Lanthanum Tribenzyl Complexes as Convenient Starting Materials for Organolanthanum Chemistry

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Simple tribenzyl complexes of lanthanum, \([\text{La}(\text{CH}_2\text{C}_6\text{H}_4-4-\text{R})_3(\text{THF})_3](\text{R} = \text{H (1a), Me (1b)})\), were prepared in a remarkably straightforward fashion from \(\text{LaBr}_3(\text{THF})_4\) and potassium benzyl reagents. Single-crystal X-ray diffraction revealed a fac arrangement of the three THF ligands and \(\eta^2\) binding of the benzyl groups. These compounds are convenient precursors to other organolanthanum complexes. Reaction of 1a with the amine ArN\(=\text{CPhNHAr}\) (Ar = 2,6-Pr\(_2\)-C\(_6\)H\(_4\)) affords the corresponding mono(amidinate) dibenzyl derivative 2. Complex 1b reacts with LiCH\(_2\text{C}_6\text{H}_4-4-\text{Me}\) to give the THF-free anion \([\text{La}(\text{CH}_2\text{C}_6\text{H}_4-4-\text{Me})_3]^-(3)\). Reaction of 1 with 1 or 2 equiv of \([\text{PhNMe}_2\text{H}][\text{B} (\text{C}_6\text{F}_5)_4]\) (X = H, F) generate the corresponding mono- and dicaticion benzyl species \([\text{La}(\text{CH}_2\text{C}_6\text{H}_4-4-\text{R})_3(\text{THF})_n]^+(4)\) and \([\text{La}(\text{CH}_2\text{C}_6\text{H}_4-4-\text{R})(\text{THF})_n]^2+(5)\), which were structurally characterized. Scouring ethylene polymerization experiments indicate that these species are only moderately active catalysts but suggest that the monocationic dibenzyl species is more efficient. Both neutral and cationic lanthanum benzyl complexes effect the catalytic intramolecular hydroamination/cyclization of 2,2-dimethyl-4-pentenylamine. It was also observed that polycationic La species without ancillary ligands effectively catalyze the isomerization of the substrate to \(\text{(E)-2,2-dimethyl-3-pentenylamine}\).

Introduction

Homoleptic trialkyl complexes of the type \(\text{M}(\text{CH}_2\text{SiMe}_3)_3-(\text{THF})_n\) \((n = 2, 3)\) of the group 3 metals and lanthanides are valuable starting materials for organo-rare-earth-metal chemistry.\(^2\) They are readily prepared from the corresponding metal trialkyls and are sufficiently thermally stable to be handled conveniently. Unfortunately, they are only available for the rare-earth metals in the small to medium size range (Sc, Y, and Ln = Lu – Dy). For the larger lanthanide metals, such as Nd and La, salt-free neutral species of this type are only available for very large alkyl groups, in particular \(\text{CH}(\text{SiMe}_3)_3\),\(^3\) which hamper further reactivity. Recently we showed that for these metal species \((L)\text{Ln}(\text{CH}_2\text{SiMe}_3)_3\), species \((L = \text{nonanionic ligand})\) can be obtained in moderate yield from in situ procedures, reacting Ln trihalides with 3 equiv of Me\(_2\text{SiCH}_2\text{Li}\) followed by addition of LH.\(^4\) Nevertheless, readily accessible yet reactive homoleptic trialkyl complexes of these metals would be very useful.\(^5\) Early attempts to prepare homoleptic tribenzyl complexes of Nd\(^6\) and La\(^7\) were reported but were inconclusive as to the existence of these species. For the former, decomposition to the alkylidene [PhCH\(_2\)Nd=CH][Ph] was proposed, whereas for the latter decomposition to form [PhCH\(_2\)La(H)OCH=CH\(_2\)] was suggested. Very recently, Harder reported the synthesis of rare-earth tribenzyl complexes bearing intramolecularly coordinating groups on the aryl moiety.\(^8\) Here we describe a straightforward synthesis of the neutral, salt-free lanthanum tribenzyl complexes La(CH\(_2\text{Ph})_3(\text{THF})_3\) and La(CH\(_2\text{Ph}-4\text{-Me})_3(\text{THF})_3\). With several examples, their use as precursors to other neutral and cationic lanthanum benzyl complexes is illustrated. Their catalytic performance in ethylene polymerization and intramolecular hydroamination/cyclization was also briefly explored.

Results and Discussion

Synthesis and Characterization of Tribenzyllanthanum Complexes. Reaction of \(\text{LaBr}_3(\text{THF})_4\) with 3 equiv of the potassium benzylls K\(_2\text{CH}_2\text{C}_6\text{H}_4-4-\text{R}\) \((\text{R} = \text{H, Me})\) in THF solvent, followed by centrifugation and decantation (to remove (8) Harder, S. Organometallics 2005, 24, 373.


LaBr₃(THF)_₄ + 3 KCH₂C₆H₄-4-R
(R = H, Me)

La(CH₂Ph)₃(THF)₃ (1a)

La(CH₂Ph)₃(THF)₃ (1b)

Figure 1. Molecular structure of [La(CH₂Ph)₃(THF)₃] (1a), with 50% probability ellipsoids. Selected interatomic distances (Å) and angles (deg): La–C(1) = 2.649(2), La–C(2) = 2.649(2), La–C(8) = 2.694(2), La–C(9) = 2.972(2), La–C(15) = 2.639(2), La–C(16) = 2.994(2), La–O(1) = 2.6779(16), La–O(2) = 2.6630(15), La–O(3) = 2.6497(16), La–C(1)–C(2) = 88.05(13), La–C(8)–C(9) = 88.09(13), La–C(15)–C(16) = 89.53(14), O(1)–La–O(2) = 72.90(5), O(1)–La–O(3) = 74.59(5), O(2)–La–O(3) = 74.06(5).

The amido ArN=CPhNHAr (Ar = 2,6-Pr₂C₆H₄) in THF solvent generates cleanly the monoamidinate dibenzyl complex [PbC(NAr₂)₂][La(CH₂C₆H₄-R)(THF)]₃ (1b) with elimination of 1 equiv of toluene or p-xylene, respectively (Scheme 2). A preparative-scale reaction of 1a with ArN=CPhNHAr, followed by crystallization from hexane/THF, afforded [PhC(NAr₂)₂][La(CH₂C₆H₄)(THF)] (2) in 70% isolated yield. A crystal structure determination of 2 (Figure 3; crystal data and collection parameters are given in Table 4) shows that in this complex one of the two remaining benzyl groups is again η²-bound to the metal, with a La–C(39)–C(40) angle of 83.3(1)°. The other, with a La–C(32)–C(33) angle of 87.0(3)°, has a phenyl group that is significantly tilted, suggesting an η¹-like bonding, with a short La–C₆ distance (La–C(34)) of 3.030(3) Å. Such an η¹ coordination mode has been observed before in lanthanide metallocene benzyl complexes.12 Probably in response to the η¹ bonding of the benzyl groups, complex 2 only contains a single coordinated THF molecule, whereas two were found in the related bis(trimethylsilyl)methyl complex [PhC(NAr₂)₂][La(CH₂SiMe₃)₂(THF)]₂.²b The room-temperature ¹³C NMR spectrum of 2 in CD₃Cl shows a single resonance for the La–CH₂ groups at δ 69.5 ppm (¹JC₂ = 136 Hz). In THF-d₅ solvent, this resonance is observed at δ 71.1 ppm (¹JC₂ = 131 Hz). The slight, but significant, reduction of the latter ¹JC₂ coupling constant relative to that in benzene may indicate (reversible) binding of an additional THF molecule in this solvent.

PhC(NAr₂)₂[La(CH₂C₆H₄-R)(THF)]₃ (3) (Scheme 2), obtained by crystallization from THF/hexane as red-orange crystals in 52% yield. The room-temperature solution NMR spectra of 3 are

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simple, indicative of a symmetrically averaged structure of the La-tetrabenzy1 anion. In a comparison of the spectra of 1b and 3, the benzyl methylene 1H and 13C NMR resonances in 3 are shifted upfield (δ 1.11 and 62.0 ppm, respectively, vs δ 1.36 and 66.0 ppm in 1b). The 1JCH coupling constant in 3 of 139 Hz is significantly larger than the 131 Hz for 1b.

Generation and Structure of Cationic Lanthanum Benzyl Complexes. Complexes 1a and 1b can be used as precursors to cationic lanthanum benzyl complexes. Reactions of the tribenzyl complexes 1a and 1b with 1 or 2 equiv of the Brønsted acid [PhNMe2H][B(C6F5)4] in THF-d8 solvent generate cleanly (as seen by NMR spectroscopy) the ionic species [La(CH2C6H4-R)2(THF-d8)n][B(C6F5)4] (R = H (4a), Me (4b)) and [La(CH2C6H4-R)(THF-d8)m][B(C6F5)4]2 (R = H (5a), Me (5b)), respectively, accompanied by liberation of toluene or p-xylene and free PhNMe2.

Compounds 4 and 5 are related to the mono- and dicationic alkyl species [Ln(CH2SiMe3)2(THF)]+ and [Ln(CH2SiMe3)- (THF)2]2+ of the smaller rare-earth metals (Ln = Sc, Y, Tb–Lu) reported by Okuda et al. The 13C NMR spectrum of 4a shows a single resonance for the La–CH2 groups at δ 71.3 ppm (JCH = 134 Hz). In the dication 5a, the corresponding resonance is found at δ 78.9 ppm (JCH = 130 Hz).

The couple 4b/5b follows the same trend in chemical shift for the benzyl methylene groups. The La–CH2 13C NMR resonances move downfield from 70.6 ppm (JCH = 134 Hz) in
the monocation 4b to 78.0 ppm ($J_{CH} = 130$ Hz) for the dication 5b. This trend is also observed in the respective $^1$H NMR spectra. The triad from the neutral 1a over the monocation 4a to the dication 5a displays the La–CH$_2$ resonances at $\delta$ 1.41, 1.74, and 1.85 ppm, respectively, in response to the increased positive charge at the metal center. For the p-tolyl species these chemical shifts are observed from the neutral complex 1b (1.36 ppm) via the monocation 4b (1.63 ppm) to the dication 5b (1.79 ppm). Reaction of 1a or 1b with 3 equiv of [HNMe$_2$H]-[B(C$_6$F$_5$)$_4$] in THF-d$_8$ appears to generate the alkyl-free species [La(THF)$_3$]$^{3+}$[B(C$_6$F$_5$)$_4$]$^{3-}$. This is based on the disappearance of all resonances of lanthanum-bound benzyl groups and the emergence of 3 equiv of either toluene or p-xylene, as seen by $^1$H NMR spectroscopy. Reaction of the dibenzyl complex 2 with [HNMe$_2$H][B(C$_6$F$_5$)$_4$] in THF-d$_8$ solvent cleanly generates the ionic species [[PhC(NAr)$_2$][La(CH$_2$Ph)(THF-d$_8$)][B(C$_6$F$_5$)$_4$] (6). Its $^{13}$C NMR spectrum shows the remaining benzyl methylene resonance at $\delta$ 78.2 ppm ($J_{CH} = 130$ Hz).

To facilitate the crystallization of the ionic lanthanum benzyl species to allow single-crystal structure determinations, the corresponding tetraphenylborate salts were prepared using the Bronsted acid [HNMe$_2$Ph][BPh$_4$]. Reactions of the tribenzyl complexes 1a,b with 1 equiv of [HNMe$_2$Ph][BPh$_4$] in THF solvent at ambient temperature produce clear solutions. Cooling these solutions to $-30$ °C afforded the ion pairs [La(THF)$_2$][B(C$_6$H$_5$)$_4$] (R = H (4a'), Me (4b')) in about 70% yield as plate-shaped crystals. Similarly, reaction of 1b with 2 equiv of [HNMe$_2$Ph][BPh$_4$] in THF, followed by cooling to $-30$ °C, afforded crystals of 5b' in 61% yield (Scheme 3). The corresponding parent benzyl dication 5a' appears to be much less soluble and precipitates as an oil that gradually solidified upon rinsing with hexanes.

The molecular structure of the cation of 4a', [La(CH$_2$Ph)$_2$](THF)$_4$]$,^+$, is shown in Figure 5 (crystal data and collection parameters are given in Table 4). Three THF molecules (O11–O13) coordinate to the lanthanum center in a facial arrangement with La–O distances of 2.579(2)–2.589(2) Å. These La–O bond lengths are much shorter than those in the neutral precursor

![Molecular structure of [La(CH$_2$Ph)$_2$](THF)$_4$][B(C$_6$H$_5$)$_4$] (4a'), with 50% probability ellipsoids. Selected interatomic distances (Å) and angles (deg): La(1)–C(18) = 2.649(4), La(1)–C(19) = 2.936(3), La(1)–C(110) = 3.052(2), La(1)–C(11) = 2.592(2), La(1)–C(12) = 2.595(2), La(1)–C(17) = 2.057(2), La(1)–O(11) = 2.589(2), La(1)–O(12) = 2.584(2), La(1)–O(13) = 2.579(2), La(1)–O(14) = 2.554(2); La(1)–C(11)–C(12) = 89.8(2), La(1)–C(18)–C(19) = 86.7(2), O(11)–La(1)–O(12) = 74.78(7), O(11)–La(1)–O(13) = 74.63(7), O(12)–La(1)–O(13) = 79.57(7).]

1a (average La–O = 2.664 Å). The fourth THF molecule is located at the other side of the cation and essentially replaces the abstracted benzyl group. The remaining two benzyl ligands are tilted to suggest an $\eta^1$ bonding mode. The two short La–C(ortho) distances are 3.057(2) and 3.052(2) Å for C(17) and C(110), respectively. The La–CH$_2$ bond distances in 4a' are 2.649(4) and 2.592(2) Å are somewhat longer than those in the seven-coordinate complexes [[P(C$_6$H$_5$)$_2$-2-HNMe$_2$][(CH(SiMe$_3$)$_2$)-(SiMe$_3$CH$_2$)][La(THF)$_3$][BPh$_4$]$_{13}$ and [[PhC(NAr)$_2$][La(CH$_2$SiMe$_3$)][THF]]$_2$[BPh$_4$].$^{ab}$ where the La–CH$_3$ bond distances are 2.485(9) and 2.510(4) Å, respectively. The multihapto bonding
Figure 6. Molecular structure of [La(CH2Ph-4Me)(THF)6]2− ([B(C6F5)4]2) with 50% probability ellipsoids. Selected interatomic distances (Å) and angles (deg): La(1)−C(11) = 2.534(3), La(1)−C(12) = 2.968(3), La(1)−O(17) = 3.136(3), La(1)−O(11) = 2.6835(19), La(1)−O(12) = 2.588(2), La(1)−O(13) = 2.595(4)(19), La(1)−O(14) = 2.5632(19), La(1)−O(15) = 2.5754(19), La(1)−O(16) = 2.5127(19), La(1)−C(11)−C(12) = 92.27(17), O(11)−La(1)−O(12) = 69.17(6), O(11)−La(1)−O(16) = 71.58(6), O(12)−La(1)−O(13) = 77.39(6), O(13)−La(1)−O(15) = 73.90(6), O(15)−La(1)−O(16) = 73.66(6), O(14)−La(1)−C(11) = 150.84(8), O(14)−La(1)−C(12) = 163.45(8).

The overall geometry of the cation in 4a′ does not distort the overall geometry of the cation relative to that in the six-coordinate yttrium dialkyl species [Y(CH2SiMe3)2(THF)4]+, which is closer to a regular octahedron.1b

Whereas the overall geometry of the cation in 4a′ is still closely related to that in the parent tribenzyl 1a, this is no longer the case for the dication in 5b′. The molecular structure of this cation is shown in Figure 6 (crystal data and collection parameters are given in Table 4) and can be described as a capped pentagonal bipyramidal. The structure of 5b′ is related to that of the dicaticonic yttrium complex [YMe(THF)6][BPh4]2′ reported by Okuda et al.,1h where the alkyl group is located in the apical position of the pentagonal bipyramid. The iso6 carbon atom C(12) of the benzyl group and O(14) occupy the axial positions and the benzyl methylene carbon atom C(12) then caps the edge of two trigonal planes defined by C(12)−O(12)−O(13) and C(12)−O(13)−O(15). The benzyl ligand is bound essentially in an η1 fashion to the lanthanum center; the shortest distance to one of the aromatic ortho carbon atoms is 3.136(8) Å. The lanthanum−methylene carbon bond distance of 2.534(3) Å is the shortest La−C bond length in the series studied here. As in the structure of 4a′, there are no obvious interactions between the dicaticonic lanthanum center and the two tripehetylborate anions in the lattice.

**Catalysis Studies of Neutral and Cationic Lanthanum Benzyl Complexes.** (a) Ethylene Polymerization. While caticonic alkyl complexes of the transition metals have long been known as highly active catalysts for olefin polymerization, related species of the rare-earth metals have only recently become available.14 In the few comparative studies on olefin polymerization by cationic lanthanide species that include lanthanum derivatives, these showed very poor activities compared to the intermediate size metals.3b,15 We have examined the new lanthanum benzyl compounds for their activity in ethylene polymerization. Caticonic and dicaticionic catalysts were generated in toluene solvent by reacting complex 1b (which is more soluble than 1a) with 1 or 2 equiv of the Bronsted acid [PhNMe2H][B(C6F5)4]. Similarly, the caticonic amidinate benzyl species was generated from 2 and 1 equiv of [PhNMe2H][B(C6F5)4]. All experiments were performed in the presence of TiBAO (isobutylalumoxane, La/Al = 1/10) at 50 °C in toluene solvent. The results are given in Table 1. The neutral complexes 1b and 2, under the given conditions, were themselves inactive for ethene polymerization.

The caticonic species derived from 1b show low activities, but the monocaticonic species is clearly the more active of the two.16 The activity of the caticonic amidinate benzyl species is higher than that observed previously with the cation generated from [PhCNar2]La(CH2SiMe3)2(THF)2b17 which may be associated with the coordination of an additional THF molecule in the latter. The polydispersities of the polymers obtained are broad, an indication that the ethylene polymerization behavior of these catalysts with very large metal centers is not straightforward.

(b) Intramolecular Hydroamination/Cyclization. Another reaction that can be efficiently catalyzed by organolanthanide catalysts is the intramolecular hydroamination/cyclization of aminomethanes.17−19 Although for catalytic olefin polymerization it has been well established that caticonic catalysts generally show higher activities than related neutral species, this situation is not as clear-cut for the intramolecular hydroamination/cyclization reaction. The few comparative studies that have been carried out suggest that the relative reactivity of caticonic catalysts relative to their neutral congeners is highly dependent on the ancillary ligand system.20,21 We have compared the activities of the various lanthanum benzyl species reported here in the hydroamination/cyclization of the commonly used standard substrate 2,2-dimethyl-4-pentenylamine to give 2-methyl-4,4-dimethylpyrrolidine. The results are given in Table 2. All caticonic species were generated in situ from the listed compounds by reaction with [PhNMe2H][B(C6F5)4].

A comparison of the neutral vs caticonic amidinate lanthanum benzyl species shows that both reactions are zeroth order in substrate (characteristic of rate-determining intramolecular alkyltransfer).

### Table 1. Catalytic Ethylene Polymerization Experiments

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<th>Mw/Mn</th>
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<td>89.5</td>
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*Conditions: toluene solvent (30 mL), 50 °C, 10 μmol of La, 5 bar of ethylene pressure, 15 min run time. A = 100 μmol of Al, B = 10 μmol of [PhNMe2H][B(C6F5)4].

15 Although for catalytic olefin polymerization


ene insertion into the metal—amide bond; Scheme 4). The cationic species is nearly 2 orders of magnitude slower than the neutral catalyst. This observation is similar to that made by us on the related amidinate ([trimethylsilyl)methyl]yttrium, the neutral catalyst. This observation is similar to that made by us on the related amidinate ([trimethylsilyl)methyl]yttrium system. Nevertheless, although the Y and La neutral catalysts display similar activities, the cationic La catalyst is 3 times faster than its analogue with the smaller metal Y.

Although the activity of the neutral tribenzyl 1b was difficult to quantify due to its poor solubility,22 the mono- and dicationic derivatives showed good activities (comparable to that of the neutral amidinate catalyst). The monocationic system is nearly twice as active as the dicationic derivative.

As the tribenzyl complex 1b contains three coordinated THF molecules, we attempted to use the anionic tetrabenzy1 complex 3 to generate unsolvated lanthanum benzyl cations by reaction with ammonium salts. These molecules containing active protons can provide derivatives with anionic ancillary ligands, and solvated cationic benzyl derivatives can be obtained by reaction with ammonium salts. These lanthanum benzyl species are active for some of the best known reactions catalyzed by rare-earth-metal compounds (ethene polymerization, hydroamination/cyclization).

As the synthesis of salt-free rare-earth organometallics is usually most problematic for the largest metal, lanthanum, it is likely that related tribenzyl species will also be readily available for the smaller sized rare-earth metals. They should provide a convenient starting point for studies addressing the effect of rare-earth-metal ionic radius on reactivity.

Experimental Section

General Considerations. All experiments were carried out under an inert atmosphere of purified N2 using standard Schlenk and glovebox techniques, unless mentioned otherwise. Toluene, pentane, diethyl ether, and THF were distilled from Na or Na/K alloy before use or purified by percolation under a nitrogen atmosphere over columns of alumina, molecular sieves, and supported copper oxygen scavenger (BASF R3-11). Benzene-d6 and THF-d6 were dried over Na/K alloy and vacuum-transferred before use. Bromobenzene-d5 was degassed and dried over CaH2. KCH2Ph-4-R (R = H, Me) and [PhC(N-2,6-Pr3 C6 H3 )2]H24 were prepared according to published procedures. [PhNMMe2][B(C6F5)4] (Strem) was used as purchased. TIBAO was prepared by careful partial hydrolysis of Bu3Al (Witco) in toluene. For the polymerization experiments, the toluene solvent (Aldrich anhydrous, 99.5%) as well as the ethene (AGA, polymer grade) were passed over columns of oxygen scavenger (BASF R3-11) and molecular sieves (4 Å) before being passed to the reactor. NMR spectra were recorded on Varian Unity 500, VXR 300, and Gemini 200 spectrometers. Gel permeation chromatography (GPC) analysis of the polyethylene was carried out by A. Jekel (University of Groningen) on a Polymer Laboratories Ltd. (PL-GPC210) chromatograph using 1,2,4-trichlorobenzene (TCB) as the mobile phase at 150 °C. Elemental analyses were performed at the Microanalytical Department of H. Kolbe (Mülheim an der Ruhr).

Synthesis of K(CH2Ph-4-Me). To a suspension of potassium tert-butoxide (5.6 g, 50 mmol) in xylene (100 mL) and hexanes (100 mL) was added 4-n-butyl lithium (20 mL, 2.5 M solution in hexanes). The reaction mixture turned orange. The first order in substrate and proceeds, under the chosen conditions, essentially to completion in 2 h (Table 3). Isomerization of this and related aminoalkene substrates was observed previously as a side reaction in the nBuLi-catalyzed hydroamination/cyclization and attributed to allylic deprotonation/reprotonation.23 In case of the La polycationic species, the strong Lewis acidity of the metal center and the presence of amines (substrate, product, and PhNMMe2) in the reaction mixture may combine in promoting this isomerization.

Conclusions

The lanthanum tribenzyl complexes 1 provide easily prepared neutral and salt-free homoleptic trialkyl complexes that are sufficiently reactive to serve as convenient starting materials for organolanthanum chemistry. Reactions with organic molecules containing active protons can provide derivatives with anionic ancillary ligands, and solvated cationic benzyl derivatives can be obtained by reaction with ammonium salts. These lanthanum benzyl species are active for some of the best known reactions catalyzed by rare-earth-metal compounds (ethene polymerization, hydroamination/cyclization).

<table>
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<th>time/h</th>
<th>conversion/%</th>
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<tr>
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<td>31</td>
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*e Conditions: C6D5Br solvent (total volume 0.5 mL), 50 °C, 10 μmol of catalyst and [PhNMMe2][B(C6F5)4] (B) activator where appropriate, 1.0 mmol of substrate. *Determined by 1H NMR. * Over the first 50% conversion. * In C6D6 solvent. * Not determined, due to the poor solubility of the catalyst.

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Scheme 4

**Scheme 4**

![Scheme 4](image)

**Table 2. Catalytic Hydroamination/Cyclization of 2,2-Dimethyl-4-pentenylamine by Neutral and Cationic Lanthanum Benzyl Complexes**

<table>
<thead>
<tr>
<th>catalyst</th>
<th>time/h</th>
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<td>1b</td>
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(22) Tsurugi, H.; Bambirra, S.; Hessen, B. Unpublished results. When [Y(CH2SiMe3)3][THF]2 was exposed to solutions of the substrate 2,2-dimethyl-4-pentenylamine in C6D6, cloudy suspensions were obtained, which (remarkably) give clear solutions when [PhNMMe2][B(C6F5)4] was added.

reaction mixture was stirred for 4 h at room temperature. After filtration, the orange solid was washed by continuous extraction with hot hexanes (LiOBru removal) and dried under vacuum, yielding 6.5 g (46 mmol, 93%) of KCH₂Ph-4-Me as a red, pyrophoric solid. ³H NMR (300 MHz, THF-d₈, 20 °C): δ 5.97 (d, 1JHH = 7.5 Hz, 2H, Ar-H), 3.62 (s, 3 H, Me). ¹³C NMR (75.4 MHz, THF-d₈, 20 °C): δ 154.5 (Ar Cipso), 131.0 (d, 1JCH = 153.6 Hz, Ar CH), 122.8 (d, 1JCH = 152.8 Hz, Bz CH), 117.6 (d, 1JCH = 157.8 Hz, Bz CH), 71.1 (tt, 1JCH = 130.6 Hz, LaCH₂), 30.2 (d, 1JCH = 126.6 Hz, Pr Me), 26.8 (qu, 1JCH = 125.0 Hz, Pr Me), 24.7 (qu, 1JCH = 124.8 Hz, Pr Me).

(b) Preparative Scale. Solid 1a (0.3 g, 0.50 mmol) and [PhC(N2,6-Pr₂C₆H₄)₂]Li (0.22 g, 0.50 mmol) were mixed and dissolved in THF (30 mL). The solution was stirred at ambient temperature for 1 h, after which the volatiles were removed in vacuo. The residue was dissolved in hexanes (5 mL) with some added THF (ca. 1.0 mL). Cooling to ~30 °C afforded the crystalline title compound (0.29 g, 0.35 mmol, 70%). ³H NMR (300 MHz, CD₂Cl₂, 20 °C): δ 7.19–7.15 (m, 2 H, Ar H), 7.03 (m, 5 H, Ph), 6.96 (tt, 3JHH = 7.2 Hz, 4 H, Bz m-H), 6.69–6.66 (m, 4 H, Ar H), 6.53 (d, 1JHH = 6.9 Hz, 2 H, Bz p-H), 6.20 (sept, 3JHH = 6.7 Hz, 4 H, CMe₂), 3.06 (m, 4 H, Ar CH₂), 2.34 (s, 4 H, LaCH₂). 1.32 (d, 1JHH = 6.7 Hz, 12 H, Pr Me), 1.12 (m, 4 H ß-THF), 1.03 (d, 1JHH = 6.7 Hz, 12 H, Pr Me). ¹³C NMR (75.4 MHz, CD₂Cl₂, 20 °C): δ 173.2 (NCCN), 150.2 (Bz C), 144.8 (Ph C), 141.5 (Ar C), 132.9 (Ar C), 131.9 (d, 1JHH = 156.2 Hz, Bz CH), 130.6 (d, 1JHH = 160.3 Hz, Ar CH), 128.9 (d, 1JHH = 154.1 Hz, Ph CH), 127.0 (d, 1JHH = 152.1 Hz, Ph CH), 124.1 (d, 1JHH = 160.4 Hz, Ph CH), 123.8 (d, 1JHH = 156.2 Hz, Ar CH), 121.0 (d, 1JHH = 152.1 Hz, Bz CH), 116.2 (d, 1JHH = 160.3 Hz, Bz CH), 69.4 (t, 1JCH = 135.8 Hz, LaCH₂), 68.7 (t, 1JCH = 147.6 Hz, ß-THF), 28.8 (d, 1JCH = 125.8 Hz, Pr CH), 25.5 (qu, 1JCH = 125.2 Hz, Pr Me), 25.4 (qu, 1JCH = 132.2 Hz, ß-THF), 23.5 (qu, 1JCH = 125.2 Hz, Pr Me). Anal. Calc. for Ca₂H₆La₂O₄ (mol wt 832.94): C, 70.66; H, 7.38; N, 3.36. Found: C, 70.48; H, 7.32; N, 3.24.

Reactions of 1b with ArN=C=PhNH₂. Solid 1b (670 mg, 1.00 mmol) and [PhC(N2,6-Pr₂C₆H₄)₂]Li (440 mg, 1.00 mmol) were mixed together and dissolved in 0.6 mL of THF-d₈. NMR spectroscopy showed clean conversion to [(PhC(NAr)₂La(CH₂Ph)₃(THF)] and 1 equiv of p-xylene. ¹³C NMR (300 MHz, THF-d₈, 20 °C): δ 6.94 (m, 2 H, Ar H), 6.90 (m, 5 H, Ph), 6.83 (m, 4 H, Ar H), 6.75 (d, 1JHH = 7.5 Hz, 4 H, Bz m-H), 6.30 (d, 1JHH = 7.5 Hz, 4 H, Bz o-H), 3.42 (sept, 3JHH = 6.6 Hz, 4 H, CMe₂), 1.79 (s, 4 H, LaCH₂), 1.18 (d, 1JHH = 6.6 Hz, 12 H, Pr Me), 0.85 (d, 1JHH = 6.6 Hz, 12 H, Pr Me). ¹³C NMR (125.7 MHz, THF-d₈, 20 °C): δ 174.4 (NCCN), 149.5 (Bz C), 146.7 (Ph C), 143.2 (Ar C), 134.7 (Ar C), 132.9 (d, 1JHH = 160.0 Hz, Bz CH), 130.3 (d, 1JHH = 156.2 Hz, Ar CH), 128.3 (d, 1JHH = 158.2 Hz, Ph CH), 126.3 (d, 1JHH = 157.5 Hz, Ph CH), 125.0 (d, 1JHH = 158.7 Hz, Ph CH), 125.1 (d, 1JHH = 151.4 Hz, Ar CH), 123.0 (d, 1JHH = 152.8 Hz, Bz CH), 69.8 (t, 1JCH = 130.5 Hz, LaCH₂), 30.1 (d, 1JCH = 126.6 Hz, Pr CH), 26.6 (qu, 1JCH = 125.0 Hz, Pr Me), 24.8 (qu, 1JCH = 124.8 Hz, Pr Me), 21.6 (qu, 1JCH = 126.8 Hz, Bz Me).

Synthesis of [La(CH₂Ph)₃(THF)]₂. Solid 1b (670 mg, 1.00 mmol) and LiCH₂Ph-4-Me (112 mg, 1.00 mmol) were mixed and THF (5 mL) was added with stirring. The red solution was stirred for 1 h, after which the solution was layered with hexanes (30 mL). Cooling to ~30 °C yielded the title compound as red-orange crystals (450 mg, 52%). ¹³C NMR (300 MHz, THF-d₈, 20 °C): δ 6.51 (d, 8H, 1JHH = 7.9 Hz, Ar m-H), 5.70 (d, 3JHH = 7.9 Hz, 8H, Ar o-H), 2.06 (s, 12 H, Me), 1.11 (s, 8H, LaCH₂). ¹³C NMR (75.4 MHz, THF-d₈, 20 °C): δ 150.0 (Ar C), 132.7 (d, 1JCH = 152.0 Hz, Ar CH), 121.9 (Ar C), 120.7 (d, 1JCH = 153.0 Hz, Ar CH), 62.0 (t, 1JCH = 139.6 Hz, LaCH₂), 21.8 (qu, 1JCH = 124.8 Hz, Pr Me).
125.5 Hz, Ar Me). Anal. Calcd for C₆₀H₇₈Br₈O₅ (mol wt 854.91):

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Reactions of 1a with 1 Equiv of [HNMe₂Ph][B(C₆F₅)₄]:

- Solid [La(CH₂Ph)₃(THF)₃] (31 mg, 50.0 μmol) and [HNMe₂Ph][B(C₆F₅)₄] (40 mg, 50.0 μmol) were mixed, and THF-d₅ (0.6 mL) was added. The obtained solution was transferred to an NMR tube and analyzed by NMR spectroscopy, which showed full conversion to the ionic species [La(CH₂Ph)₃(THF)₃][B(C₆F₅)₄] (4a).

- Reaction of 1a with 1 Equiv of [HNMe₂Ph][B(C₆F₅)₄]. Solid [La(CH₂Ph)₃(THF)₃] (31 mg, 50.0 μmol) and [HNMe₂Ph][B(C₆F₅)₄] (80 mg, 100.0 μmol) were mixed, and THF-d₅ (0.6 mL) was added. The obtained solution was transferred to an NMR tube and analyzed by NMR spectroscopy, which showed full conversion to the ionic species [La(CH₂Ph)₃(THF)₃][B(C₆F₅)₄] (4a).

Synthesis of [La(CH₂Ph)₃(THF)][B(C₆F₅)₄]:

- THF (0.5 mL) was added to a mixture of 63 mg (100 μmol) of 1a and 44 mg (100 μmol) of [HNMe₂Ph][B(C₆F₅)₄]. The resulting yellow solution was cooled to −30°C for 3 days, producing yellow crystals of the title compound (69 mg, 69 μmol, 75%).

- THF (0.5 mL) was added to a mixture of 63 mg (100 μmol) of 1a and 44 mg (100 μmol) of [HNMe₂Ph][B(C₆F₅)₄]. The resulting yellow solution was cooled to −30°C for 3 days, producing yellow crystals of the title compound (69 mg, 69 μmol, 75%).
spectroscopy, which showed full conversion to the ionogenic species [La(CH2Ph-4-Me)(THF-d8)]2[BF4]d. The resulting light yellow solution was cooled to −30 °C for 3 days, producing yellowish crystals of 4b. 1H NMR (300 MHz, THF-d8, 20 °C): δ 6.78 (d, JHH = 7.3 Hz, 2 H, Ar H), 6.18 (d, JHH = 7.7 Hz, 2 H, Ar o-H), 2.14 (s, 6 H, Me), 1.59 (s, 4 H, LaCH2). 13C NMR (75.4 MHz, THF-d8, 20 °C): δ 149.2 (Ar CH), 132.8 (Ar Ce), 78.0 (t, 1JCH = 129.7 Hz, LaCH2), 21.1 (q, 1JCH = 126.6 Hz, Me).

**Synthesis of [La(CH2Ph-4-Me)(THF)]2[B(C6F5)4] (4b)**. THF (0.5 mL) was added to a mixture of 67 mg (100 μmol) of 1b and 44 mg (100 μmol) of [HNMe2Ph][BPh4]. The resulting light yellow solution was cooled to −30 °C for 3 days, producing yellowish crystals of 4b. 1H NMR (75.4 MHz, THF-d8, 20 °C): δ 6.87 (d, JHH = 7.5 Hz, 4 H, Ar H), 6.18 (d, JHH = 7.7 Hz, 2 H, Ar o-H), 2.14 (s, 6 H, Me), 1.59 (s, 4 H, LaCH2). 13C NMR (75.4 MHz, THF-d8, 20 °C): δ 166.1 (q, 1JC = 48.7 Hz, BPh4 Cipso), 148.5 (Ar Cipso), 133.5 (d, JCH = 155.2 Hz, Ar m-C), 128.9 (Ar CMe), 124.0 (d, JCH = 153.0 Hz, Ar o-C), 70.4 (t, 1JCH = 131.0 Hz, LaCH2), 21.6 (q, 1JCH = 125.0 Hz, Me). Anal. Calc'd for C60H78BLaO5 (mol wt 1028.99): C, 70.04; H, 7.64.

**Procedure for Ethylene Polymerization**. Polymerizations were performed in a 50 mL glass mini-clave (Büchi AG, Switzerland) with a magnetic stirrer. Before use, the reactor was dried at 80 °C in a vacuum oven for at least 2 h. In a drybox, the miniclave was charged with 1b or 2 (10 μmol), [HNMe2Ph][B(C6F5)4] (where appropriate 10 μmol or 20 μmol), 30 mL of toluene, and TiBAO (100 μmol of Al). The reactor was taken out of the drybox, heated at 50 °C in an oil bath, and pressurized with 5 bar of ethylene. The pressure was kept constant during the reaction by replenishing the flow. The reaction mixture was stirred for 15 min and then vented. The polymer was repeatedly rinsed with acidified methanol and dried in a vacuum oven.

**Procedure for Intramolecular Hydroamination/Cyclization**. All samples for the hydroamination/cyclization reactions were prepared in a N2-filled glovebox. Typically, an NMR tube equipped with a Teflon (Young) valve was charged with the (pre)catalyst (10 μmol), the activator [HNMe2Ph][B(C6F5)4] (10 μmol, where appropriate), ferrocene (as internal standard, 100 μmol), and the aminolane substrate 2,2-dimethyl-4-pentenylamine (1000 μmol) dissolved in C6D6 or C6D6Br (total volume 0.5 mL). The reactions were followed in time, either directly in the NMR spectrometer (thermostated at 50 °C unless mentioned otherwise; measurements taken in an array of regular intervals) or warmed in an electric oven at 50 °C and transferred to the spectrometer periodically. Conversions were determined by 1H NMR following the decrease of the olefinic resonances of the substrate relative to the ferrocene internal standard (single-pulse spectra). The product 2-methyl-4,4-dimethylpyrrolidine was identified by 1H NMR and GC-MS in comparison with literature data.