.1(2)−111.1(3)°) angle in **3**−**5** is about 4° smaller than in the corresponding phenyl amidinate compound [Ln(PEBA)$_2$(μ-Cl)]$_2$,[35] indicating the expected steric influence of the substituent in the ligand backbone. As a result, the average bite angle in **5** (average 57.48°) is about 1° smaller than that in [Ln(PEBA)$_2$(μ-Cl)]$_2$ (58.51(9)°).[35]

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **2** and **3** show the expected signals and coupling patterns. In contrast, the NMR

DOI: 10.1021/acs.organomet.6b00523
Organometallics XXXX, XXX, XXX−XXX

spectra of **5** show broad signals at room temperature, probably owing to small rotation barriers of the ligand side groups, but at 60 °C the expected signals and splitting patterns are observed.

In compound **6**, the byproduct of the salt metathesis, lithium chloride, could not be separated completely and 1 equiv of lithium chloride is coordinated to the samarium atom, giving it a 6-fold coordination. Compound **6** crystallizes in the orthorhombic space group $P2_12_12_1$ with four molecules in the unit cell (Figure 6). As observed for **3**–**5**, the metal center is 6-fold coordinated by two (*S*)-PETA ligands and two chlorine atoms. In contrast to **3**–**5** the chlorine atoms do not bridge to a second lanthanide atom but to a lithium ion. The Sm–N bond distances are in the expected range of 2.414(2)–2.436(2) Å. In contrast to the comparable neodymium complex **5** the Cl1–Sm–Cl2 bond angle (80.58(3)°) is about 5° larger (Cl1–Nd1–Cl2 = 75.31(3)° in **5**), indicating the reduced steric demand of the $Li(THF)_2$ unit.

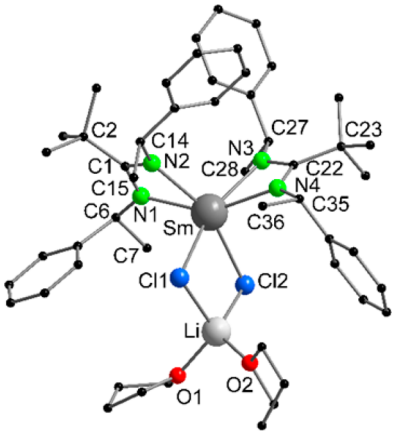
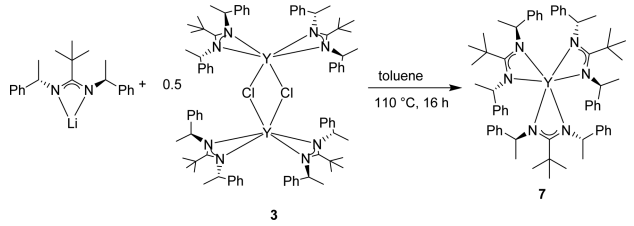


Figure 6. Solid-state structure of $[\{(S)\text{-PETA}\}_2Sm(\mu\text{-}Cl)_2Li(THF)_2]$ (**6**). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sm–Cl1 2.7440(8), Sm–Cl2 2.7602(8), Sm–N1 2.414(3), Sm–N2 2.436(2), Sm–N3 2.414(2), Sm–N4 2.436(2), Cl1–Li 2.345(7), Cl2–Li 2.365(7), N1–C1 1.351(4), N1–C6 1.471(4), N2–C1 1.339(4), N2–C14 1.471(4), N3–C22 1.357(4), N3–C27 1.474(3), N4–C22 1.340(4), N4–C35 1.469(4), C1–C2 1.558(4); Cl1–Sm–Cl2 80.58(3), Cl1–Sm–Li 40.11(11), Cl2–Sm–Li 40.52(11), N1–Sm–N2 54.46(8), N3–Sm–N4 54.29(8), Cl1–Li–Cl2 98.2(2), Li Cl1 Sm 91.0(2), Li–Cl2–Sm 90.2(2), N1–C1–N2 111.2(3), N3–C22–N4 110.2(2).

Synthesis of Tris(amidinate) Complex. With the analogous PEBA amidinate ligand, having a phenyl group at the central NCN unit, the homoleptic tris(amidinate) complex $[\{(S)\text{-PEBA}\}_3Sm]$ with samarium was isolated and characterized.[35] For smaller lanthanides, a tris(amidinate) complex could not be isolated, owing to steric strain of the ligands at the metal center. With the PETA amidinate ligand, having a *tert*-butyl group at the central NCN unit, the tris(amidinate) complex $[\{(S)\text{-PETA}\}_3Y]$ (**7**) with yttrium as the center metal could be isolated. This is not surprising, since the yttrium atom is smaller than the samarium atom and the PETA ligand has a smaller bite angle. The homoleptic yttrium complex was accessible in one step from the bis(amidinate) complex **3** and (*S*)-LiPETA (Scheme 7). The synthesis was carried out in hot toluene for better separation of the metathesis salt lithium chloride.

Compound **7** was characterized by single-crystal X-ray diffraction. It crystallizes in the chiral trigonal space group $P3_2$ with three molecules of the complex and three molecules of toluene in the unit cell (Figure 7). The yttrium atom is 6-fold coordinated by six nitrogen atoms of the amidinate ligands in a distorted-octahedral fashion. The four-membered metallacycles, formed by the ligand and the yttrium atom (N–C–N–Y), are slightly rotated with respect to each other, forming a propeller-type structure. As a result, a helical chirality is observed, which is typical for octahedral tris(chelate) complexes. In the solid state, we exclusively observed one diastereomer that had the Λ configuration along the helical axis.[54] Thus, the molecule is chiral at the metal center, which is in agreement with the data obtained for the analogous complex $[\{(S)\text{-PEBA}\}_3Sm]$.[35] The center metal is completely shielded by the ligands. The metal–nitrogen distances of complex **7** (Y–N1 = 2.379(5) Å, Y–N2 = 2.413(5) Å, Y–N3 = 2.390(5) Å, Y–N4 = 2.412(5) Å, Y–N5 = 2.413(5) Å, and Y–N6 = 2.360(6) Å) show one longer and one shorter bond, indicating a slightly asymmetric coordination of the amidinate in the solid state. However, NMR spectra in benzene solution only show one set of signals for each of the methine (^{1}H NMR, δ 5.26 ppm; $^{13}C\{^1H\}$ NMR, δ 56.9 ppm) and methyl groups (^{1}H NMR, δ 1.88 ppm; $^{13}C\{^1H\}$ NMR, δ 28.3 ppm), indicating a symmetric coordination in solution. However, the signals in the ^{1}H NMR spectrum are broad and not well resolved.

Scheme 7. Synthesis of Tris(amidinate) Complex 7



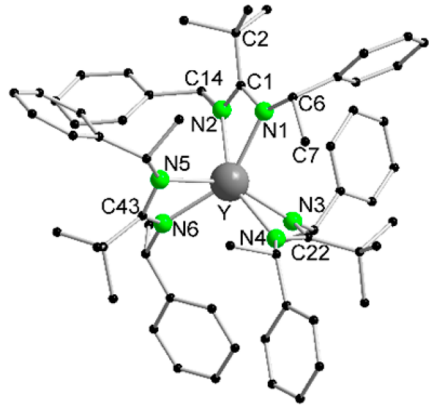


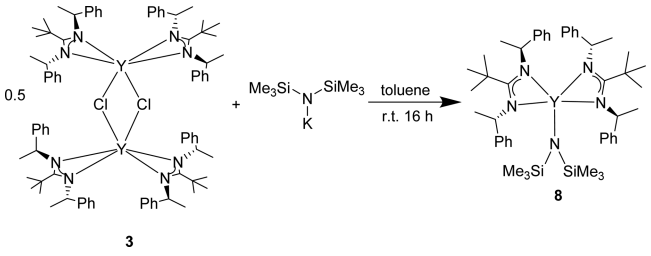
Figure 7. Solid-state structure of $[\{(S)\text{-PETA}\}_3Y]$ (**7**). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y–N1 2.379(5), Y–N2 2.413(5), Y–N3 2.390(5), Y–N4 2.412(5), Y–N5 2.413(5), Y–N6 2.360(6), N1–C1 1.329(8), N2–C1 1.353(8), N3–C22 1.344(8), N4–C22 1.346(8), N5–C43 1.360(8), N6–C43 1.341(9), C1–C2 1.556(9); N1–Y–N2 55.5(2), N1–C1–N2 112.7(6), N3–Y–N4 55.07(2), N3–C22–N4 111.2(6), N5–Y–N6 55.3(2), N5–C43–N6 110.2(6).

Synthesis of Amido and Alkyl Complexes. For catalytic applications, the introduction of a suitable leaving group is essential. Thus, we desired to substitute the chloro ligand in the bis(amidinate)-chloro complexes **2**–**6** by the common alkyl or amido group $\{N(SiMe_3)_2\}^-$ or $\{CH(SiMe_3)_2\}^-$.[3] This was not

DOI: 10.1021/acs.organomet.6b00523
Organometallics XXXX, XXX, XXX–XXX

successful in all cases. With the chiral (*S*)-PEBA ligand, amido complexes of yttrium and lutetium but no alkyl complexes are known.[34,35] To access an amido complex, compound **3** was reacted with 1 equiv of $KN(SiMe_3)_2$ in toluene to give the corresponding chiral amido complex of composition $[\{(S)\text{-PETA}\}_2Y\{N(SiMe_3)_2\}]$ (**8**) (Scheme 8). The ^1H and $^{13}C\{^1H\}$ NMR spectra of **8** show the expected set of signals and coupling patterns.

Scheme 8. Synthesis of the Amido Complex 8



Single crystals were grown from a saturated *n*-heptane solution, and the solid-state structure of **8** was established by single-crystal X-ray diffraction (Figure 8). Compound **8**

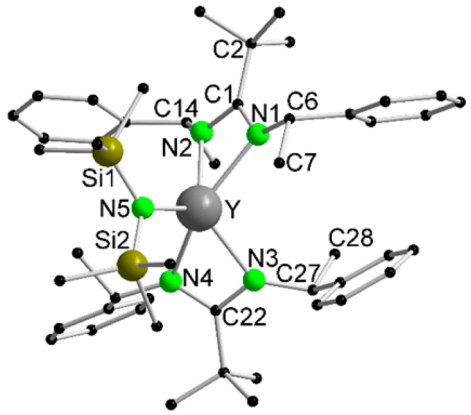
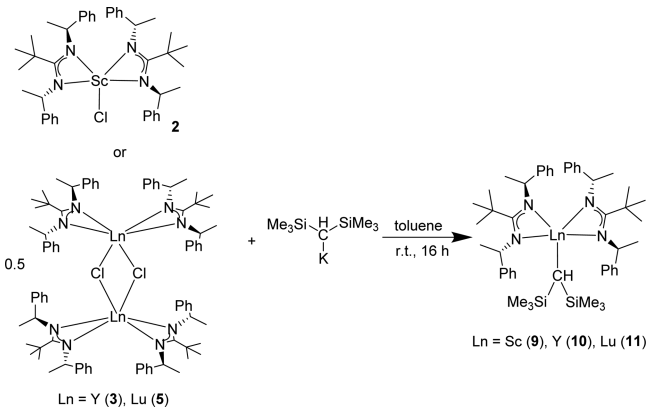


Figure 8. Solid-state structure of $[\{(S)\text{-PETA}\}_2Y\{N(SiMe_3)_2\}]$ (**8**). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å0 and angles (deg): Y–N1 2.369(5), Y–N2 2.341(5), Y–N3 2.337(5), Y–N4 2.384(5), Y–N5 2.270(5), Si1–N5 1.718(6), Si2–N5 1.728(5), N1–C1 1.344(8), N2–C1 1.349(7), N1–C6 1.456(8), N2–C14 1.460(8), N3–C22 1.337(8), N4–C22 1.341(8), C1–C2 1.573(9); N1–Y–N2 56.2(2), N3–Y–N4 55.5(2), N1–C1–N2 110.9(5), N3–C22–N4 110.4(6), C6–N1–Y 131.0(4), C14–N2–Y 133.4(4), Si1–N5–Si2 116.8(3), Si1–N5–Y 122.3(3), Si2–N5–Y 120.8(3).

crystallizes in the monoclinic space group $P2_1$ with four molecules of the complex and two molecules of *n*-heptane in the unit cell. The yttrium atom is 5-fold coordinated by five nitrogen atoms of the two amidinate ligands and the amido group. The two amidinates coordinate slightly asymmetrically to the metal atom (Y–N1 = 2.369(5) Å, Y–N2 = 2.341(5) Å, Y–N3 = 2.337(5) Å, and Y–N4= 2.384(5) Å). The angles of the (*S*)-PETA ligand are almost equal (N1–C1–N2 = 110.9(5)° and N3–C22–N4 = 110.4(6)°) and are slightly smaller than in the analogous (*S*)-PEBA compound $[\{(S)\text{-PETA}\}_2Y\{N(SiMe_3)_2\}]$ (116.5(4)°).[35] The $N(SiMe_3)_2$ group coordinates symmetrically (Si1–N5–Y = 122.3(3)°, Si2–N5–Y = 120.8(3)°) and is arranged in an eclipsed fashion with respect to the PETA ligands. The yttrium–nitrogen distance of the amido group (Y–N5 = 2.270(5) Å) is shorter than the yttrium–nitrogen distances to the PETA ligands and therefore is the shortest yttrium–nitrogen distance within compound **8**.

Since it is known in lanthanide chemistry that alkyl groups are more reactive and thus better leaving groups than amido groups, we were interested in introducing an alkyl group as a leaving group in the precatalyst. Although alkyl-functionalized lanthanide complexes using the (*S*)-PEBA ligand are not known, the analogous (*S*)-PETA compounds are straightforwardly available. Reaction of the bis(amidinate) chloro complexes **2**, **3**, and **5** described above with freshly prepared $KCH(SiMe_3)_2$[55] resulted in the desired complexes of composition $[\{(S)\text{-PETA}\}_2Ln\{CH(SiMe_3)_2\}]$ (Ln = Sc (**9**), Y (**10**), Lu (**11**)) in good yields (Scheme 9). All of these

Scheme 9. Synthesis of Alkyl Complexes 9–11



complexes were fully characterized by standard analytical/spectroscopic techniques, and for complex **11** single crystals were grown from a saturated *n*-pentane solution. Compound **11** crystallizes in the monoclinic space group *I*2 with eight molecules of the complex and four molecules of *n*-pentane in the unit cell (Figure 9). Some slight disorder is observed in one

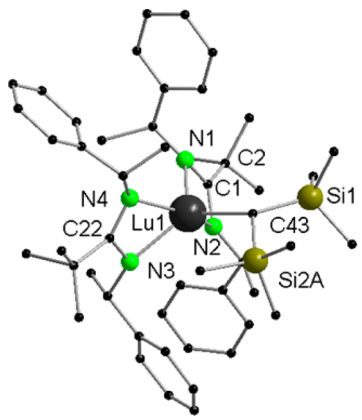
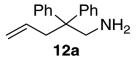
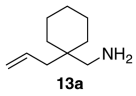
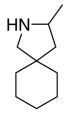
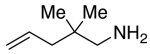
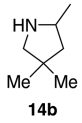
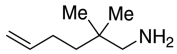
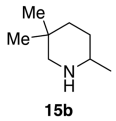
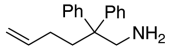
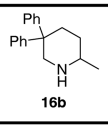
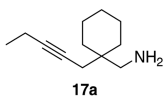
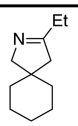
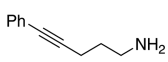
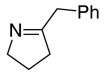


Figure 9. Solid-state structure of $[\{(S)\text{-PETA}\}_2Lu\{CH(SiMe_3)_2\}]$ (**11**). Hydrogen atoms and disorder are omitted for clarity. Only one molecule is shown. Selected bond lengths (Å) and angles (deg): Lu1–N1 2.304(7), Lu1–N2 2.326(6), Lu1–N3 2.280(7), Lu1–N4 2.356(6), Lu1–C43 2.382(8), Si1–C43 1.866(9), av. Si2–C43 1.87, N1–C1 1.343(10), N2–C1 1.338(10), C1–C2 1.561(12), N2–C14 1.469(9), N3–C22 1.353(10), N4–C22 1.343(11); N1–Lu1–N2 57.2(2), N3–Lu1–N4 57.3(3), N1–C1–N2 111.6(8), N3–C22–N4 111.2(8), average Si1–C43–Si2 112.5, Si1–C43–Lu1 124.7(4), average Si2–C43–Lu1 117.5.

DOI: 10.1021/acs.organomet.6b00523
Organometallics XXXX, XXX, XXX–XXX

Table 1. Hydroamination of Aminoalkenes and Aminoalkynes Catalyzed by Compounds 8−11[a]

	Substrate	Prod.	Cat.	t [h]	Yield[d] [%]	ee[e] [%]
1	 **12a**	 **12b**	**8**	9[b]	98	10 (*S*)[f]
2			**9**	3[c]	97	36 (*S*)[f]
3			**10**	1[b]	99	19 (*S*)[f]
4			**11**	2.5[b]	98	48 (*S*)[f]
5	 **13a**	 **13b**	**9**	4[c]	quant	31 (*S*)[f]
6			**10**	3[b]	quant	13 (*S*)[f]
7			**11**	2[c]	quant	36 (*S*)[f]
8	 **14a**	 **14b**	**9**	40[c]	95	14 (*S*)[f]
9			**10**	16[b]	98	13 (*S*)[f]
10			**11**	6[c]	quant	42 (*S*)[f]
11	 **15a**	 **15b**	**9**	78[c]	98	rac[g]
12			**10**	13[c]	quant	rac[g]
13			**11**	12[c]	quant	11[g] (*R*)[f]
14	 **16a**	 **16b**	**9**	14[c]	96	rac[g]
15			**10**	9[c]	quant	5[g] (*R*)[f]
16			**11**	7[c]	quant	n.d.[g][h]
17	 **17a**	 **17b**	**11**	2.5[b]	quant	---
18	 **18a**	 **18b**	**11**	81[c]	97	---

[a]Conditions: catalyst loading (15 mg, 5 mol %), C_6D_6. [b]Conditions: reaction temperature: 20 °C. [c]Conditions: reaction temperature 40 °C. [d]Calculated by ^{1}H NMR spectroscopy with ferrocene as internal standard. [e]Enantiomeric excess determined by ^{19}F NMR of Mosher amides. The values determined by chiral HPLC analysis of 1-naphthoyl amides are slightly higher (1−5%), entry 2 (10% higher). [f]Absolute configurations. [g]Enantiomeric excess determined by chiral HPLC analysis of 1-naphthoylamides. [h]No reproducible data were obtained.

of the independent molecules. The lutetium atom is 5-fold coordinated by four nitrogen atoms of the PETA ligands and one carbon atom of the alkyl group. The bonding parameters are discussed here only for one independent molecule. The lutetium−carbon distance (Lu1−C43 = 2.382(8) Å) is in the range of those for related compounds, e.g. [{$Me_2Si(\eta^5$-$C_5H_4)(\eta^5$-$C_5Me_4)$}Lu{$CH(SiMe_3)_2$}] (2.365(7) Å).[56] One (*S*)-PETA ligand coordinates symmetrically, whereas the other amidinate binds asymmetrically to the lutetium atom. The alkyl group coordinates slightly asymmetrically (Si1−C43−Lu1 = 124.7(4)° and average Si2−C43−Lu1 = 117.5°). The reason for this might be crystal-packing effects rather than agostic interactions, which are observed in [{$Me_2Si(\eta^5$-$C_5H_4)$-$(\eta^5$-$C_5Me_4)$}Lu{$CH(SiMe_3)_2$}][56] and the homoleptic amido complex [Lu{$N(SiMe_3)_2$}$_3$].[57]

The NMR spectra of **9**−**11** at room temperature show multiple sets of signals for the methine and methyl groups, which is in agreement with the asymmetric coordination mode observed in the solid-state structure. Recording ^{1}H and ^{13}C{^{1}H} NMR spectra at 353 K in deuterated THF solution in a sealed NMR tube resulted in the expected symmetric set of signals for the methine and methyl groups, indicating a symmetrical or quickly fluctuating coordination mode in THF solution. As result of the increased temperature, minor amounts of decomposition products were observed. Two signals were seen for the two $SiMe_3$ groups at room temperature and elevated temperatures, suggesting a rotation barrier around the metal−carbon bond. The ^{1}H NMR resonance of the methine alkyl group depends on the nature of the rare-earth-metal atom. With decreasing ion radius, the NMR signal is shifted to lower magnetic field (Y, −1.22 ppm; Lu, −1.16 ppm; Sc, −0.27 ppm). Furthermore, the coordination of the alkyl group to the metal center in solution was proven by measuring the NMR proton−yttrium and carbon−yttrium coupling. Thus, a doublet with a proton−yttrium coupling of $^2J_{H,Y}$ = 2.4 Hz and a carbon−yttrium coupling of $^1J_{C-Y}$ = 53 Hz was observed for the Y-*CH* group. The observed chemical shifts and coupling constants agree with those in the literature: e.g., in [{PhC(N-$(CH_2)_3NMe_2$)($NSiMe_3$)}Y{$CH(SiMe_3)_2$}$_2$].[58] The alkyl complexes **9**−**11** are unexpectedly stable in hydrocarbon solvents and only show minor decomposition after high-temperature

DOI: 10.1021/acs.organomet.6b00523
Organometallics XXXX, XXX, XXX−XXX

NMR spectra are measured in THF solution with collection of data over several hours.

Catalytic Hydroamination/Cyclization Studies. The catalytic hydroamination reaction is the addition of an organic amine or, in general, a nitrogen−hydrogen bond to an unsaturated carbon−carbon multiple bond in one step. This straightforward synthetic approach is superior to most of the classical amine synthesis, which consist of multistep reactions especially in laboratory-scale synthesis. The formation of byproducts and large amounts of chemical waste can be minimized by the catalytic hydroamination reaction. Although this reaction is thermodynamically feasible under normal conditions, the high reaction barrier is a significant problem for practical use. For a larger number of metals hydroamination catalysts have been developed. The progress in this area over the past decade has been reviewed extensively.[59−83] The enantioselective hydroamination reaction catalyzed by metallocene complexes of the rare-earth elements was pioneered in the 1990s by Marks and co-workers[60,84−87] and has then been extended to nonmetallocene rare-earth-element catalysts.[88] Parallel to this development, enantioselective catalysts based on other metals have also been reported.[83,89−95] However, there is still a great demand for catalysts that can enantioselectively transform a broad range of substrates at moderate temperatures with low catalyst loadings.

The amido and alkyl complexes **8**−**11** have been investigated as catalysts for the asymmetric intramolecular hydroamination of amino alkenes and amino alkynes. Because these catalysts have the same structural composition with two chiral amidinate ligands and one leaving group, the effect of the metal ion radius on the enantioselectivity can be determined. In addition to that, compounds **8** and **10** only differ in their leaving group and this effect can also be studied. The catalytic hydroamination experiments were carried out under rigorous anaerobic conditions in C_6D_6 at 20 or 40 °C with catalyst loadings of 5 mol %. The conversion was followed by ^{1}H NMR spectroscopy with ferrocene as an internal standard, and the ee values of the cyclized amino alkenes were determined by ^{19}F NMR spectroscopy of their corresponding Mosher (methoxy-(trifluoromethyl)phenylacetyl)amides.[88,96] In addition, the ee values were also measured by chiral HPLC analysis of the corresponding 1-naphthoylamides, which resulted in slightly higher values.[97] The results are shown in Table 1.

All investigated compounds **8**−**11** showed good activity, and all of the substrates were converted regioselectively into their corresponding cyclic products under mild reaction conditions in very good yield. As expected, the yttrium alkyl **10** is more catalytically active than the yttrium amide **8** by a factor of 9 (Table 1, entries 1 and 3). In addition, the ee value of **10** is higher in comparison to **8** as catalyst. Therefore, only the yttrium alkyl compound **10** was further investigated in favor of the yttrium amide complex **8**. In general, the yttrium alkyl **10** (entries 1−10) was the most reactive catalyst in cyclization of pyrrolidines, whereas the lutetium alkyl **11** was more reactive in cyclization of piperidines (entries 11−16). The scandium alkyl **9**, having the smallest metal ion radius in this series, showed the least reactivity. Thus, all catalytic experiments with this compound were carried out at 40 °C to get full conversion within reasonable reaction times. The suggested turnover-limiting step is the olefin insertion/cyclization step, which is sterically sensitive.[85,98] The differences in the reactivities of substrates **12a**−**14a**, which contain different bulky substituents at the position β to the amino group (entries 1−10), can be explained by the Thorpe−Ingold effect.[99]

Compound **11** turned out being the best choice between catalytic activity and enantioselectivity, and the highest ee values of 48 (*S*) were obtained with substrate **12a** (entry 4). However, the observed ee's are lower than those for the related PEBA ligand systems [{(*S*)-PEBA}$_2$Ln{N(SiMe$_3$)$_2$}] (Ln = Y, Lu).[35,36]

The high catalytic activity also led us to investigate **11** for the hydroamination/cyclization reactions of two internal alkynes (entries 17 and 18), which form achiral Schiff bases as products. Quantitative formation of spirocycle **17b** was observed at 20 °C in 2.5 h. For substrate **18a**, the reaction temperature was increased to 40 °C and after 81 h almost quantitative formation of spirocycle **18b** was completed.

SUMMARY

We have developed and fully characterized the new chiral amidine (*S*)-HPETA. By using the lithium amidinate ((*S*)-LiPETA) a series of new chiral rare-earth amidinate complexes with the PETA ligand were synthesized. This includes mono-, bis-, and tris(amidinate) complexes. The mono- and bis-(amidinate) complexes were readily available in a one-step synthesis protocol, whereas the tris(amidinate) complex was obtained in a two-step protocol.

The bis(amidinate) chloro complexes of the lanthanides were of particular interest for further reactions. With these compounds as starting materials, reactive leaving groups such as an amido or alkyl group for σ-bond metathesis were introduced by salt metathesis reactions with KN(SiMe$_3$)$_2$ and freshly prepared KCH(SiMe$_3$)$_2$, leading to new chiral lanthanide amido and alkyl compounds. To the best of our knowledge the first chiral lanthanide amidinate alkyl complex was obtained.

The compounds [{(*S*)-PETA}$_2$Ln{E(SiMe$_3$)$_2$}] (E = N, Ln = Y; E = CH, Ln = Sc, Y, Lu) were used as homogeneous catalysts for the asymmetric intramolecular hydroamination of amino alkenes and amino alkynes. All catalysts showed very good catalytic activity and regioselectivity. The lutetium alkyl compound combined high activity with good enantioselectivity.

EXPERIMENTAL SECTION[52,100]

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 glovebox. 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 a 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 or 400 MHz NMR and Ascend 400 MHz FT-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 instrument. Mass spectra were recorded at 70 eV on a Finnigan MAT 8200 instrument. Elemental analysis was performed on an Elementar vario EL or microcube instrument. $LnCl_3$[101] and KCH(SiMe$_3$)$_2$[55] were prepared according to literature procedures. KN(SiMe$_3$)$_2$ was sublimed before use.

(*S*)-*N*-(1-Phenylethyl)pivalamide (I). To a reaction mixture of 10.00 mL (9.40 g, 78 mmol) of (*S*)-1-phenylethylamine in 80 mL of an aqueous sodium hydroxide solution (10%) was added 10.0 mL

DOI: 10.1021/acs.organomet.6b00523
Organometallics XXXX, XXX, XXX−XXX

(9.82 g, 81 mmol) of pivaloyl chloride dropwise with vigorous stirring. After 1 h of stirring at room temperature the colorless precipitate that formed was filtered off, washed several times with water, and then dried in vacuo. 11.09 g (54 mmol, 70%) of (*S*)-*N*-(1-phenylethyl)-pivalamide was obtained as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$, 290 K): δ (ppm) 7.35−7.18 (m, 5 H, Ph), 6.00 (br, 1 H, N*H*), 5.10 (br, 1 H, C*H*), 1.47 (d, ^3J = 6.6 Hz, 3 H, CH_3), 1.23 (s, 9 H, *t*Bu). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 290 K): δ (ppm) 160.2 (*C*O), 148.0 (*i*-Ph), 128.6 (Ph), 127.1 (Ph), 125.7 (Ph), 54.7 (CH), 34.0 (*t*Bu-*C*), 29.4 (*t*Bu-CH_3), 22.2 (CH_3).

(*S*)-*N*-(1-Phenylethyl)pivalimidoyl Chloride (II). A mixture of (*S*)-*N*-(1-phenylethyl)pivalamide (11.09 g, 54 mmol) and 10.4 mL (9.61 g, 90 mmol) of 2,6-lutidine was dissolved in 150 mL of dry CH_2Cl_2 and cooled to 0 °C. 4.64 mL (6.85 g, 54 mmol) of oxalyl chloride, dissolved in 50 mL of dry CH_2Cl_2, was slowly added dropwise to the reaction mixture within 1 h. The reaction mixture turned reddish brown. The mixture was stirred for 30 min at 0 °C, and after it was warmed to room temperature, it was stirred for another 30 min. The volatile components were removed in vacuo. A 150 mL portion of dry *n*-pentane was added to the dark brown residue, and the mixture was stirred for 1 h. The suspension was filtered, and the volatile components of the filtrate were removed under vacuum. The resulting brown oil was distilled in vacuo at 64 °C (1.8×10^{-2} mbar) to give 5.36 g (24 mmol, 44%) of colorless (*S*)-*N*-(1-phenylethyl)-pivalimidoyl chloride. ^{1}H NMR (300 MHz, $CDCl_3$, 290 K): δ (ppm) 7.59−7.41 (m, 5 H, Ph), 5.12 (q, ^3J = 6.7 Hz, 1 H, C*H*), 1.58 (d, ^3J = 6.7 Hz, 3 H, CH_3), 1.45 (s, 9 H, *t*Bu). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 290 K): δ (ppm) 147.2 (*C*Cl), 143.6 (*i*-Ph), 128.4 (Ph), 126.9 (Ph), 126.5 (Ph), 62.0 (CH), 43.9 (*t*Bu-*C*), 28.3 (*t*Bu-CH_3), 23.7 (CH_3). The data agree with those in the literature.[47]

(*S,S*)-*N,N*′-Bis(1-phenylethyl)pivalamidine ((*S*)-HPETA). The imidoyl chloride **II** was dissolved in 40 mL of dry toluene, and 3.1 mL (2.90 g, 24 mmol) of (*S*)-1-phenylethylamine was added dropwise. The reaction mixture was refluxed for 12 h. After the mixture was cooled to −30 °C, the solvent was decanted from the highly viscous oil. The oily residue was dried in vacuo and washed with 50 mL of *n*-pentane. The solid was recrystallized from hot toluene to give 4.49 g (13 mmol, 54%) of colorless (*S*)-HPETA·HCl. IR (ATR): ν (cm^{-1}) 3146 (br), 2967 (w), 2929 (w), 1599 (m), 1492 (m), 1448 (m), 1375 (w), 1293 (w), 1226 (w), 1116 (w), 1077 (w), 1026 (w), 819 (w), 756 (m), 695 (s), 541 (m). Anal. Calcd for $C_{21}H_{29}N_2Cl{\cdot}1/2C_7H_8$ (390.99): C, 75.26; H, 8.51; N, 7.16. Found: C, 74.84; H, 8.46; N, 7.19. $[\alpha]_D^{24}$ −189.6° (*c* 0.18, CH_2Cl_2). (*S*)-HPETA·HCl was dissolved in 50 mL of CH_2Cl_2 and treated with 50 mL of a saturated sodium bicarbonate solution. After 1 h of vigorous stirring, the phases were separated and the water layer was extracted twice with 30 mL of CH_2Cl_2. The combined organic layers were dried over magnesium sulfate and filtered, and then the solvent was removed in vacuo to give (*S*)-HPETA as a colorless oil. Yield: 3.90 g (13 mmol, 97%) (overall yield: 16%). MS (EI, 70 eV): *m*/*z* (%) 308 ([M]$^+$, 14), 293 ([M − CH_3]$^+$, 2), 203 ([M − PhEt]$^+$, 33), 189 ([M − PhEtCH_3]$^+$, 5), 120 ([PhEtN]$^+$, 86), 105 ([PhEt]$^+$, 100), 77 ([Ph]$^+$, 11), 57 ([*t*Bu]$^+$, 9), 42 ([C_2H_4N]$^+$, 5). IR (ATR): ν (cm^{-1}) 3485 (w), 3026 (w), 2962 (m), 2921 (w), 1631 (m), 1602 (w), 1490 (w), 1476 (m), 1447 (m), 1397 (w), 1363 (m), 1251 (w), 1190 (m), 1066 (w), 1025 (m), 755 (s), 697 (s), 543 (m). Anal. Calcd for $C_{21}H_{28}N_2$ (308.46): C, 81.77; H, 9.15; N, 9.08. Found: C, 81.96; H, 8.94; N, 9.22.

((*S*)-1-Phenylethyl)carbodiimide ((*S*)-PEC). To a solution of 4.13 g (69 mmol) of urea in 50 mL of isoamyl alcohol was added 21.3 mL (20.0 g, 165 mmol) (*S*)-1-phenylethylamine. The reaction mixture was refluxed for 12 h. After the mixture was cooled to room temperature, the colorless precipitate that formed was filtered off and dried in vacuo overnight. 17.10 g (64 mmol, 93%) of 1,3-bis((*S*)-1-phenylethyl)urea was obtained as a colorless powder. The product and 20.1 g (76 mmol) of triphenylphosphine were suspended in 40 mL of dry CH_2Cl_2. Then, 6.20 mL (9.80 g, 64 mmol) of tetrachlorocarbon and 8.83 mL (6.45 g, 64 mmol) of triethylamine were added and the reaction mixture was refluxed for 8 h. All volatiles were removed in vacuo, and the residue was extracted five times with 100 mL of dry *n*-pentane. The solvent was removed in vacuo, and the resulting oil was purified via vacuum distillation at 97 °C (3.2×10^{-2} mbar) to give (*S*)-PEC as a colorless oil. Yield: 9.0 g (36 mmol, 56%) (overall yield: 52%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) 7.38−7.29 (m, 10 H, Ph), 4.60 (q, ^3J = 6.8 Hz, 2 H, C*H*), 1.52 (d, ^3J = 6.8 Hz, 6 H, CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ (ppm) 143.7 (NCN), 140.5 (*i*-Ph), 128.6 (*m*-Ph), 127.4 (*p*-Ph), 126.1 (*o*-Ph), 56.8 (*C*H), 24.7 (CH_3). MS (EI, 70 eV): *m*/*z* (%) 250 ([M]$^+$, 19), 235 ([M − CH_3]$^+$, 35), 145 ([M − PhEt]$^+$, 3), 131 ([M − PhEtN]$^+$, 15), 105 ([PhEt]$^+$, 100), 91 ([Bz]$^+$, 12), 77 ([Ph]$^+$, 78), 51 ([C_4H_3]$^+$, 22). IR (ATR): ν (cm^{-1}) 3514 (br), 3085 (w), 3062 (w), 3029 (w), 2973 (w), 2926 (w), 2868 (w), 2109 (m), 1950 (w), 1876 (w), 1808 (w), 1752 (w), 1717 (w), 1603 (w), 1493 (w), 1451 (m), 1372 (w), 1341 (w), 1299 (w), 1276 (m), 1203 (w), 1179 (w), 1157 (w), 1067 (m), 1028 (w), 1007 (w), 995 (w), 981 (w), 911 (w), 880 (w), 816 (w), 754 (m), 696 (s), 650 (w), 628 (m), 596 (w), 533 (m). Anal. Calcd for $C_{21}H_{28}N_2$ (250.34): C, 81.56; H, 7.25; N, 11.19. Found: C, 81.49; H, 6.97; N, 11.24. $[\alpha]_D^{25}$ 11.1° (*c* 2.68, CH_2Cl_2).

Lithium *N,N*′-Bis((*S*)-1-phenylethyl)pivalamidinate ((*S*)-LiPE-TA). A 4.9 mL portion (1.7 M in *n*-pentane, 8.31 mmol) of *tert*-butyllithium was added dropwise to a solution of 2.00 mL (2.08 g, 8.31 mmol) of (*S*)-PEC in 25 mL of dry diethyl ether. The reaction mixture turned deep red. The mixture was stirred at room temperature for 1 h. All volatiles were removed in vacuo, and the residue was washed with 20 mL of *n*-pentane to give (*S*)-LiPETA as an orange powder. Yield: 2.21 g (7.03 mmol, 85%). ^{1}H NMR (400 MHz, D_8-THF, 298 K): δ (ppm) 7.35−7.33 (m, 4 H, *m*-Ph), 7.11−7.07 (m, 4 H, *o*-Ph), 6.98−6.95 (m, 2 H, *p*-Ph), 5.14 (q, ^3J = 6.3 Hz, 2 H, C*H*), 1.25 (d, ^3J = 6.3 Hz, 6 H, CH_3), 1.17 (s, 9 H, *t*Bu). ^{13}C{^{1}H} NMR (101 MHz, D_8-THF, 298 K): δ (ppm) 167.2 (NCN), 154.1 (*i*-Ph), 128.2 (*m*-Ph), 128.1 (*o*-Ph), 125.3 (*p*-Ph), 56.3 (*C*H), 39.3 (*t*BuC), 31.1 (*t*BuCH$_3$), 26.7 (CH_3). MS (EI, 70 eV): *m*/*z* (%) 308 ([M − Li]$^+$, 86), 293 ([M − LiCH_3]$^+$, 58), 257 ([M − *t*Bu]$^+$, 1), 251 ([M − Li*t*Bu]$^+$, 8), 203 ([M − LiPhEt]$^+$, 93), 189 ([M − PhEtCH_3]$^+$, 71), 147 ([M − LiPhEt − *t*Bu]$^+$, 71), 120 ([PhEtN]$^+$, 99), 105 ([PhEt]$^+$, 100), 91 ([Bz]$^+$, 78), 77 ([Ph]$^+$, 72), 57 ([*t*Bu]$^+$, 85), 42 ([C_2H_4N]$^+$, 99). IR (ATR): ν (cm^{-1}) 3060 (w), 3025 (w), 2962 (w), 2923 (w), 2868 (w), 1631 (m), 1481 (m), 1445 (m), 1400 (w), 1365 (w), 1255 (w), 1197 (w), 1066 (w), 1019 (m), 910 (w), 876 (w), 799 (w), 756 (m), 697 (s), 598 (w), 539 (w).

Mono(amidinate)iodolanthanum Complex. *[{(S)-PETA}La(μ-I)$_4$Li$_2$(thf)$_4$] (**1**).* THF (ca. 10 mL) was condensed at −78 °C onto a mixture of 223 mg (0.428 mmol) of LaI_3 and 135 mg (0.428 mmol) of (*S*)-LiPETA. The reaction mixture was refluxed for 2 h and was stirred overnight at room temperature. The solvent was removed in vacuo, and the residue was extracted with 10 mL of hot toluene. The solvent was removed in vacuo, and the residue was washed with 10 mL of *n*-pentane. The product was crystallized from hot toluene to yield 210 mg (0.167 mmol, 39%) of **1**. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ (ppm) 7.84−7.82 (m, 4 H, Ph), 7.40−7.35 (m, 4 H, Ph), 7.14−7.09 (m, 2 H, Ph), 5.39 (q, $^3J_{H,H}$ = 6.6 Hz, 2 H, C*H*), 3.79−3.75 (m, 16 H, OCH_2), 2.23 (d, $^3J_{H,H}$ = 6.6 Hz, 6 H, CH_3) 1.37−1.33 (m, 16 H, OCH$_2$CH_2), 1.20 (s, 9 H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 298 K): δ (ppm) 181.4 (NCN), 148.4 (*i*-Ph), 129.0 (Ph), 127.5 (Ph), 126.6 (Ph), 69.5 (OCH_2), 56.6 (CH), 41.9 (*C*(CH$_3$)$_3$), 30.7 (C(CH_3)$_3$), 28.0 (CH_3), 25.4 (OCH$_2$CH_2). IR (ATR): ν (cm^{-1}) 3357 (m), 3058 (w), 3027 (w), 2974 (m), 2877 (m), 1612 (vs), 1548 (w), 1493 (m), 1448 (s), 1397 (w), 1379 (w), 1335 (w), 1300 (w), 1275 (w), 1201 (w), 1146 (w), 1121 (w), 1072 (w), 1041 (vs), 913 (w), 890 (s), 758 (m), 728 (w), 700 (vs), 669 (w), 610 (w), 588 (w), 544 (w), 367 (w). Anal. Calcd for $C_{37}H_{59}N_2O_4I_4Li_2La$ (1256.28 g/mol): C, 35.37; H, 4.73, N, 2.23. Found: C, 35.84, H, 4.60, N, 2.09.

Bis(amidinate)chlorolanthanide Complexes. *[{(S)-PETA}$_2$ScCl] (**2**).* THF (ca. 10 mL) was condensed at −78 °C onto a mixture of 76 mg (0.503 mmol) of $ScCl_3$ and 317 mg (1.007 mmol) of (*S*)-LiPETA, and the reaction mixture was refluxed for 6 h. 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 of *n*-pentane. The product was crystallized from hot toluene to yield 140 mg (0.201 mmol, 40%) of **2**. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ

DOI: 10.1021/acs.organomet.6b00523
Organometallics XXXX, XXX, XXX−XXX

(ppm) 7.50 (d, $^3J_{H,H}$ = 7.5 Hz, 8 H, *o*-Ph), 7.25 (t, $^3J_{H,H}$ = 7.5 Hz, 8 H, *m*-Ph), 7.08 (t, $^3J_{H,H}$ = 7.5 Hz, 4 H, *p*-Ph), 4.83 (q, $^3J_{H,H}$ = 6.6 Hz, 4 H, C*H*), 1.73 (d, $^3J_{H,H}$ = 6.6 Hz, 12 H, CH_3), 1.06 (s, 18 H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 298 K): δ (ppm) 187.3 (NCN), 148.2 (*i*-Ph), 128.6 (Ph), 127.0 (Ph), 126.5 (Ph), 55.9 (CH), 41.2 (C(CH$_3$)$_3$), 30.0 (C(CH_3)$_3$), 27.5 (CH_3). EI-MS (70 eV): *m*/*z* (%) 694 ([M]$^+$, 6), 659 ([M − Cl]$^+$, 13), 607 ([M − *t*Bu − 2 CH$_3$]$^+$, 10), 601 ([M − Cl − *t*Bu]$^+$, 21), 589 ([M − PhEt]$^+$, 100), 501 (17), 449 ([M − 2 *t*Bu − PhEtNC]$^+$, 7), 425 (15), 410 (14). IR (ATR): ν (cm^{-1}) 3482 (w), 3082 (w), 3059 (w), 3024 (w), 2964 (m), 2925 (w), 2870 (w), 1947 (w), 1872 (w), 1803 (w), 1772 (w), 1631 (m), 1602 (w), 1583 (w), 1543 (w), 1490 (m), 1476 (w), 1446 (w), 1430 (w), 1401 (w), 1361 (m), 1336 (w), 1297 (m), 1253 (w), 1189 (w), 1156 (m), 1074 (w), 1026 (m), 966 (w), 909 (w), 841 (w), 791 (w), 758 (m), 697 (vs), 670 (w), 624 (w), 612 (w), 587 (w), 537 (w), 509 (w), 476 (m), 417 (w), 365 (s). Anal. Calcd for $C_{42}H_{54}N_4ClSc\cdot{}^1/_3$ LiCl (709.36 g/mol): C, 71.10; H, 7.67; N, 7.90. Found: C, 71.12; H, 7.38; N, 7.93.

[{(S)-PETA}$_2$YCl]$_2$ (**3**). THF (ca. 10 mL) was condensed at −78 °C onto a mixture of 79 mg (0.406 mmol) of YCl_3 and 255 mg (0.812 mmol) of (*S*)-LiPETA, and the reaction mixture was stirred overnight at room temperature. The solvent was removed in vacuo, and the residue was extracted with 10 mL of hot toluene. The solvent was removed in vacuo, and the product was crystallized from hot toluene to yield 123 mg (0.166 mmol, 41%) of **3**. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ (ppm) 7.73−7.70 (m, 4 H, Ph), 7.38−7.33 (m, 4 H, Ph), 7.16−7.08 (m, 12 H, Ph), 5.33 (q, $^3J_{H,H}$ = 5.7 Hz, 2 H, C*H*), 4.21 (q, $^3J_{H,H}$ = 6.0 Hz, 2 H, C*H*), 2.04 (d, $^3J_{H,H}$ = 6.3 Hz, 6 H, CH_3), 1.18 (s, 18 H, C(CH_3)$_3$), 0.68 (d, $^3J_{H,H}$ = 6.3 Hz, 6 H, CH_3). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 298 K): δ (ppm) 184.2 (d, $^2J_{C,Y}$ = 1.5 Hz, NCN), 150.8 (*i*-Ph), 146.7 (*i*-Ph), 127.9 (Ph), 127.1 (Ph), 125.9 (Ph), 56.0 (CH), 54.6 (CH), 41.1 (d, $^3J_{C,Y}$ = 3.9 Hz, C(CH$_3$)$_3$), 30.5 (C(CH_3)$_3$), 29.5 (CH$_3$), 25.5 (CH$_3$). IR (ATR): ν (cm^{-1}) 3482 (w), 3083 (w), 3059 (w), 3023 (w), 2966 (m), 2923 (w), 2870 (w), 1945 (w), 1877 (w), 1807 (w), 1631 (m), 1601 (w), 1583 (w), 1549 (w), 1491 (m), 1446 (w), 1420 (w), 1406 (m), 1363 (m), 1322 (w), 1299 (m), 1271 (w), 1253 (w), 1220 (w), 1187 (m), 1151 (m), 1069 (m), 1027 (m), 968 (w), 909 (w), 843 (w), 794 (w), 753 (m), 698 (vs), 673 (w), 613 (w), 589 (w), 529 (w), 500 (w), 456 (w), 396 (m), 363 (w). Anal. Calcd for $C_{42}H_{54}N_4ClY$ (739.26 g/mol): C, 68.24; H, 7.36; N, 7.58. Found: C, 67.88; H, 7.23; N, 7.23.

[{(S)-PETA}$_2$NdCl]$_2$ (**4**). THF (ca. 10 mL) was condensed at −78 °C onto a mixture of 95 mg (0.378 mmol) of $NdCl_3$ and 237 mg (0.755 mmol) of (*S*)-LiPETA, and the reaction mixture was stirred overnight at room temperature. The solvent was removed in vacuo, and the residue was 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 80 mg (0.101 mmol, 27%) of **4**. IR (ATR): ν (cm^{-1}) 3482 (w), 3060 (w), 3026 (w), 2963 (m), 2922 (w), 2869 (w), 1967 (w), 1869 (w), 1717 (w), 1699 (w), 1684 (w), 1653 (w), 1630 (s), 1583 (w), 1558 (w), 1541 (w), 1490 (s), 1476 (m), 1448 (m), 1397 (w), 1363 (m), 1277 (w), 1252 (w), 1191 (m), 1147 (w), 1066 (m), 1026 (m), 937 (w), 909 (w), 843 (w), 755 (m), 697 (vs), 668 (w), 613 (w), 543 (m), 368 (w). Anal. Calcd for $C_{42}H_{54}N_4ClNd$ (794.60 g/mol): C, 63.48; H, 6.85; N, 7.05. Found: C 63.71; H, 6.89; N, 6.96.

[{(S)-PETA}$_2$LuCl]$_2$ (**5**). THF (ca. 10 mL) was condensed at −78 °C onto a mixture of 179 mg (0.64 mmol) of $LuCl_3$ and 400 mg (1.27 mmol) of (*S*)-LiPETA, and the reaction mixture was stirred overnight at room temperature. The solvent was removed in vacuo, and the residue was extracted with 10 mL of hot toluene. The solvent was removed in vacuo, and the residue was washed with 10 mL of *n*-pentane. The product was crystallized from hot toluene to yield 202 mg (0.25 mmol, 39%) of **5**. ^{1}H NMR (300 MHz, D_8-THF, 332 K): δ (ppm) 7.62 (m, 8 H, *o*-Ph), 6.96 (m, 12 H, *m*,*p*-Ph), 5.20 (q, ^3J = 6.7 Hz, 4 H, C*H*), 1.62 (d, ^3J = 6.7 Hz, 12 H, CH_3), 1.12 (s, 18 H, *t*Bu). ^{13}C{^{1}H} NMR (75 MHz, D_8-THF, 332 K): δ (ppm) 181.3 (NCN), 150.0 (*i*-Ph), 127.3 (*m*-Ph), 127.2 (*o*-Ph), 124.6 (*p*-Ph), 55.9 (CH), 40.8 (*t*Bu-C), 30.9 (*t*Bu-CH$_3$), 25.3 (CH$_3$). MS (EI, 70 eV): *m*/*z* (%) 785 ([M − Cl]$^+$, 80), 718 ([M − PhEt]$^+$, 80), 516 ([M − (PETA)]$^+$, 85), 481 ([(PETA)Lu]$^+$, 2), 308 ([PETA]$^+$, 2), 293 ([PETA − CH$_3$]$^+$, 100), 203 ([(PETA) − PhEt]$^+$, 10), 120 ([PhEtN]$^+$, 53), 105 ([PhEt]$^+$, 100), 91 ([Bz]$^+$, 7), 77 ([Ph]$^+$, 21), 57 ([*t*Bu]$^+$, 30). IR (ATR): ν (cm^{-1}) 3059 (w), 3025 (w), 2963 (w), 2922 (w), 2869 (w), 1629 (m), 1551 (w), 1489 (m), 1447 (m), 1401 (w), 1365 (w), 1326 (w), 1298 (w), 1253 (w), 1187 (w), 1152 (w), 1068 (w), 1022 (w), 909 (w), 754 (m), 696 (s), 616 (w), 544 (w). Anal. Calcd for $C_{42}H_{54}N_4ClLu$ (825.32 g/mol): C, 61.12; H, 6.59; N, 6.79. Found: C, 61.51; H, 6.52; N, 6.54.

[{(S)-PETA}$_2$Sm(μ-Cl)$_2$Li(thf)$_2$] (**6**). THF (ca. 10 mL) was condensed at −78 °C onto a mixture of 163 mg (0.64 mmol) of $SmCl_3$ and 400 mg (1.27 mmol) of (*S*)-LiPETA, and the reaction mixture was stirred overnight at room temperature. The solvent was removed in vacuo, and the residue was extracted with 10 mL of toluene. The solvent was removed in vacuo, and the residue was washed with 10 mL of *n*-pentane. The product was crystallized from THF/*n*-pentane to yield 148 mg (0.15 mmol, 24%) of **6**. MS (EI, 70 eV): *m*/*z* (%) 843 ([M]$^+$, 1), 766 ([M − LiCl$_2$]$^+$, 15), 709 ([M − LiCl$_2$ − *t*Bu]$^+$, 23), 496 ([(PETA)SmCl]$^+$, 20), 308 ([PETA]$^+$, 100), 293 ([PETA − CH$_3$]$^+$, 100), 251 ([PETA − *t*Bu]$^+$, 65), 203 ([(PETA) − PhEt]$^+$, 100), 189 ([(PETA) − PhEtCH$_3$]$^+$, 100), 147 ([(PETA) − PhEt − *t*Bu]$^+$, 100), 120 ([PhEtN]$^+$, 100), 105 ([PhEt]$^+$, 100), 91 ([Bz]$^+$, 100), 77 ([Ph]$^+$, 100), 57 ([*t*Bu]$^+$, 100). IR (ATR): ν (cm^{-1}) 3058 (w), 3024 (w), 2963 (w), 2922 (w), 2871 (w), 1625 (m), 1551 (w), 1489 (m), 1447 (m), 1398 (w), 1364 (w), 1301 (w), 1275 (w), 1252 (w), 1185 (w), 1147 (w), 1068 (w), 1044 (w), 1024 (w), 908 (w), 845 (w), 755 (m), 697 (s), 665 (w), 611 (w), 586 (w), 545 (w). Anal. Calcd for $C_{50}H_{70}LiN_4O_2Cl_2Sm$ (987.32 g/mol): C, 60.82; H, 7.15; N, 5.67. Found: C, 60.37; H, 7.09; N, 5.57.

Tris(amidinate)yttrium Complex. *[{(S)-PETA}$_3$Y]* (**7**). Toluene (ca. 10 mL) was condensed at −78 °C onto a mixture of 300 mg (0.406 mmol) of **3** and 128 mg (0.406 mmol) of (*S*)-LiPETA, and the reaction mixture was refluxed overnight. The solvent was removed in vacuo, and the residue was extracted with 10 mL of *n*-pentane. The product was crystallized from toluene/*n*-pentane to yield 43 mg (0.043 mmol, 11%) of **7**. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ (ppm) 7.49 (br, 12 H, Ph), 7.02−6.91 (m, 18 H, Ph), 5.26 (br q, $^3J_{H,H}$ = 5.6 Hz, 6 H, C*H*), 1.88 (br, 18 H, CH_3), 1.21 (s, 27 H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ (ppm) 184.2 (NCN), 149.4 (*i*-Ph), 128.4 (Ph), 127.4 (Ph), 125.9 (Ph), 56.9 (CH), 41.3 (C(CH$_3$)$_3$), 31.7 (C(CH$_3$)$_3$), 28.3 (CH$_3$). − EI-MS (70 eV): *m*/*z* (%) 931 ([M − Ph]$^+$, 8), 700 ([M − PETA]$^+$, 81), 644 ([M − PETA − *t*Bu]$^+$, 65), 598 ([M − PETA − PhEt]$^+$, 100), 541 ([M − PETA − PhEt − *t*Bu]$^+$, 11). Anal. Calcd for $C_{63}H_{81}N_6Y\cdot 1/2C_7H_8$ (1057.33 g/mol): C, 75.54; H, 8.10; N, 7.95. Found: C, 75.79; H, 8.17; N, 7.99.

Amido Complex. *[{(S)-PETA}$_2$Y{N(SiMe$_3$)$_2$}]* (**8**). Toluene (ca. 10 mL) was condensed at −78 °C onto a mixture of 428 mg (0.579 mmol) of **3** and 115 mg (0.579 mmol) of KN(SiMe$_3$)$_2$, and the reaction mixture was stirred overnight at room temperature. The solvent was removed in vacuo, and the residue was extracted with 10 mL of *n*-pentane. The solvent was removed in vacuo, and the product was crystallized from a saturated *n*-heptane solution to yield 410 mg (0.474 mmol, 82%) of **8**. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ (ppm) 7.45−7.44 (m, 4 H, Ph), 7.28−7.27 (m, 4 H, Ph), 7.13−6.92 (m, 12 H, Ph), 5.07 (q, $^3J_{H,H}$ = 6.0 Hz, 4 H, C*H*), 1.66 (d, $^3J_{H,H}$ = 6.0 Hz, 6 H, CH_3), 1.43 (d, $^3J_{H,H}$ = 6.0 Hz, 6 H, CH_3), 1.16 (s, 18 H, C(CH_3)$_3$), 0.53 (s, 18H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K): δ (ppm) 183.4 (d, $^2J_{C,Y}$ = 1.5 Hz, NCN), 149.1 (*i*-Ph), 147.2 (*i*-Ph), 127.3 (Ph), 126.9 (Ph), 126.8 (Ph), 126.5 (Ph), 126.1 (Ph), 56.2 (CH), 54.9 (CH), 41.2 (d, $^3J_{C,Y}$ = 3.9 Hz, C(CH$_3$)$_3$), 30.9 (C(CH$_3$)$_3$), 28.0 (CH$_3$), 26.8 (CH$_3$), 5.9 (Si(CH$_3$)$_3$). EI-MS (70 eV): *m*/*z* (%) 863 ([M]$^+$, 1), 848 ([M − Me]$^+$, 3), 703 ([M − N(SiMe$_3$)$_2$]$^+$, 12), 556 ([M − PETA]$^+$, 91), 368 (22), 308 ([HPETA]$^+$, 88), 293 ([HPETA − Me]$^+$, 47), 236 ([HPETA − Me − *t*Bu]$^+$, 56), 203 ([HPETA − PhEt]$^+$, 96), 189 ([HPETA − PhEt − Me]$^+$, 66), 146 ([HPETA − PhEt − *t*Bu]$^+$, 96), 130 ([PETA − PhEt − *t*Bu − Me]$^+$, 73), 120 ([PhEtNH]$^+$, 100), 105 ([PhEt]$^+$, 99). IR (ATR): ν (cm^{-1}) 3483 (w), 3061 (w), 3024 (w), 2964 (s), 1945 (w), 1886 (w), 1805 (w), 1771 (w), 1633 (m), 1602 (w), 1491 (m), 1446 (w), 1422 (m), 1403 (vs), 1362 (m), 1319 (w), 1296 (s), 1273 (w), 1242 (m), 1187 (m), 1142

DOI: 10.1021/acs.organomet.6b00523
Organometallics XXXX, XXX, XXX−XXX

(m), 1065 (w), 1027 (w), 1011 (w), 947 (vs), 910 (w), 874 (m), 845 (w), 826 (s), 794 (w), 779 (w), 751 (s), 723 (w), 698 (vs), 667 (m), 613 (m), 588 (w), 526 (w), 493 (w), 456 (w), 397 (w), 377 (s). Anal. Calcd for $C_{48}H_{72}N_5Si_2Y$ (864.20 g/mol): C, 66.71; H, 8.40; N, 8.10. Found: C, 65.74; H, 7.73; N, 7.86.

Alkyl Complexes. *[{(S)-PETA}$_2$Sc{CH(SiMe$_3$)$_2$}] (**9**).* Toluene (ca. 10 mL) was condensed at −78 °C onto a mixture of 239 mg (0.344 mmol) of **2** and 68 mg (0.344 mmol) of KCH(SiMe$_3$)$_2$, and the reaction mixture was stirred overnight at room temperature. The solvent was removed in vacuo, and the residue was extracted with 10 mL of *n*-pentane. The solvent was removed in vacuo to yield 164 mg (0.200 mmol, 58%) of **9** as a colorless powder. ^{1}H NMR (300 MHz, D$_8$-THF, 353 K): δ (ppm) 7.35 (d, $^3J_{H,H}$ = 7.5 Hz, 8 H, *o*-Ph), 7.14 (t, $^3J_{H,H}$ = 7.5 Hz, 8 H, *m*-Ph), 7.04 (t, $^3J_{H,H}$ = 7.5 Hz, 4 H, *p*-Ph), 5.08 (br, 4 H, C*H*), 1.66 (br, 12 H, CH_3), 1.18 (s, 18 H, C(CH_3)$_3$), 0.17 (s, 9 H, Si(CH_3)$_3$), 0.16 (s, 9 H, Si(CH_3)$_3$), −0.27 (s, 1 H, C*H*(SiMe$_3$)$_2$). ^{13}C{^{1}H} NMR (75 MHz, D$_8$-THF, 353 K): δ (ppm) 148.7 (*i*-Ph), 128.8 (Ph), 127.8 (Ph), 126.8 (Ph), 56.9 (CH), 41.6 (C(CH$_3$)$_3$), 31.6 (C(CH$_3$)$_3$), 31.4 (CH(SiMe$_3$)$_2$), 28.3 (CH$_3$), 6.8 (Si(CH$_3$)$_3$), 6.5 (Si(CH$_3$)$_3$). (the NCN carbon atom was not detected). The complex shows some decomposition in NMR solution. EI-MS (70 eV): *m*/*z* (%) 804 ([M − CH$_3$]$^+$, 5), 659 ([M − CH(SiMe$_3$)$_2$]$^+$, 100), 601 ([M − CH(SiMe$_3$)$_2$ − *t*Bu]$^+$, 33), 555 ([M − CH(SiMe$_3$)$_2$ − PhEt]$^+$, 20), 533 (19), 527 ([M − CH(SiMe$_3$)$_2$ − PhEt − 2 CH$_3$]$^+$, 15), 497 ([M − CH(SiMe$_3$)$_2$ − PhEt − *t*Bu]$^+$, 9), 451 ([M − CH(SiMe$_3$)$_2$ − *t*Bu − PhEt − 3 CH$_3$]$^+$, 13), 425 ([M − CH(SiMe$_3$)$_2$ − PhEt − 2 *t*Bu − CH$_3$]$^+$, 15), 412 ([M − CH(SiMe$_3$)$_2$ − PhEt − 2 *t*Bu − 2 CH$_3$]$^+$, 39). IR (ATR): ν (cm^{-1}) 3483 (w), 3060 (w), 3025 (w), 2960 (s), 2925 (w), 1945 (w), 1871 (w), 1804 (w), 1632 (s), 1602 (w), 1558 (w), 1490 (m), 1477 (w), 1447 (m), 1401 (m), 1365 (w), 1322 (w), 1299 (m), 1274 (w), 1250 (m), 1188 (m), 1146 (w), 1066 (w), 1026 (m), 909 (w), 837 (s), 754 (m), 725 (w), 697 (s), 662 (w), 589 (w), 459 (w), 401 (w). Anal. Calcd for $C_{49}H_{73}N_4Si_2Sc$ (819.26 g/mol): C, 71.84; H, 8.98; N, 6.84. Found: C, 70.97; H, 8.52; N, 6.75.

*[{(S)-PETA}$_2$Y{CH(SiMe$_3$)$_2$}] (**10**).* Toluene (ca. 10 mL) was condensed at −78 °C onto a mixture of 257 mg (0.348 mmol) of **3** and 69 mg (0.348 mmol) KCH(SiMe$_3$)$_2$, and the reaction mixture was stirred overnight at room temperature. The solvent was removed in vacuo, and the residue was extracted with 10 mL of *n*-pentane. The solvent was removed in vacuo to yield 200 mg (0.232 mmol, 67%) of **10** as a colorless powder. ^{1}H NMR (300 MHz, D$_8$-THF, 353 K): δ (ppm) 7.34 (d, $^3J_{H,H}$ = 7.2 Hz, 8 H, *o*-Ph), 7.18 (t, $^3J_{H,H}$ = 7.2 Hz, 8 H, *m*-Ph), 7.08 (t, $^3J_{H,H}$ = 7.2 Hz, 4 H, *p*-Ph), 5.06 (q, $^3J_{H,H}$ = 6.6 Hz, 4 H, C*H*), 1.52 (d, $^3J_{H,H}$ = 6.6 Hz, 12 H, CH_3), 1.19 (s, 18 H, C(CH_3)$_3$), 0.12 (s, 9 H, Si(CH_3)$_3$), 0.11 (s, 9 H, Si(CH_3)$_3$), −1.22 (d, $^2J_{H,Y}$ = 2.4 Hz, 1 H, C*H*(SiMe$_3$)$_2$). ^{13}C{^{1}H} NMR (75 MHz, D$_8$-THF, 353 K): δ (ppm) 185.2 (d, $^2J_{C,Y}$ = 1.7 Hz, NCN), 184.4 (d, $^2J_{C,Y}$ = 1.3 Hz, NCN), 152.5 (*i*-Ph), 148.9 (*i*-Ph), 129.0 (Ph), 128.8 (Ph), 127.7 (Ph), 127.3 (Ph), 127.0 (Ph), 126.4 (Ph), 56.3 (CH), 42.1 (d, $^3J_{C,Y}$ = 3.7 Hz, C(CH$_3$)$_3$), 31.5 (C(CH$_3$)$_3$), 31.4 (d, $^1J_{C,Y}$ = 53.0 Hz, CH(SiMe$_3$)$_2$), 28.2 (CH$_3$), 6.5 (Si(CH$_3$)$_3$), 6.3 (Si(CH$_3$)$_3$). The complex shows some decomposition in NMR solution. IR (ATR): ν (cm^{-1}) 3484 (w), 3061 (w), 3026 (w), 2959 (s), 2923 (w), 1945 (w), 1872 (w), 1804 (w), 1632 (s), 1478 (s), 1447 (m), 1398 (w), 1366 (m), 1297 (w), 1251 (s), 1193 (m), 1053 (m), 1022 (w), 938 (w), 908 (w), 841 (s), 756 (s), 697 (s), 541 (m). Anal. Calcd for $C_{49}H_{73}N_4Si_2Y$ (863.21 g/mol): C, 68.18; H, 8.52; N, 6.49. Found: C, 68.60; H, 8.26; N, 6.42.

*[{(S)-PETA}$_2$Lu{CH(SiMe$_3$)$_2$}] (**11**).* Toluene (ca. 10 mL) was condensed at −78 °C onto a mixture of 348 mg (0.421 mmol) of **5** and 84 mg (0.421 mmol) of KCH(SiMe$_3$)$_2$,and the reaction mixture was stirred overnight at room temperature. The solvent was removed in vacuo, and the residue was extracted with 10 mL of *n*-pentane. The solvent was removed in vacuo to yield 260 mg (0.274 mmol, 65%) of **11** as a colorless powder. Single crystals were grown from a saturated *n*-pentane solution. ^{1}H NMR (300 MHz, D$_8$-THF, 353 K): δ (ppm) 7.34 (d, $^3J_{H,H}$ = 7.2 Hz, 8 H, *o*-Ph), 7.16 (t, $^3J_{H,H}$ = 7.2 Hz, 8 H, *m*-Ph), 7.07 (t, $^3J_{H,H}$ = 7.2 Hz, 4 H, *p*-Ph), 5.20 (br, 4 H, C*H*), 1.51 (br, 12 H, CH_3), 1.20 (s, 18 H, C(CH_3)$_3$), 0.14 (s, 9 H, Si(CH_3)$_3$), 0.13 (s, 9 H, Si(CH_3)$_3$), −1.16 (s, 1 H, C*H*(SiMe$_3$)$_2$). ^{13}C{^{1}H} NMR (75 MHz, D$_8$-THF, 353 K): δ (ppm) 148.8 (*i*-Ph), 128.9 (Ph), 127.7 (Ph), 126.9 (Ph), 56.3 (CH), 44.3 (C(CH$_3$)$_3$), 42.6 (CH(SiMe$_3$)$_2$), 31.5 (C(CH$_3$)$_3$), 28.1 (CH$_3$), 6.9 (Si(CH$_3$)$_3$), 6.5 (Si(CH$_3$)$_3$). (the NCN carbon atom was not detected). The complex shows some decomposition in NMR solution. EI-MS (70 eV): *m*/*z* (%) 789 ([M − CH(SiMe$_3$)$_2$]$^+$, 61), 731 ([M − CH(SiMe$_3$)$_2$ − *t*Bu]$^+$, 26), 602 ([Lu + PETA + PhEtN]$^+$, 32), 577 (100), 564 (49), 551 (92), 536 (76), 523 (83), 508 (50), 495 (46). IR (ATR): ν (cm^{-1}) 3483 (w), 3061 (w), 3026 (w), 2962 (s), 2922 (w), 2869 (w), 1944 (w), 1870 (w), 1793 (w), 1653 (w), 1632 (s), 1602 (w), 1583 (w), 1559 (w), 1490 (w), 1476 (s), 1448 (m), 1397 (w), 1363 (m), 1340 (w), 1278 (w), 1251 (m), 1191 (m), 1065 (w), 1026 (m), 938 (w), 908 (w), 842 (s), 756 (s), 697 (vs), 668 (w), 636 (w), 614 (w), 543 (m), 465 (w), 365 (w), 356 (w). Anal. Calcd for $C_{49}H_{73}N_4Si_2Lu$ (949.27 g/mol): C, 62.00; H, 7.75, N, 5.90. Found: C, 61.81; H, 7.59; N, 5.86.

Hydroamination Reactions. The catalyst was weighed into a NMR tube under an argon atmosphere. C_6D_6 (about 0.5 mL) was condensed into the NMR tube, and the mixture was frozen at −196 °C. The reactant was injected onto the solid mixture, and the whole sample was melted and mixed just before insertion into the core of the NMR machine (t_0). The ratio between the reactant and the product was calculated by comparison of the integrations of the corresponding signals in the ^{1}H NMR spectrum. Ferrocene was used as an internal standard for the kinetic measurements. The substrates 2,2-diphenylpent-4-enylamine (**12a**),[96] *C*-(1-allylcyclohexyl)methylamine (**13a**),[96] 2,2-dimethylpent-4-en-1-amine (**14a**),[96] 2,2-dimethylhex-5-en-1-amine (**15a**),[88] 2,2-diphenylhex-5-en-1-amine (**16a**),[102] [1-(pent-2-ynyl)cyclohexyl]methanamine (**17a**),[98] and 5-phenylpent-4-yn-1-amine (**18a**)[103] were synthesized according to literature procedures. The ^{1}H NMR data of 2-methyl-4,4-diphenylpyrrolidine (**12b**),[96] 3-methyl-2-azaspiro[4.5]decane (**13b**),[96] 2,4,4-trimethylpyrrolidine (**14b**),[96] 2,5,5-trimethylpiperidine (**15b**),[88] 2-phenyl-4,4-diphenylpiperidine (**16b**),[102] 3-propyl-2-azaspiro[4.5]dec-2-ene (**17b**),[98] and 2-benzyl-1-pyrroline (**18b**)[103] conformed with literature data.

General Procedure for the Preparation of Mosher Amides. The cyclic amine (0.1−0.2 mmol) was dissolved in dry $CDCl_3$ (0.5 mL) in an NMR tube. Then, Et_3N (2 equiv) and (*S*)-(+)-α-methoxy-α-trifluoromethylphenylacetic acid chloride (2−5 equiv) were added. Afterward, the enantiomeric excess was determined by ^{19}F NMR spectroscopy at 60−70 °C.[88] Mosher adducts: **12b**, ^{19}F NMR ($CDCl_3$, 70 °C) δ −69.2 (major isomer), −70.3 ppm (minor isomer); **13b**, ^{19}F NMR ($CDCl_3$, 70 °C) δ −69.7 (major isomer), −70.5 ppm (minor isomer); **14b**, ^{19}F NMR ($CDCl_3$, 60 °C) δ −69.7 (major isomer), −70.6 ppm (minor isomer). The ^{19}F NMR spectrum of the Mosher adducts of compound **15b** and **16b** showed an indefinable mixture of products, and the enantiomeric excess of compounds **17b** and **18b** was determined by chiral HPLC analysis of the corresponding 1-naphthoylamide.

Determination of Enantiomeric Excess by Chiral HPLC Analysis. The hydroamination products were derivatized as 1-naphthoyl amides by treating with 1-naphthoyl chloride (1 equiv) and Et_3N (3 equiv) in CH_2Cl_2.[97] The ee values of the products were determined by HPLC analysis on a chiral stationary phase column (Regis (*R*,*R*)-β-Gem1 column, i.d. 4.6 mm, length 250 mm, particle size 5 mm). The HPLC conditions and ee values are shown in Table S1 in the Supporting Information.

X-ray Crystallographic Studies of Compounds (*S*)-HPETA·HCl, (*S*)-LiPETA·LiCl, 1−8, and 11. Suitable crystals of (*S*)-HPETA HCl, (*S*)-LiPETA·LiCl, **1**−**8**, and **11** 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.[104] 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 minimizing the function $(F_o - F_c)^2$, where the weight was defined as $4F_o^2/2(F_o^2)$ and F_o and F_c were the observed and calculated structure factor amplitudes, respectively, by using the program SHELXL.[104] 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

DOI: 10.1021/acs.organomet.6b00523
Organometallics XXXX, XXX, XXX−XXX

Fourier map calculations, as well as the magnitude of the residual electron densities, were of no chemical significance.

Crystal data for (S)-HPETA·HCl: $2(C_{21}H_{29}N_2)\cdot C_7H_8\cdot 2Cl$, M_r = 781.95, a = 8.4967(5) Å, b = 17.3514(7) Å, c = 16.4202(11) Å, β = 102.371(5)°, V = 2364.6(2) Å^3, T = 150 K, space group $P2_1$, Z = 2, μ(Mo Kα) = 0.172 mm^{-1}, 34885 reflections measured, 9329 independent reflections (R_{int} = 0.0473). The final R1 value was 0.0485 ($I > 2\sigma(I)$). The final $R_w(F^2)$ value was 0.0974 ($I > 2\sigma(I)$). The final R1 value was 0.0647 (all data). The final $R_w(F^2)$ value was 0.1031 (all data). The goodness of fit on F^2 was 1.015. Flack parameter: 0.02(3).

Crystal data for (S)-LiPETA·LiCl: $C_{29}H_{43}ClLi_2N_2O_2$, M_r = 500.98, a = 12.7412(5) Å, b = 24.4396(15) Å, c = 9.3499(4) Å, V = 2911.5(2) Å^3, T = 110 K, space group $P2_12_12$, Z = 4, μ(Mo Kα) = 0.158 mm^{-1}, 9938 reflections measured, 5578 independent reflections (R_{int} = 0.0513). The final R1 value was 0.1247 ($I > 2\sigma(I)$). The final $R_w(F^2)$ value was 0.2987 ($I > 2\sigma(I)$). The final R1 value was 0.1488 (all data). The final $R_w(F^2)$ value was 0.3127 (all data). The goodness of fit on F^2 was 1.082. Flack parameter: 0.2(3).

Crystal data for **1***:* $C_{37}H_{59}I_4LaLi_2N_2O_4$, M_r = 1256.25, a = 11.33320(10) Å, b = 11.4658(2) Å, c = 36.0610(4) Å, V = 4685.92(11) Å^3, T = 150 K, space group $P2_12_12_1$, Z = 4, μ(Mo Kα) = 3.581 mm^{-1}, 117235 reflections measured, 9247 independent reflections (R_{int} = 0.0660). The final R1 value was 0.0502 ($I > 2\sigma(I)$). The final $R_w(F^2)$ value was 0.1300 ($I > 2\sigma(I)$). The final R1 value was 0.0552 (all data). The final $R_w(F^2)$ value was 0.1397 (all data). The goodness of fit on F^2 was 1.104. Flack parameter: −0.004(15).

Crystal data for **2***:* $C_{42}H_{54}ClN_4Sc$, M_r = 695.30, a = 12.4537(13) Å, b = 16.5826(16) Å, c = 18.5953(12) Å, V = 3840.2(6) Å^3, T = 150 K, space group $P2_12_12_1$, Z = 4, μ(Mo Kα) = 0.295 mm^{-1}, 13707 reflections measured, 7593 independent reflections (R_{int} = 0.0943). The final R1 value was 0.0593 ($I > 2\sigma(I)$). The final $R_w(F^2)$ value was 0.0788 ($I > 2\sigma(I)$). The final R1 value was 0.1441 (all data). The final $R_w(F^2)$ value was 0.0978 (all data). The goodness of fit on F^2 was 0.902. Flack parameter: 0.04(5).

Crystal data for **3***:* $C_{84}H_{108}Cl_2N_8Y_2\cdot 2(C_7H_8)$, M_r = 1662.76, a = 10.8692(2) Å, b = 14.5825(3) Å, c = 15.6131(3) Å, α = 93.542(2)°, β = 106.261(2)°, γ = 107.213(2)°, V = 2240.87(8) Å^3, T = 150 K, space group $P1$, Z = 1, μ(Mo Kα) = 1.398 mm^{-1}, 100319 reflections measured, 17078 independent reflections (R_{int} = 0.0300). The final R1 value was 0.0234 ($I > 2\sigma(I)$). The final $R_w(F^2)$ value was 0.0564 ($I > 2\sigma(I)$). The final R1 value was 0.0267 (all data). The final $R_w(F^2)$ value was 0.0576 (all data). The goodness of fit on F^2 was 1.019. Flack parameter: −0.029(2).

Crystal data for **4***:* $C_{84}H_{108}Cl_2N_8Nd_2\cdot 2C_7H_8$, M_r = 1773.42, a = 10.9693(2) Å, b = 14.7087(2) Å, c = 15.8593(2) Å, α = 93.1880(10)°, β = 106.4590(10)°, γ = 107.3440(10)°, V = 2314.79(6) Å^3, T = 205 K, space group $P1$, Z = 1, μ(Mo Kα) = 1.215 mm^{-1}, 80060 reflections measured, 17608 independent reflections (R_{int} = 0.0166). The final R1 value was 0.0181 ($I > 2\sigma(I)$). The final $R_w(F^2)$ value was 0.0465 ($I > 2\sigma(I)$). The final R1 value was 0.0189 (all data). The final $R_w(F^2)$ value was 0.0467 (all data). The goodness of fit on F^2 was 1.006. Flack parameter: −0.016(5).

Crystal data for **5***:* $C_{84}H_{108}Cl_2Lu_2N_8\cdot 2C_7H_8$, M_r = 1834.88, a = 10.9769(2) Å, b = 14.6162(2) Å, c = 15.5983(3) Å, α = 93.3340(10)°, β = 106.5800(10)°, γ = 107.3700(10)°, V = 2260.88(7) Å^3, T = 200 K, space group $P1$, Z = 1, μ(Mo Kα) = 2.279 mm^{-1}, 58940 reflections measured, 17115 independent reflections (R_{int} = 0.0183). The final R1 value was 0.0235 ($I > 2\sigma(I)$). The final $R_w(F^2)$ value was 0.0600 ($I > 2\sigma(I)$). The final R1 value was 0.0249 (all data). The final $R_w(F^2)$ value was 0.0607 (all data). The goodness of fit on F^2 was 1.030. Flack parameter: −0.012(6).

Crystal data for **6***:* $C_{50}H_{70}Cl_2LiN_4O_2Sm$, M_r = 987.29, a = 14.6919(2) Å, b = 16.0293(2) Å, c = 21.4446(3) Å, V = 5050.22(12) Å^3, T = 200 K, space group $P2_12_12_1$, Z = 4, μ(Mo Kα) = 1.308 mm^{-1}, 54484 reflections measured, 9926 independent reflections (R_{int} = 0.0443). The final R1 value was 0.0187 ($I > 2\sigma(I)$). The final $R_w(F^2)$ value was 0.0416 ($I > 2\sigma(I)$). The final R1 value was 0.0214 (all data). The final $R_w(F^2)$ value was 0.0422 (all data). The goodness of fit on F^2 was 0.974. Flack parameter: −0.028(3).

Crystal data for **7***:* $C_{63}H_{81}N_6Y$, M_r = 1011.24, a = 13.3096(6) Å, b = 13.3096(6) Å, c = 29.3910(15) Å, V = 4508.9(5) Å^3, T = 150 K, space group $P3_2$, Z = 3, μ(Mo Kα) = 1.011 mm^{-1}, 20791 reflections measured, 11790 independent reflections (R_{int} = 0.0501). The final R1 value was 0.0417 ($I > 2\sigma(I)$). The final $R_w(F^2)$ value was 0.0806 ($I > 2\sigma(I)$). The final R1 value was 0.0807 (all data). The final $R_w(F^2)$ value was 0.0890 (all data). The goodness of fit on F^2 was 0.832. Flack parameter: −0.022(5).

Crystal data for **8***:* $C_{48}H_{72}N_5Si_2Y\cdot C_7H_{16}$, M_r = 964.39, a = 16.5999(4) Å, b = 11.5487(2) Å, c = 28.9601(7) Å, β = 94.457(2)°, V = 5535.1(2) Å^3, T = 100 K, space group $P2_1$, Z = 4, μ(Mo Kα) = 1.135 mm^{-1}, 45880 reflections measured, 21383 independent reflections (R_{int} = 0.0854). The final R1 value was 0.0520 ($I > 2\sigma(I)$). The final $R_w(F^2)$ value was 0.0918 ($I > 2\sigma(I)$). The final R1 value was 0.0880 (all data). The final $R_w(F^2)$ value was 0.1037 (all data). The goodness of fit on F^2 was 0.935. Flack parameter: −0.021(4).

Crystal data for **11***:* $C_{49}H_{73}LuN_4Si_2\cdot 0.5C_5H_{12}$, M_r = 985.33, a = 21.7416(7) Å, b = 11.4890(2) Å, c = 43.5432(14) Å, β = 104.408(2)°, V = 10534.5(5) Å^3, T = 200 K, space group $I2$, Z = 8, μ(Mo Kα) = 1.955 mm^{-1}, 104944 reflections measured, 20655 independent reflections (R_{int} = 0.0860). The final R1 value was 0.0356 ($I > 2\sigma(I)$). The final $R_w(F^2)$ value was 0.0597 ($I > 2\sigma(I)$). The final R1 value was 0.0692 (all data). The final $R_w(F^2)$ value was 0.0673 (all data). The goodness of fit on F^2 was 0.874. Flack parameter: −0.026(5).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00523.

Catalytic data, crystallographic data for (*S*)-HPETA HCl, (*S*)-LiPETA·LiCl, **1**−**8**, and **11**, and NMR and IR data (PDF)

Crystallographic data for (*S*)-HPETA HCl, (*S*)-LiPETA·LiCl, **1**−**8**, and **11** (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail for P.W.R.: roesky@kit.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

T.S.B. thanks the Helmholtz Research School Energy-Related Catalysis (VH-KO-403) and the Fonds der Chemischen Industrie (190481) for support. Ms. S. Schneider is acknowledged for her help in collecting single-crystal X-ray diffraction data. This work was also supported by the Landesstiftung Baden-Württemberg GmbH (7714.14-0301-3) and the KIT.

■ REFERENCES

(1) Trifonov, A. A. *Coord. Chem. Rev.* **2010**, *254*, 1327−1347.
(2) Edelmann, F. T. *Chem. Soc. Rev.* **2012**, *41*, 7657−7672.
(3) Edelmann, F. T. *Adv. Organomet. Chem.* **2008**, *57*, 183−352.
(4) Chlupatý, T.; Růžička, A. *Coord. Chem. Rev.* **2016**, *314*, 103−113.
(5) Elkin, T.; Eisen, M. S. *Catal. Sci. Technol.* **2015**, *5*, 82−95.
(6) Barry, S. T. *Coord. Chem. Rev.* **2013**, *257*, 3192−3201.
(7) Edelmann, F. T. *Chem. Soc. Rev.* **2009**, *38*, 2253−2268.
(8) Wedler, M.; Knösel, F.; Pieper, U.; Stalke, D.; Edelmann, F. T.; Amberger, H.-D. *Chem. Ber.* **1992**, *125*, 2171−2181.
(9) Cole, M. L.; Deacon, G. B.; Forsyth, C. M.; Junk, P. C.; Konstas, K.; Wang, J.; Bittig, H.; Werner, D. *Chem. - Eur. J.* **2013**, *19*, 1410−1420.
(10) Cole, M. L.; Junk, P. C. *Chem. Commun.* **2005**, 2695−2697.

DOI: 10.1021/acs.organomet.6b00523
Organometallics XXXX, XXX, XXX−XXX

(11) Cole, M. L.; Deacon, G. B.; Junk, P. C.; Konstas, K. *Chem. Commun.* **2005**, 1581−1583.
(12) Cole, M. L.; Deacon, G. B.; Forsyth, C. M.; Junk, P. C.; Konstas, K.; Wang, J. *Chem. - Eur. J.* **2007**, *13*, 8092−8110.
(13) Cole, M. L.; Junk, P. C. *New J. Chem.* **2005**, *29*, 135−140.
(14) Cole, M. L.; Deacon, G. B.; Forsyth, C. M.; Konstas, K.; Junk, P. C. *Dalton Trans.* **2006**, 3360−3367.
(15) Edelmann, F. *Struct. Bonding (Berlin, Ger.)* **2010**, *137*, 109−163.
(16) Junk, P. C.; Cole, M. L. *Chem. Commun.* **2007**, 1579−1590.
(17) Edelmann, F. T. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2466−2488.
(18) Edelmann, F. T. *Coord. Chem. Rev.* **1994**, *137*, 403−481.
(19) Hagadorn, J. R.; Arnold, J. *Organometallics* **1996**, *15*, 984−991.
(20) Edelmann, F. T. *J. Alloys Compd.* **1994**, *207-208*, 182−188.
(21) Bambirra, S.; van Leusen, D.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Chem. Commun.* **2003**, 522−523.
(22) Zhang, L.; Nishiura, M.; Yuki, M.; Luo, Y.; Hou, Z. *Angew. Chem., Int. Ed.* **2008**, *47*, 2642−2645.
(23) Bambirra, S.; Bouwkamp, M. W.; Meetsma, A.; Hessen, B. *J. Am. Chem. Soc.* **2004**, *126*, 9182−9183.
(24) Bambirra, S.; Tsurugi, H.; van Leusen, D.; Hessen, B. *Dalton Trans.* **2006**, 1157−1161.
(25) Brunner, T. S.; Hartenstein, L.; Roesky, P. W. *J. Organomet. Chem.* **2013**, *730*, 32−36.
(26) Li, J.; Huang, S.; Weng, L.; Liu, D. *J. Organomet. Chem.* **2006**, *691*, 3003−3010.
(27) Koterwas, L. A.; Fettinger, J. C.; Sita, L. R. *Organometallics* **1999**, *18*, 4183−4190.
(28) Averbuj, C.; Tish, E.; Eisen, M. S. *J. Am. Chem. Soc.* **1998**, *120*, 8640−8646.
(29) Brunner, H.; Lukassek, J.; Agrifoglio, G. *J. Organomet. Chem.* **1980**, *195*, 63−76.
(30) Brunner, H.; Agrifoglio, G.; Bernal, I.; Creswick, M. W. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 641−642.
(31) Bertogg, A.; Togni, A. *Organometallics* **2006**, *25*, 622−630.
(32) Brunner, H.; Agrifoglio, G. *Monatsh. Chem.* **1980**, *111*, 275−287.
(33) Nelkenbaum, E.; Kapon, M.; Eisen, M. S. *J. Organomet. Chem.* **2005**, *690*, 3154−3164.
(34) Benndorf, P.; Preuß, C.; Roesky, P. W. *J. Organomet. Chem.* **2011**, *696*, 1150−1155.
(35) Benndorf, P.; Kratsch, J.; Hartenstein, L.; Preuss, C. M.; Roesky, P. W. *Chem. - Eur. J.* **2012**, *18*, 14454−14463.
(36) Benndorf, P.; Jenter, J.; Zielke, L.; Roesky, P. W. *Chem. Commun.* **2011**, *47*, 2574−2576.
(37) Kratsch, J.; Kuzdrowska, M.; Schmid, M.; Kazeminejad, N.; Kaub, C.; Oña-Burgos, P.; Guillaume, S. M.; Roesky, P. W. *Organometallics* **2013**, *32*, 1230−1238.
(38) Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471−6473.
(39) Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337−339.
(40) Edelmann, F. T. Scandium, Yttrium, and the Lanthanide and Actinide Elements, Excluding their Zero Oxidation State Complexes. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, G. A., Wilkinson, G., Eds.; Elsevier: Oxford, U.K., 1995; pp 11−212.
(41) Evans, W. J. Organometallic Lanthanide Chemistry. In *Advances in Organometallic Chemistry*; Stone, F. G. A., Robert, W., Eds.; Academic Press: New York, 1985; Vol. *24*, pp 131−177.
(42) Atwood, J. L.; Hunter, W. E.; Wayda, A. L.; Evans, W. J. *Inorg. Chem.* **1981**, *20*, 4115−4119.
(43) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203−219.
(44) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51−56.
(45) Thompson, M. E.; Bercaw, J. E. *Pure Appl. Chem.* **1984**, *56*, 1−11.
(46) Vaughan, W. R.; Carlson, R. D. *J. Am. Chem. Soc.* **1962**, *84*, 769−774.
(47) Cunico, R. F.; Pandey, R. K. *J. Org. Chem.* **2005**, *70*, 5344−5346.
(48) Drabowicz, J.; Pacholczyk, M. *Phosphorus, Sulfur Silicon Relat. Elem.* **1987**, *29*, 257−263.
(49) Schlama, T.; Gouverneur, V.; Mioskowski, C. *Tetrahedron Lett.* **1996**, *37*, 7047−7048.
(50) Hiatt, R. R.; Shaio, M.-J.; Georges, F. *J. Org. Chem.* **1979**, *44*, 3265−3266.
(51) Appel, R.; Kleinstück, R.; Ziehn, K.-d. *Chem. Ber.* **1971**, *104*, 1335−1336.
(52) Brunner, T. S. Dissertation, Karlsruher Institut für Technologie (KIT), 2015.
(53) Schmidt, J. A. R.; Arnold, J. *Chem. Commun.* **1999**, 2149−2150.
(54) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley-Interscience: New York, 1988; p 54.
(55) Hitchcock, P. B.; Khvostov, A. V.; Lappert, M. F. *J. Organomet. Chem.* **2002**, *663*, 263−268.
(56) Stern, D.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 9558−9575.
(57) Scarel, G.; Wiemer, C.; Fanciulli, M.; Fedushkin, I. L.; Fukin, G. K.; Domrachev, G. A.; Lebedinskii, Y.; Zenkevich, A.; Pavia, G. *Z. Anorg. Allg. Chem.* **2007**, *633*, 2097−2103.
(58) Bambirra, S.; Brandsma, M. J. R.; Brussee, E. A. C.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **2000**, *19*, 3197−3204.
(59) Roesky, P. W.; Müller, T. E. *Angew. Chem., Int. Ed.* **2003**, *42*, 2708−2710.
(60) Hong, S.; Marks, T. J. *Acc. Chem. Res.* **2004**, *37*, 673−686.
(61) Hultzsch, K. C. *Org. Biomol. Chem.* **2005**, *3*, 1819−1824.
(62) Han, X.; Widenhoefer, R. A. *Angew. Chem., Int. Ed.* **2006**, *45*, 1747−1749.
(63) Aillaud, I.; Collin, J.; Hannedouche, J.; Schulz, E. *Dalton Trans.* **2007**, 5105−5118.
(64) Brunet, J.-J.; Chu, N.-C.; Rodriguez-Zubiri, M. *Eur. J. Inorg. Chem.* **2007**, *2007*, 4711−4722.
(65) Lee, A. V.; Schafer, L. L. *Eur. J. Inorg. Chem.* **2007**, *2007*, 2245−2255.
(66) Severin, R.; Doye, S. *Chem. Soc. Rev.* **2007**, *36*, 1407−1420.
(67) Andrea, T.; Eisen, M. S. *Chem. Soc. Rev.* **2008**, *37*, 550−567.
(68) Dorta, R. Iridium-Catalyzed Hydroamination. In *Iridium Complexes in Organic Synthesis*; Wiley-VCH: Weinheim, Germany, 2009; pp 145−172.
(69) Zi, G. *Dalton Trans.* **2009**, 9101−9109.
(70) Duncan, A. N.; Widenhoefer, R. A. *Synlett* **2010**, *2010*, 419−422.
(71) Hesp, K. D.; Stradiotto, M. *J. Am. Chem. Soc.* **2010**, *132*, 18026−18029.
(72) Li, T.; Jenter, J.; Roesky, P. W. *Struct. Bonding (Berlin, Ger.)* **2010**, *137*, 165−228.
(73) Reznichenko, A. L.; Hultzsch, K. C. Asymmetric Hydroamination. In *Chiral Amine Synthesis*; Wiley-VCH: Weinheim, Germany, 2010; pp 341−375.
(74) Taylor, J. G.; Adrio, L. A.; Hii, K. K. *Dalton Trans.* **2010**, *39*, 1171−1175.
(75) Zi, G. *J. Organomet. Chem.* **2011**, *696*, 68−75.
(76) Jenter, J.; Lühl, A.; Roesky, P. W.; Blechert, S. *J. Organomet. Chem.* **2011**, *696*, 406−418.
(77) Li, T.; Schulz, S.; Roesky, P. W. *Chem. Soc. Rev.* **2012**, *41*, 3759−3771.
(78) Hannedouche, J.; Schulz, E. *Chem. - Eur. J.* **2013**, *19*, 4972−4985.
(79) Nishina, N.; Yamamoto, Y. *Top. Organomet. Chem.* **2012**, *43*, 115−143.
(80) Reznichenko, A.; Hultzsch, K. *Top. Organomet. Chem.* **2011**, *43*, 51−114.
(81) Manzano, R.; Wurm, T.; Rominger, F.; Hashmi, A. S. K. *Chem. - Eur. J.* **2014**, *20*, 6844−6848.
(82) Yang, W.; Hashmi, A. S. K. *Chem. Soc. Rev.* **2014**, *43*, 2941−2955.
(83) Müller, T. E.; Hultzsch, K. C.; Yus, M.; Foubelo, F.; Tada, M. *Chem. Rev.* **2008**, *108*, 3795−3892.

DOI: 10.1021/acs.organomet.6b00523
Organometallics XXXX, XXX, XXX−XXX

(84) Gagne, M. R.; Brard, L.; Conticello, V. P.; Giardello, M. A.; Stern, C. L.; Marks, T. J. *Organometallics* **1992**, *11*, 2003−2005.
(85) Gagne, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 275−294.
(86) Giardello, M. A.; Conticello, V. P.; Brard, L.; Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10241−10254.
(87) Huang, L.; Arndt, M.; Gooßen, K.; Heydt, H.; Gooßen, L. J. *Chem. Rev.* **2015**, *115*, 2596−2697.
(88) Gribkov, D. V.; Hultzsch, K. C.; Hampel, F. *J. Am. Chem. Soc.* **2006**, *128*, 3748−3759.
(89) Hultzsch, K. C. *Adv. Synth. Catal.* **2005**, *347*, 367−391.
(90) Gott, A. L.; Clarke, A. J.; Clarkson, G. J.; Scott, P. *Organometallics* **2007**, *26*, 1729−1737.
(91) Zhang, X.; Emge, T. J.; Hultzsch, K. C. *Angew. Chem., Int. Ed.* **2012**, *51*, 394−398.
(92) Shen, X.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2010**, *49*, 564−567.
(93) Ogata, T.; Ujihara, A.; Tsuchida, S.; Shimizu, T.; Kaneshige, A.; Tomioka, K. *Tetrahedron Lett.* **2007**, *48*, 6648−6650.
(94) Manna, K.; Xu, S.; Sadow, A. D. *Angew. Chem., Int. Ed.* **2011**, *50*, 1865−1868.
(95) Wood, M. C.; Leitch, D. C.; Yeung, C. S.; Kozak, J. A.; Schafer, L. L. *Angew. Chem., Int. Ed.* **2007**, *46*, 354−358.
(96) Martinez, P. H.; Hultzsch, K. C.; Hampel, F. *Chem. Commun.* **2006**, 2221−2223.
(97) Hong, S.; Tian, S.; Metz, M. V.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 14768−14783.
(98) Rastätter, M.; Zulys, A.; Roesky, P. W. *Chem. - Eur. J.* **2007**, *13*, 3606−3616.
(99) Jung, M. E.; Piizzi, G. *Chem. Rev.* **2005**, *105*, 1735−1766.
(100) Benndorf, P. Dissertation, Karlsruher Institut für Technologie (KIT), 2010.
(101) Taylor, M. D.; Carter, C. P. *J. Inorg. Nucl. Chem.* **1962**, *24*, 387−391.
(102) Crimmin, M. R.; Arrowsmith, M.; Barrett, A. G. M.; Casely, I. J.; Hill, M. S.; Procopiou, P. A. *J. Am. Chem. Soc.* **2009**, *131*, 9670−9685.
(103) Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 9295−9306.
(104) Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112−122.

DOI: 10.1021/acs.organomet.6b00523
Organometallics XXXX, XXX, XXX−XXX