Lanthanum Tribenzyl Complexes as Convenient Starting Materials for Organolanthanum Chemistry

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Simple tribenzyl complexes of lanthanum, [La($CH_2C_6H_4$-4-R)$_3$(THF)$_3$] (R = H (**1a**), Me (**1b**)), were prepared in a remarkably straightforward fashion from $LaBr_3(THF)_4$ and potassium benzyl reagents. Single-crystal X-ray diffraction revealed a fac arrangement of the three THF ligands and η^2 binding of the benzyl groups. These compounds are convenient precursors to other organolanthanum complexes. Reaction of **1a** with the amidine ArN═CPhNHAr (Ar = 2,6-$Pr^i_2C_6H_3$) affords the corresponding mono(amidinate) dibenzyl derivative **2**. Complex **1b** reacts with $LiCH_2C_6H_4$-4-Me to give the THF-free anion [La($CH_2C_6H_4$-4-Me)$_4$]$^-$ (**3**). Reactions of **1** with 1 or 2 equiv of [$PhNMe_2H$][B(C_6X_5)$_4$] (X = H, F) generate the corresponding mono- and dicationic benzyl species [La($CH_2C_6H_4$-4-R)$_2$(THF)$_4$]$^+$ (**4**) and [La($CH_2C_6H_4$-4-R)(THF)$_6$]$^{2+}$ (**5**), which were structurally characterized. Scouting ethylene polymerization experiments indicate that these species are only modestly 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 (*E*)-2,2-dimethyl-3-pentenylamine.

Introduction

Homoleptic trialkyl complexes of the type M(CH_2SiMe_3)$_3$(THF)$_n$ (n = 2, 3) of the group 3 metals and lanthanides[1] are valuable starting materials for organo-rare-earth-metal chemistry.[2] They are readily prepared from the corresponding metal trihalides 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 CH($SiMe_3$)$_2$,[3] which hamper further reactivity. Recently we showed that for these metals various (L)Ln(CH_2SiMe_3)$_2$ species (L = monoanionic ligand) can be obtained in moderate yield from in situ procedures, reacting Ln trihalides with 3 equiv of Me_3SiCH_2Li 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 [$PhCH_2Nd$═CHPh] was proposed, whereas for the latter decomposition to form [$PhCH_2La$(H)OCH═CH_2-(THF)$_2$] 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_2Ph)$_3$(THF)$_3$ and La(CH_2-Ph-4-Me)$_3$(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 $LaBr_3(THF)_4$ with 3 equiv of the potassium benzyls $KCH_2C_6H_4$-4-R (R = H, Me)[9] in THF solvent, followed by centrifugation and decantation (to remove

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[3] (a) Ln[CH($SiMe_3$)$_2$]$_3$ (Ln = La, Sm): Hitchcock, P. B.; Lappert, M. F.; Smith, R. G.; Bartlett, R. A.; Power, P. P. *J. Chem. Soc. Chem. Commun.* **1988**, 1007. (b) Ln[CH($SiMe_3$)$_2$]$_3$ (Ln = Y, Lu): Schaverien, C. J.; Orpen, A. G. *Inorg. Chem.* **1991**, *30*, 4968.

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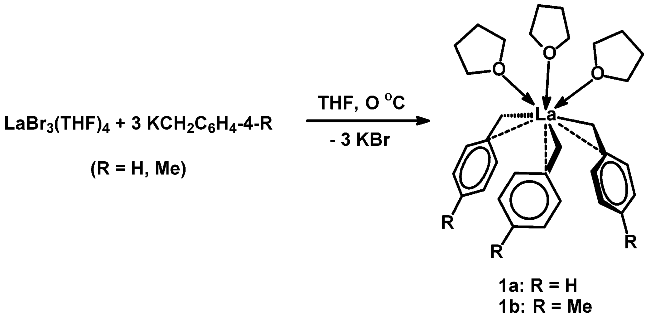
10.1021/om060262v CCC: $33.50

Scheme 1



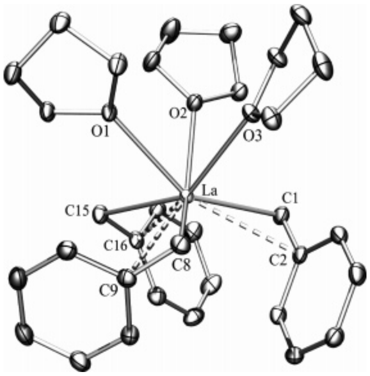


Figure 1. Molecular structure of $[La(CH_2Ph)_3(THF)_3]$ (**1a**), with 50% probability ellipsoids. Selected interatomic distances (Å) and angles (deg): La−C(1) = 2.648(2), La−C(2) = 2.968(2), La−C(8) = 2.649(2), La−C(9) = 2.972(2), La−C(15) = 2.639(2), La−C(16) = 2.994(2), La−O(1) = 2.6779(16), La−O(2) = 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 KBr) and subsequent crystallization from THF/hexane, afforded $La(CH_2Ph)_3(THF)_3$ (**1a**) and $[La(CH_2C_6H_4\text{-}4\text{-}Me)_3(THF)_3]$ (**1b**) as analytically pure orange-yellow crystals in 57% and 45% isolated yields, respectively (Scheme 1). A crystal structure determination of **1a** (Figure 1; crystal data and collection parameters are given in Table 4) revealed that the metal center is bound to three η^2-benzyl groups, with $La-CH_2-C_{ipso}$ angles of 88.0−89.5(1)°, and three THF molecules. The latter are located in a facial arrangement on one side of the molecule, with O−La−O angles of 72.90−74.59(5)°. The *p*-tolyl derivative **1b** is essentially isostructural with **1a**, with comparable bond lengths and angles around the lanthanum center (Figure 2). Due to the η^2 coordination of the benzyl ligands to lanthanum, the structures of **1a**,**b** deviate from the octahedral geometry observed for $[Y(CH_2SiMe_3)_3(THF)_3]$.[1f] The latter readily loses one THF molecule to adopt the trigonal-bipyramidal geometry more common for the small- to medium-sized group 3 and lanthanide members.[10]

Complexes **1a**,**b** are rather poorly soluble in hydrocarbon solvents but quite soluble in THF. In THF-d_8, both compounds show one singlet ^1H NMR resonance for the benzyl methylene protons, suggesting an averaged structure in solution of at least C_{3v} symmetry. The benzyl methylene ^{13}C NMR resonances are found at δ 67.2 ppm ($^1J_{CH} = 133$ Hz; **1a**) and δ 66.0 ppm ($^1J_{CH} = 131$ Hz; **1b**).

Reactivity with an Amidine and a Lithium Benzyl Reagent. NMR tube reactions of the tribenzyl complexes **1a**,**b** with the amidine ArN═CPhNHAr (Ar = 2,6-$Pr^i_2C_6H_3$)[11] in THF solvent generates cleanly the monoamidinate dibenzyl complexes $[PhC(NAr)_2]La(CH_2C_6H_4\text{-}R)_2(THF)_n$ (R = H, Me) 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 $[PhC(NAr)_2]La(CH_2C_6H_5)_2(THF)$ (**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 η^2-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 η^3-like bonding, with a short $La-C_o$ distance (La−C(34)) of 3.030(3) Å. Such an η^3 coordination mode has been observed before in lanthanide metallocene benzyl complexes.[12] Probably in response to the η^n 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 $[PhC(NAr)_2]La(CH_2SiMe_3)_2(THF)_2$.[4b] The room-temperature ^{13}C NMR spectrum of **2** in C_6D_6 shows a single resonance for the $La-CH_2$ groups at δ 69.5 ppm ($^1J_{CH} = 136$ Hz). In THF-d_8 solvent, this resonance is observed at δ 71.1 ppm ($J_{CH} = 131$ Hz). The slight, but significant, reduction of the latter $^1J_{CH}$ coupling constant relative to that in benzene may indicate (reversible) binding of an additional THF molecule in this solvent.

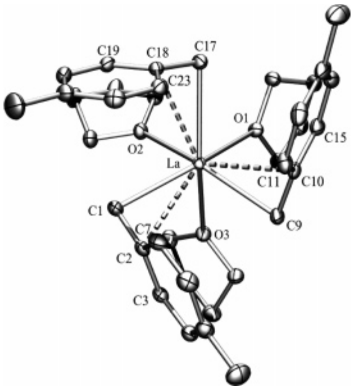


Figure 2. Top view of the molecular structure of $[La(CH_2C_6H_4\text{-}4\text{-}Me)_3(THF)_3]$ (**1b**), with 50% probability ellipsoids. Selected interatomic distances (Å) and angles (deg): La−C(1) = 2.6163(19), La−C(2) = 2.961(2), La−C(9) = 2.627(2), La−C(10) = 2.989(2), La−C(17) = 2.634(2), La−C(18) = 2.960(2), La−O(1) = 2.7067(14), La−O(2) = 2.6971(16), La−O(3) = 2.6732(16); La−C(1)−C(2) = 88.76(12), La−C(8)−C(9) = 89.57(12), La−C(17)−C(18) = 87.96(11), O(1)−La−O(2) = 74.97(4), O(1)−La−O(3) = 71.96(4), O(2)−La−O(3) = 75.27(5).

Reaction of the tribenzyl complex **1b** with 1 equiv of $LiCH_2C_6H_4\text{-}4\text{-}Me$ in THF generates the ionic compound $[La(CH_2C_6H_4\text{-}4\text{-}Me)_4][Li(THF)_4]$ (**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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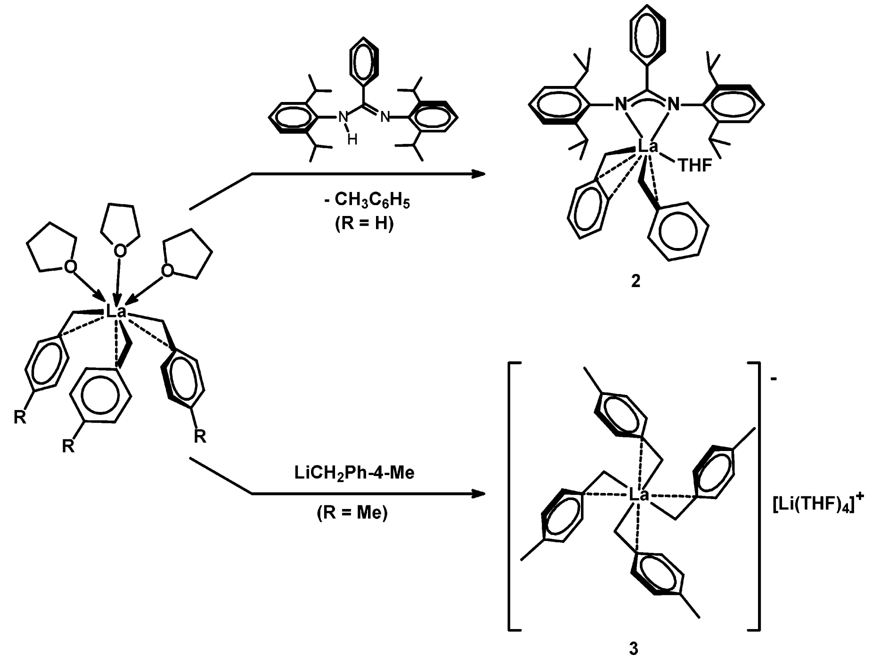
Scheme 2



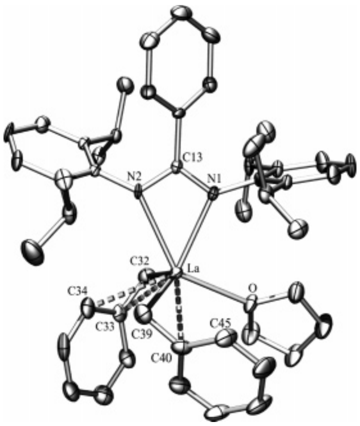


Figure 3. Molecular structure of $[PhC(NAr)_2]La(CH_2Ph)_2(THF)$ (**2**), with 50% probability ellipsoids. Selected interatomic distances (Å) and angles (deg): La−C(32) = 2.590(5), La−C(33) = 2.897(5), La−C(34) = 3.030(3), La−C(38) = 3.813(2), La−C(39) = 2.632(3), La−C(40) = 2.847(5), La−C(45) = 3.401(5), La−N(1) = 2.497(3), La−N(2) = 2.581(3), La−O(1) = 2.557(3); La−C(32)−C(33) = 87.0(3), La−C(39)−C(40) = 83.3(2).

simple, indicative of a symmetrically averaged structure of the La−tetrabenzyl anion. In a comparison of the spectra of **1b** and **3**, the benzyl methylene ^1H and ^{13}C 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 $^1J_{CH}$ coupling constant in **3** of 139 Hz is significantly larger than the 131 Hz for **1b**. Single-crystal X-ray diffraction of **3** (Figure 4; crystal data and collection parameters are given in Table 4) shows the four benzyl ligands in the anion to be η^2-bound to the metal. A similar complex, but with a Me_3Si substituent on the 2-position of the benzyl group, $[La(CH_2C_6H_4\text{-}2\text{-}SiMe_3)_4][Li(THF)_4]$, was recently reported by Harder.[8] The average $La-CH_2$ and $La\cdots C_{ipso}$ distances in **3** of 2.64 and 2.88 Å, respectively, are somewhat shorter than those in the more sterically congested *o*-$SiMe_3$ analogue (2.69 and 2.94 Å).

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 the Brønsted acid $[PhNMe_2H][B(C_6F_5)_4]$ in THF-d_8 solvent generate cleanly (as seen by NMR spectroscopy) the ionic species $[La(CH_2C_6H_4\text{-}R)_2(THF\text{-}d_8)_n][B(C_6F_5)_4]$ (R = H (**4a**), Me (**4b**)) and $[La(CH_2C_6H_4\text{-}R)(THF\text{-}d_8)_m][B(C_6F_5)_4]_2$ (R = H (**5a**), Me (**5b**)), respectively, accompanied by liberation of toluene or *p*-xylene and free $PhNMe_2$.

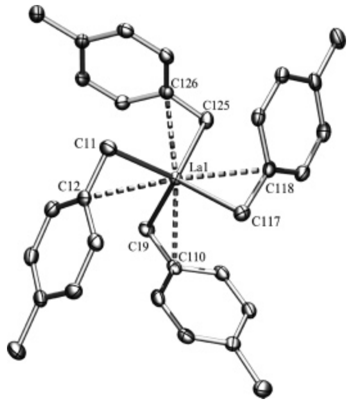
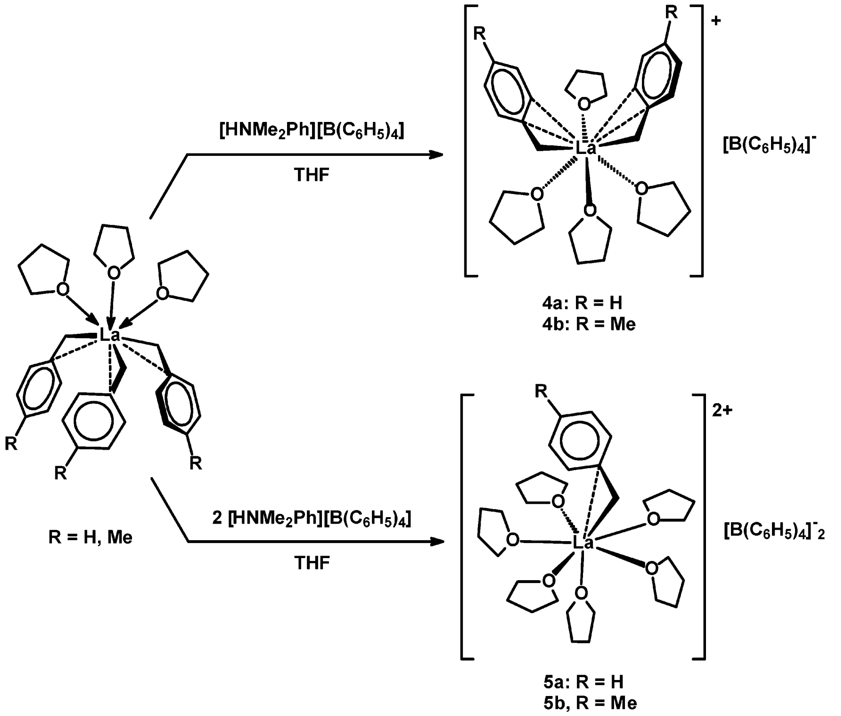


Figure 4. Molecular structure of $[La(CH_2C_6H_4\text{-}4\text{-}Me)_4][Li(THF)_4]$ (**3**), with 50% probability ellipsoids. The cation is omitted for clarity. Selected interatomic distances (Å) and angles (deg): La(1)−C(11) = 2.616(3), La(1)−C(12) = 3.004(3), La(1)−C(19) = 2.635(2), La(1)−C(110) = 2.835(2), La(1)−C(117) = 2.658(3), La(1)−C(118) = 2.871(2), La(1)−C(125) = 2.658(3), La(1)−C(126) = 2.839(2); La(1)−C(11)−C(12) = 90.80(14), La(1)−C(19)−C(110) = 82.78(13), La(1)−C(117)−C(118) = 83.36(15), La(1)−C(125)−C(126) = 81.97(14).

Compounds **4** and **5** are related to the mono- and dicationic alkyl species $[Ln(CH_2SiMe_3)_2(THF)_n]^+$ and $[Ln(CH_2SiMe_3)(THF)_m]^{2+}$ of the smaller rare-earth metals (Ln = Sc, Y, Tb−Lu) reported by Okuda et al.[1g,h] The ^{13}C NMR spectrum of **4a** shows a single resonance for the $La-CH_2$ groups at δ 71.3 ppm (J_{CH} = 134 Hz). In the dication **5a**, the corresponding resonance is found at δ 78.9 ppm (J_{CH} = 130 Hz).

The couple **4b**/**5b** follows the same trend in chemical shift for the benzyl methylene groups. The $La-CH_2$ ^{13}C NMR resonances move downfield from 70.6 ppm (J_{CH} = 134 Hz) in

Scheme 3



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 δ 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 [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] in THF-d_8 appears to generate the alkyl-free species [La(THF)$_x$]$^{3+}$[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 [PhNMe$_2$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)$_n$}[B(C$_6$F$_5$)$_4$] (**6**). Its ^{13}C NMR spectrum shows the remaining benzyl methylene resonance at δ 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 Brønsted 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(CH$_2$C$_6$H$_4$-4-R)$_2$(THF)$_4$][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 **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 η^3 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′** of 2.649(4) and 2.592(2) Å are somewhat longer than those in the seven-coordinate complexes [[P(C$_6$H$_4$-2-H$_2$NMe$_2$){CH(SiMe$_3$)(SiMe$_2$CH$_2$)}]La(THF)$_4$][BPh$_4$][13] and [{PhC(NAr)$_2$}La(CH$_2$SiMe$_3$)(THF)$_4$][BPh$_4$],[4b] where the La−CH$_2$ bond distances are 2.485(9) and 2.510(4) Å, respectively. The multihapto bonding

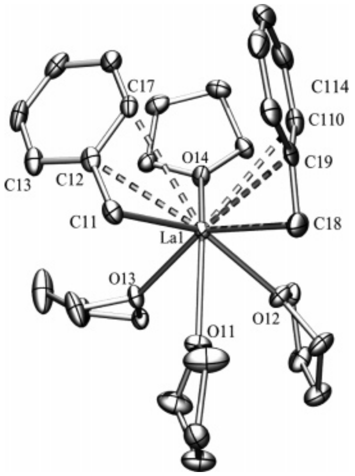


Figure 5. Molecular structure of [La(CH$_2$Ph)$_2$(THF)$_4$][B(C$_6$H$_5$)$_4$] (**4a′**), with 50% probability ellipsoids. Selected interatomic distances (Å) and angles (deg): La(1)−C(18) = 2.649(4), La(1)−C(19) = 2.936(3), La(1)−C(110) = 3.052(2), La(1)−C(11) = 2.592(2), La(1)−C(12) = 2.959(2), La(1)−C(17) = 3.057(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).

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[13] Izod, K.; Liddle, S. T.; Clegg, W. *Chem. Commun.* **2004**, 1748.

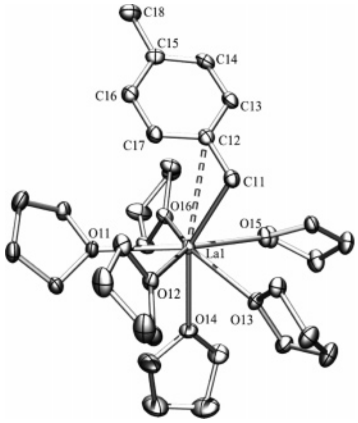

Figure 6. Molecular structure of $[La(CH_2Ph\text{-}4Me)(THF)_6][B(C_6H_5)_4]_2$ (**5b′**), with 50% probability ellipsoids. Selected interatomic distances (Å) and angles (deg): La(1)−C(11) = 2.534(3), La(1)−C(12) = 2.968(3), La(1)−C(17) = 3.136(3), La(1)−O(11) = 2.6835(19), La(1)−O(12) = 2.588(2), La(1)−O(13) = 2.5954(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).

of the benzyl groups in **4a′** distorts the overall geometry of the cation relative to that in the six-coordinate yttrium dialkyl species $[Y(CH_2SiMe_3)_2(THF)_4]^+$, which is closer to a regular octahedron.[1h]

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 bipyramid. The structure of **5b′** is related to that of the dicationic yttrium complex $[YMe(THF)_6][BPh_4]_2$ reported by Okuda et al.,[1h] where the alkyl group is located in the apical position of the pentagonal bipyramid. The ipso 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 η^2 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 dicationic lanthanum center and the two tetraphenylborate anions in the lattice.

Catalysis Studies of Neutral and Cationic Lanthanum Benzyl Complexes. (a) Ethylene Polymerization. While cationic 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 catalysis by cationic lanthanide species that include lanthanum derivatives, these showed very poor activities compared to the intermediate size metals.[4b,15] We have examined the new lanthanum benzyl compounds for their activity in ethylene polymerization. Cationic and dicationic catalysts were generated in toluene solvent by reacting complex **1b** (which is more soluble than **1a**) with 1 or 2 equiv of the Brønsted acid $[PhNMe_2H][B(C_6F_5)_4]$. Similarly, the cationic amidinate benzyl species was generated from **2** and 1 equiv of $[PhNMe_2H][B(C_6F_5)_4]$. 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.

Table 1. Catalytic Ethylene Polymerization Experiments[a]

precursor	yield (g)	activity[d]	$10^{-3}M_w$	M_w/M_n
1b/TiBAO[b]	0	none		
2/TiBAO[b]	0	none		
1b/TiBAO[b]/B[c]	0.79	63	338.4	9.8
1b/TiBAO[b]/2B	0.45	36	367.9	9.3
2/TiBAO[b]/B[c]	0.74	59	89.5	14.6

[a] Conditions: toluene solvent (30 mL), 50 °C, 10 μmol of La, 5 bar of ethylene pressure, 15 min run time. [b] 100 μmol of Al. [c] B = 10 μmol of $[HNMe_2Ph][B(C_6F_5)_4]$. [d] In units of kg of PE (mol of La)$^{-1}$ h^{-1} bar^{-1}.

The cationic species derived from **1b** show low activites, but the monocationic species is clearly the more active of the two.[16] The activity of the cationic amidinate benzyl species is higher than that observed previously with the cation generated from $[PhC(NAr)_2]La(CH_2SiMe_3)_2(THF)_2$,[4b] 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 aminoalkenes.[17−19] Although for catalytic olefin polymerization it has been well established that cationic 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 cationic 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 cationic species were generated in situ from the listed compounds by reaction with $[PhNMe_2H][B(C_6F_5)_4]$.

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

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(14) For recent reviews see: (a) Arndt, S.; Okuda, *J. Adv. Synth. Catal.* **2005**, *347*, 339. (b) Gromada, J., Carpentier, J.-F.; Mortreux, A. *Coord. Chem. Rev.* **2004**, *248*, 397.

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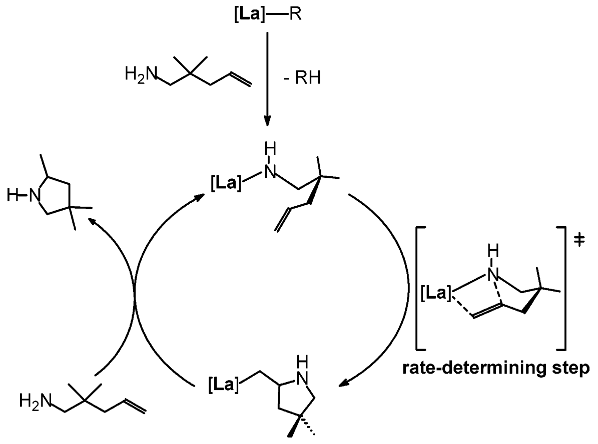
Table 2. Catalytic Hydroamination/Cyclization of 2,2-Dimethyl-4-pentenylamine by Neutral and Cationic Lanthanum Benzyl Complexes[a]

catalyst	time/h	conversn[b]/%	k/s^{-1} [c]
1b	10	45	*e*
1b/B	0.7	99	6.21×10^{-2}
1b/2B	1.4	99	3.43×10^{-2}
2[d]	0.8	99	3.85×10^{-2}
2/B[d]	23	50	5.10×10^{-4}
3	12	35	1.88×10^{-3}
3/1B	10	31	*e*

[a] Conditions: C_6D_5Br solvent (total volume 0.5 mL), 50 °C, 10 μmol of catalyst and $[PhNMe_2H][B(C_6F_5)_4]$ (B) activator where appropriate, 1.0 mmol of substrate. [b] Determined by ^{1}H NMR. [c] Over the first 50% conversion. [d] In C_6D_6 solvent. [e] Not determined, due to the poor solubility of the catalyst.

Scheme 4

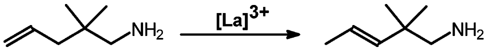


ene insertion into the metal−amide bond; Scheme 4). The cationic species is nearly 2 orders of magnitude slower than the neutral catalyst. This observation is similar to that made by us on the related amidinate ((trimethylsilyl)methyl)yttrium system.[21] Nevertheless, although the Y and La neutral catalysts 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 tetrabenzyl complex **3** to generate unsolvated lanthanum benzyl cations by reaction with the appropriate amounts of $[PhNMe_2H][B(C_6F_5)_4]$. Compound **3** itself is moderately active, and the intrinsic activity of the derived neutral species, like that of **1b**, was difficult to determine due to poor solubility. Interestingly, the combination of **3** with 2 equiv of $[PhNMe_2H][B(C_6F_5)_4]$ resulted in relatively rapid conversion of the substrate, but yielded a 1:2 mixture of 2-methyl-4,4-dimethylpyrrolidine and (*E*)-2,2-dimethyl-3-pentenylamine, the product of double-bond isomerization of the substrate.

It turns out that the cationic Lewis acidic species generated by the *full* protonation of either solvated **1b** or nonsolvated **3** can effectively isomerize 2,2-dimethyl-4-pentenylamine to 2,2-dimethyl-3-pentenylamine (eq 1). The reaction appears to be 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 *n*BuLi-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 $PhNMe_2$) in the reaction mixture may combine in promoting this isomerization.



(1)

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).

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 N_2 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-d_6 and THF-d_8 were dried over Na/K alloy and vacuum-transferred before use. Bromobenzene-d_5 was degassed and dried over CaH_2. KCH_2Ph-4-R (R = H, Me)[9] and $[PhC(N\text{-}2,6\text{-}Pr^i{}_2C_6H_3)_2]H$[24] were prepared according to published procedures. $[PhNMe_2H][B(C_6F_5)_4]$ (Strem) was used as purchased. TIBAO was prepared by careful partial hydrolysis of $Bu^i{}_3Al$ (Witco) in toluene.[25] 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 $K(CH_2Ph\text{-}4\text{-}Me)$. To a suspension of potassium *tert*-butoxide (5.6 g, 50 mmol) in xylene (100 mL) and hexanes (100 mL) was added dropwise *n*-butyllithium (20 mL, 2.5 M solution in hexanes). The reaction mixture turned orange. The

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(22) Tsurugi, H.; Bambirra, S.; Hessen, B. Unpublished results. When $[Y(CH_2SiMe_3)_3(THF)_2]$ was exposed to solutions of the substrate 2,2-dimethyl-4-pentenylamine in C_6D_6, cloudy suspensions were obtained, which (remarkably) give clear solutions when $[PhNMe_2H][B(C_6F_5)_4]$ was added.

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Table 3. Catalytic Isomerization of 2,2-Dimethyl-4-pentenylamine to (*E*)-2,2-Dimethyl-3-pentenylamine by Cationic Lanthanum Species[a]

catalyst	time/h	conversn[b]/%	k/L mol^{-1} s^{-1}
1b/3B	1.5	95	3.99×10^{-2}
3/4B	2	96	3.43×10^{-2}

[a] Conditions: C_6D_5Br solvent (total volume 0.5 mL), 50 °C, 10 μmol of catalyst, B = 10 μmol of $[PhNMe_2H][B(C_6F_5)_4]$ activator, 1.0 mmol of substrate. [b] Determined by ^1H NMR.

reaction mixture was stirred for 4 h at room temperature. After filtration, the orange solid was washed by continuous extraction with hot hexanes (LiO*t*Bu removal) and dried under vacuum, yielding 6.5 g (46 mmol, 93%) of KCH_2Ph-4-Me as a red, pyrophoric solid. ^1H NMR (300 MHz, THF-d_8, 20 °C): δ 5.97 (d, $^3J_{HH}$ = 7.5 Hz, 2H, Ar *m*-H), 5.62 (d, $^3J_{HH}$ = 7.5 Hz, 2H, Ar *o*-H), 1.94 (s, 2H, KCH_2), 1.78 (s, 3 H, Me). ^{13}C NMR (75.4 MHz, THF-d_8, 20 °C): δ 154.5 (Ar C_{ipso}), 132.0 (d, $^1J_{CH}$ = 145.8 Hz, Ar CH), 112.6 (d, $^1J_{CH}$ = 149.6 Hz, Ar CH), 105.7 (Ar *C*Me), 46.9 (t, $^1J_{CH}$ = 149.2 Hz, KCH_2), 21.7 (q, $^1J_{CH}$ = 125.3 Hz, Me).

Synthesis of Li(CH_2Ph-4-Me). Solid KCH_2Ph-4-Me (650 mg, 5.0 mmol) and LiBr (435 mg, 5 mmol) were mixed, and 50 mL of diethyl ether was added with stirring. The color of the suspension changed from red to yellow, and the mixture was stirred for 3 h. The solvent was removed in vacuo, and the solids were extracted with toluene (50 mL). The filtrate was evaporated to dryness under reduced pressure, leaving the title compound as a yellow pyrophoric powder (400 mg, 3.5 mmol, 71%). ^1H NMR (300 MHz, THF-d_8, 20 °C): δ 6.80 (d, $^3J_{HH}$ = 7.7 Hz, 2H, Ar *m*-H), 6.70 (d, $^3J_{HH}$ = 7.7 Hz, 2H, Ar *o*-H), 2.32 (s, 3 H, Me), 1.90 (s, 2H, $LiCH_2$). ^{13}C NMR (75.4 MHz, THF-d_8, 20 °C): δ 159.4 (Ar C_{ipso}), 130.4 (d, $^1J_{CH}$ = 156.0 Hz, Ar CH), 119.3 (d, $^1J_{CH}$ = 150.6 Hz, Ar CH), 115.6 (Ar *C*Me), 34.4 (t, $^1J_{CH}$ = 126.1 Hz, $LiCH_2$), 22.3 (q, $^1J_{CH}$ = 123.3 Hz, Me). Anal. Calcd for C_8H_9BLi (mol wt 112.10): C, 85.72; H, 8.09; Li, 6.19. Found: C, 85.65; H, 8.93; Li, 6.08.

Synthesis of [La(CH_2Ph)$_3$(THF)$_3$] (1a). A solution of KCH_2-Ph (1.56 g, 12.0 mmol) in 10 mL of THF was added to a suspension of $LaBr_3(THF)_4$ (2.70 g, 4.0 mmol) in THF (100 mL) at 0 °C. The resulting yellow suspension was stirred for 2 h at 0 °C, after which the mixture was centrifuged and decanted from the KBr precipitate. The solution was concentrated under reduced pressure to about 10 mL, during which a crystalline solid formed. Pentane was layered onto the mixture, and cooling to −30 °C afforded the title compound as yellow-orange crystals (1.45 g, 2.3 mmol, 57%). ^1H NMR (300 MHz, THF-d_8, 20 °C): δ 6.78 (t, 6H, $^3J_{HH}$ = 7.5 Hz, Ph *m*-H), 6.22 (t, $^3J_{HH}$ = 7.2 Hz, 3H, Ph *p*-H), 6.14 (d, $^3J_{HH}$ = 7.5 Hz, 6H, Ph *o*-H), 1.41 (s, 6H, C*H*$_2$Ph). ^{13}C NMR (300 MHz, THF-d_8, 20 °C): δ 153.0 (Ph C_{ipso}), 131.4 (d, $^1J_{CH}$ = 152.9 Hz, Ph CH), 122.7 (d, $^1J_{CH}$ = 153.0 Hz, Ph CH), 116.1 (d, $^1J_{CH}$ = 158.5 Hz, Ph CH), 67.2 (t, $^1J_{CH}$ = 133.0 Hz, $LaCH_2$). Anal. Calcd for $C_{33}H_{45}LaO_3$ (mol wt 628.62): C, 63.05; H, 7.22. Found: C, 62.85; H, 7.13.

Synthesis of [La(CH_2Ph-4-Me)$_3$(THF)$_3$] (1b). A reaction on the same scale and under the same conditions, but using KCH_2-Ph-4-Me (1.7 g, 12.0 mmol) as benzylating agent, afforded the title compound as yellow-orange crystals (1.20 g, 1.8 mmol, 45%). ^1H NMR (300 MHz, THF-d_8, 20 °C): δ 6.65 (d, $^3J_{HH}$ = 7.6 Hz, 6H, *m*-H), 6.07 (d, $^3J_{HH}$ = 7.6 Hz, 6H, *o*-H), 2.08 (s, 9 H, Me), 1.36 (s, 6H, $LaCH_2$). ^{13}C NMR (75.4 MHz, THF-d_8, 20 °C): δ 150.0 (Ar C_{ipso}), 132.0 (d, $^1J_{CH}$ = 153.3 Hz, Ar CH), 125.0 (Ar *C*Me), 123.1 (d, $^1J_{CH}$ = 150.0 Hz, Ar CH), 66.0 (t, $^1J_{CH}$ = 131.2 Hz, $LaCH_2$), 21.7 (q, $^1J_{CH}$ = 125.9 Hz, Me). Anal. Calcd for $C_{36}H_{51}LaO_3$ (mol wt 670.70): C, 64.47; H, 7.66. Found: C, 64.36; H, 7.64.

Synthesis of [PhC(NAr)$_2$]La(CH_2Ph)$_2$(THF) (2). (a) NMR-Tube Scale. Solid **1a** (63.0 mg, 100.0 μmol) and [PhC(N-2,6-$Pr^i_2C_6H_3$)$_2$]H (44.0 mg, 100.0 μmol) were mixed together and dissolved in 0.6 mL of THF-d_8. NMR spectroscopy showed clean conversion to **2** and 1 equiv of toluene. ^1H NMR (500 MHz, THF-d_8, 20 °C): δ 6.92 (m, 2 H, Ar H), 6.87 (m, 5 H, Ph), 6.84 (t, $^3J_{HH}$ = 7.5 Hz, 4 H, Bz *m*-H), 6.81 (m, 4 H, Ar H), 6.41 (d, $^3J_{HH}$ = 7.5 Hz, 4 H, Bz *o*-H), 6.32 (t, $^3J_{HH}$ = 7.5 Hz, 2 H, Bz *p*-H), 3.41 (sept, $^3J_{HH}$ = 6.6 Hz, 4 H, C*H*Me$_2$), 1.76 (s, 4 H, $LaCH_2$), 1.19 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, Pr^i Me), 0.85 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, Pr^i Me). ^{13}C NMR (125.7 MHz, THF-d_8, 20 °C): δ 174.7 (N*C*N), 153.0 (Bz C_{ipso}), 146.7 (Ph C_{ipso}), 141.5 (Ar C_{ipso}), 134.7 (Ar C), 131.9 (d, $^1J_{CH}$ = 160.0 Hz, Bz CH), 130.6 (d, $^1J_{CH}$ = 156.2 Hz, Ar CH), 129.8 (d, $^1J_{CH}$ = 158.8 Hz, Ph CH), 128.3 (d, $^1J_{CH}$ = 161.5 Hz, Ph CH), 125.2 (d, $^1J_{CH}$ = 158.7 Hz, Ph CH), 125.1 (d, $^1J_{CH}$ = 153.6 Hz, Ar CH), 122.8 (d, $^1J_{CH}$ = 152.8 Hz, Bz CH), 117.6 (d, $^1J_{CH}$ = 157.8 Hz, Bz CH), 71.1 (t, $^1J_{CH}$ = 130.6 Hz, $LaCH_2$), 30.2 (d, $^1J_{CH}$ = 126.6 Hz, Pr^i CH), 26.8 (q, $^1J_{CH}$ = 125.0 Hz, Pr^i Me), 24.7 (q, $^1J_{CH}$ = 124.8 Hz, Pr^i Me).

(b) Preparative Scale. Solid **1a** (0.31 g, 0.50 mmol) and [PhC-(N-2,6-$Pr^i_2C_6H_3$)$_2$]H (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%). ^1H NMR (300 MHz, C_6D_6, 20 °C): δ 7.19−7.15 (m, 2 H, Ar H), 7.03 (m, 5 H, Ph), 6.96 (t, $^3J_{HH}$ = 7.2 Hz, 4 H, Bz *m*-H), 6.69−6.66 (m, 4 H, Ar H), 6.53 (d, $^3J_{HH}$ = 6.9 Hz, 4 H, Bz *o*-H), 6.42 (t, $^3J_{HH}$ = 6.9 Hz, 2 H, Bz *p*-H), 3.62 (sept, $^3J_{HH}$ = 6.7 Hz, 4 H, C*H*Me$_2$), 3.06 (m, 4 H α-THF), 2.34 (s, 4 H, $LaCH_2$), 1.32 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, Pr^i Me), 1.12 (m, 4 H β-THF), 1.03 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, Pr^i Me). ^{13}C NMR (75.4 MHz, C_6D_6, 20 °C): δ 173.2 (N*C*N), 150.2 (Bz C_{ipso}), 144.8 (Ph C_{ipso}), 141.5 (Ar C_{ipso}), 132.9 (Ar C), 131.9 (d, $^1J_{CH}$ = 156.2 Hz, Bz CH), 130.6 (d, $^1J_{CH}$ = 160.3 Hz, Ar CH), 128.9 (d, $^1J_{CH}$ = 154.1 Hz, Ph CH), 127.0 (d, $^1J_{CH}$ = 152.1 Hz, Ph CH), 124.1 (d, $^1J_{CH}$ = 160.4 Hz, Ph CH), 123.8 (d, $^1J_{CH}$ = 156.2 Hz, Ar CH), 121.0 (d, $^1J_{CH}$ = 152.1 Hz, Bz CH), 116.2 (d, $^1J_{CH}$ = 160.3 Hz, Bz CH), 69.4 (t, $^1J_{CH}$ = 135.8 Hz, $LaCH_2$), 68.7 (t, $^1J_{CH}$ = 147.6 Hz, α-THF), 28.8 (d, $^1J_{CH}$ = 125.8 Hz, Pr^i CH), 25.5 (q, $^1J_{CH}$ = 125.2 Hz, Pr^i Me), 25.4 (t, $^1J_{CH}$ = 132.2 Hz, β-THF), 23.5 (q, $^1J_{CH}$ = 125.2 Hz, Pr^i Me). Anal. Calcd for $C_{49}H_{61}LaN_2O$ (mol wt 832.94): C, 70.66; H, 7.38; N, 3.36. Found: C, 70.48; H, 7.32; N, 3.24.

Reaction of 1b with ArN═CPhNHAr. Solid **1b** (67.0 mg, 100.0 μmol) and [PhC(N-2,6-$Pr^i_2C_6H_3$)$_2$]H (44.0 mg, 100.0 μmol) were mixed together and dissolved in 0.6 mL of THF-d_8. NMR spectroscopy showed clean conversion to {[PhC(NAr)$_2$]La(CH_2-Ph-4-Me)$_2$(THF)$_x$} and 1 equiv of *p*-xylene. ^1H NMR (300 MHz, THF-d_8, 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, $^3J_{HH}$ = 7.5 Hz, 4 H, Bz *m*-H), 6.30 (d, $^3J_{HH}$ = 7.5 Hz, 4 H, Bz *o*-H), 3.42 (sept, $^3J_{HH}$ = 6.6 Hz, 4 H, C*H*Me$_2$), 1.79 (s, 4 H, $LaCH_2$), 1.18 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, Pr^i Me), 0.85 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, Pr^i Me). ^{13}C NMR (125.7 MHz, THF-d_8, 20 °C): δ 174.4 (N*C*N), 149.5 (Bz C_{ipso}), 146.7 (Ph C_{ipso}), 143.2 (Ar C_{ipso}), 134.7 (Ar C), 132.9 (d, $^1J_{CH}$ = 160.0 Hz, Bz CH), 130.3 (d, $^1J_{CH}$ = 156.2 Hz, Ar CH), 128.3 (d, $^1J_{CH}$ = 158.2 Hz, Ph CH), 126.3 (d, $^1J_{CH}$ = 157.5 Hz, Ph CH), 125.0 (d, $^1J_{CH}$ = 158.7 Hz, Ph CH), 125.1 (d, $^1J_{CH}$ = 151.4 Hz, Ar CH), 123.0 (d, $^1J_{CH}$ = 152.8 Hz, Bz CH), 69.8 (t, $^1J_{CH}$ = 130.5 Hz, $LaCH_2$), 30.1 (d, $^1J_{CH}$ = 126.6 Hz, Pr^i CH), 26.6 (q, $^1J_{CH}$ = 125.0 Hz, Pr^i Me), 24.8 (q, $^1J_{CH}$ = 124.8 Hz, Pr^i Me), 21.6 (q, $^1J_{CH}$ = 126.8 Hz, Bz*Me*).

Synthesis of [La(CH_2Ph-4-Me)$_4$][Li(THF)$_4$] (3). Solid **1b** (670 mg, 1.0 mmol) and $LiCH_2Ph$-4-Me (112 mg, 1.0 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%). ^1H NMR (300 MHz, THF-d_8, 20 °C): δ 6.51 (d, 8H, $^3J_{HH}$ = 7.9 Hz, Ar *m*-H), 5.70 (d, $^3J_{HH}$ = 7.9 Hz, 8H, Ar *o*-H), 2.06 (s, 12 H, Me), 1.11 (s, 8H, $LaCH_2$). ^{13}C NMR (75.4 MHz, THF-d_8, 20 °C): δ 150.0 (Ar C_{ipso}), 132.7 (d, $^1J_{CH}$ = 152.0 Hz, Ar CH), 121.9 (Ar C), 120.7 (d, $^1J_{CH}$ = 153.0 Hz, Ar CH), 62.0 (t, $^1J_{CH}$ = 139.6 Hz, $LaCH_2$), 21.8 (q, $^1J_{CH}$ =

Table 4. Crystal Data and Collection Parameters of Complexes 1a,b, 2, 3, 4a′, and 5b′

	1a	**1b**	**2**	**3**	**4a′**	**5b′**
formula	$C_{36}H_{51}LaO_3$	$C_{36}H_{45}LaO_3$	$C_{49}H_{61}LaN_2O$	$[C_{32}H_{36}La]^-[C_{16}H_{32}LiO_4]^+\cdot C_4H_8O$	$[C_{30}H_{64}LaO_4]^+[C_{24}H_{20}B]^-$	$[C_{32}H_{57}LaO_6]^{2+}[C_{24}H_{20}B]^-{}_2\cdot C_4H_8O$
fw	628.62	664.66	832.94	927.02	928.83	1387.28
cryst color	yellow	orange	orange	orange	yellow	yellow
cryst size (mm)	0.51 × 0.42 × 0.37	0.53 × 0.41 × 0.33	0.31 × 0.11 × 0.07	0.37 × 0.31 × 0.26	0.41 × 0.34 × 0.10	0.49 × 0.27 × 0.25
cryst syst	monoclinic	triclinic	orthorhombic	triclinic	orthorhombic	triclinic
space group (No.)	$P2_1/c$ (14)	$P\bar{1}$ (2)	*Pbca* (61)	$P\bar{1}$ (2)	*Pbca* (61)	$P\bar{1}$ (2)
a (Å)	14.092(1)	10.5672(8)	19.961(2)	13.599(1)	18.3872(9)	13.9488(8)
b (Å)	10.443(1)	13.420(1)	15.566(1)	13.605(1)	18.3346(9)	15.7315(9)
c (Å)	20.773(2)	15.033(1)	26.987(2)	15.016(1)	27.242(1)	17.528(1)
α (deg)		64.923(1)		71.147(1)		106.521(1)
β (deg)	100.879(2)	73.314(1)		89.847(1)		96.670(1)
γ (deg)		73.363(1)		67.519(1)		98.939(1)
V (Å^3)	3002.1(5)	1816.0(2)	8385.2(12)	2406.0(3)	9183.9(7)	3590.1(4)
Z	4	2	8	2	8	2
ρ_{calcd}, g cm^{-3}	1.391	1.215	1.320	1.280	1.343	1.280
μ(Mo K$\bar{\alpha}$), cm^{-1}	14.53	12.05	10.56	9.32	9.76	6.5
F(000), e	1296	684	3472	976	3872	1456
θ range (deg)	3.33, 28.28	3.63, 28.28	2.54, 26.02	2.56, 28.28	2.48, 26.37	2.46, 28.28
R1	0.0290	0.0236	0.0423	0.0320	0.0365	0.0425
wR2 (all data)	0.0716	0.0664	0.1077	0.0790	0.0859	0.1085
index ranges (*hkl*)	±18, ±13, ±27	±14, ±17, −19 to +20	±24, ±19, −31 to +33	−18 to +17, ±18, −19 to +20	±22, ±22, −34 to +29	±18, −19 to +20, −22 to +23
T (K)	100(1)	100(1)	100(1)	100(1)	100(1)	200
GOF	1.043	1.116	1.025	1.025	1.016	1.521

125.5 Hz, Ar Me). Anal. Calcd for $C_{60}H_{78}BLaO_5$ (mol wt 854.91): C, 67.44; H, 8.02; La, 16.25; Li, 0.81. Found: C, 67.28; H, 7.88; La, 16.11; Li, 0.84.

Reaction of 1a with 1 Equiv of [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]. Solid [La(CH$_2$Ph)$_3$(THF)$_3$] (31 mg, 50.0 μmol) and [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] (40 mg, 50.0 μmol) were mixed, and THF-d_8 (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(CH$_2$Ph)$_2$(THF-d_8)$_n$][B(C$_6$F$_5$)$_4$] (**4a**), 1 equiv of toluene, and free PhNMe$_2$. ^{1}H NMR (300 MHz, THF-d_8, 20 °C): **4a**, δ 7.09 (t, $^3J_{HH}$ = 7.6 Hz, 4 H, Ph *m*-H), 6.50 (t, $^3J_{HH}$ = 7.6 Hz, 2 H, Ph *p*-H), 6.33 (d, $^3J_{HH}$ = 7.6 Hz, 4 H, Ph *o*-H), 1.74 (s, 4 H, LaCH_2); PhNMe$_2$, δ 7.12 (t, $^3J_{HH}$ = 7.8 Hz, 2 H, Ph *m*-H), 6.63 (d, $^3J_{HH}$ = 7.8 Hz, 2 H, Ph *o*-H), 6.54 (t, $^3J_{HH}$ = 7.00 Hz, 1 H, Ph *p*-H), 2.82 (s, 6H, Me); C_7H_8, δ 7.18 (t, $^3J_{HH}$ = 7.2 Hz, 2 H, Ph *m*-H), 7.11 (t, $^3J_{HH}$ = 7.2 Hz, 2 H, Ph *o*-H), 7.07 (t, $^3J_{HH}$ = 7.2 Hz, 2 H, Ph *p*-H), 2.24 (s, 3 H, Me). ^{13}C NMR (75.4 MHz, THF-d_8, 20 °C): **4a**, δ 150.5 (Ph C$_{ipso}$), 149.9 (d, $^1J_{CF}$ = 242.6 Hz, C$_6$F$_5$), 140.0 (d, $^1J_{CF}$ = 245.2 Hz, C$_6$F$_5$), 138.5 (d, $^1J_{CF}$ = 243.6 Hz, C$_6$F$_5$), 132.8 (d, $^1J_{CH}$ = 155.6 Hz, Ph CH), 123.8 (d, $^1J_{CH}$ = 156.1 Hz, Ph CH), 119.6 (d, $^1J_{CH}$ = 162.0 Hz, Ph CH), 71.3 (t, $^1J_{CH}$ = 133.7 Hz, LaCH$_2$); PhNMe$_2$, δ 152.4 (Ph C$_{ipso}$), 130.2 (d, $^1J_{CH}$ = 161.0 Hz, Ph *m*-CH), 117.7 (d, $^1J_{CH}$ = 161.0 Hz, Ph *p*-CH), 114.0 (d, $^1J_{CH}$ = 154.6 Hz, Ph *o*-CH), 41.2 (s, Me).

Reaction of 1a with 2 Equiv of [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]. Solid **1a** (31.0 mg, 50.0 μmol) and [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] (80.0 mg, 100.0 μmol) were mixed, and THF-d_8 (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(CH$_2$Ph)(THF-d_8)$_n$][B(C$_6$F$_5$)$_4$]$_2$ (**5a**), 2 equiv of toluene, and free PhNMe$_2$. ^{1}H NMR (300 MHz, THF-d_8, 20 °C): δ 7.29 (t, $^3J_{HH}$ = 7.5 Hz, 2 H, Ph *m*-H), 6.82 (t, $^3J_{HH}$ = 7.5 Hz, 1 H, Ph *p*-H), 6.65 (d, $^3J_{HH}$ = 7.2 Hz, 2 H, Ph *o*-H), 1.85 (s, 2 H, LaCH$_2$). ^{13}C NMR (75.4 MHz, THF-d_8, 20 °C): δ 148.0 (Ph C$_{ipso}$), 133.6 (d, $^1J_{CH}$ = 157.5 Hz, Ph CH), 125.4 (d, $^1J_{CH}$ = 154.1 Hz, Ph CH), 122.8 (d, $^1J_{CH}$ = 160.5 Hz, Ph CH), 78.9 (t, $^1J_{CH}$ = 130.0 Hz, LaCH$_2$).

Synthesis of [La(CH$_2$Ph)$_2$(THF)$_4$][B(C$_6$H$_5$)$_4$] (4a′). THF (0.5 mL) was added to a mixture of 63 mg (100 μmol) of **1a** and 44 mg (100 μmol) of [HNMe$_2$Ph][BPh$_4$]. The resulting yellow solution was cooled to −30 °C for 3 days, producing yellow crystals of the title compound (69 mg, 69 μmol, 75%). ^{1}H NMR (300 MHz, THF-d_8, 20 °C): δ 7.26 (br, 8H, BPh$_4$ *o*-H), 7.03 (t, $^3J_{HH}$ = 7.5 Hz, 4 H, Ph *m*-H), 6.85 (t, 7.3 Hz, 8H, BPh$_4$ *m*-H), 6.72 (t, 7.1 Hz, 4H, BPh$_4$ *p*-H), 6.50 (t, $^3J_{HH}$ = 7.5 Hz, 2 H, Ph *p*-H), 6.26 (d, $^3J_{HH}$ = 7.6 Hz, 4 H, Ph *o*-H), 1.69 (s, 4H, LaCH$_2$). ^{13}C NMR (75.4 MHz, 20 °C, THF-d_8): δ 165.8 (q, $^1J_{CB}$ = 49.6 Hz, BPh$_4$ C$_{ipso}$), 150.5 (Ph C$_{ipso}$), 137.9 (dt, $^1J_{CH}$ = 153.6, 7.3 Hz, BPh$_4$ *o*-H), 132.7 (dd, $^1J_{CH}$ = 156.6, 7.7 Hz, Ph CH), 126.7 (d, 152.5 Hz, BPh$_4$ *m*-H), 123.7 (dt, $^1J_{CH}$ = 152.0, 7.2 Hz, Ph CH), 122.7 (dt, 155.5, 8.2, 7.3 Hz, BPh$_4$ *p*-H), 119.4 (dt, $^1J_{CH}$ = 162.0, 7.4 Hz, Ph CH), 71.1 (t, $^1J_{CH}$ = 133.5 Hz, LaCH$_2$). Anal. Calcd for $C_{54}H_{66}LaBO_4$ (mol wt 928.83): C, 69.83; H, 7.16. Found: C, 69.58; H, 6.83.

Synthesis of [La(CH$_2$Ph)(THF)$_6$][B(C$_6$H$_5$)$_4$]$_2$ (5a′). THF (0.5 mL) was added to a mixture of 63 mg (100 μmol) of **1a** and 88 mg (200 μmol) of [HNMe$_2$Ph][BPh$_4$]. From the resulting yellow solution an oil precipitated. The supernatant was decanted off, and the oil was rinsed with hexanes. Drying of the residue in vacuo gave yellow microcrystalline **5a′** (69 mg, 75%). ^{1}H NMR (300 MHz, room temperature, THF-d_8, 20 °C): δ 7.11 (t, $^3J_{HH}$ = 7.4 Hz, 4 H, Ph *m*-H), 6.80 (t, $^3J_{HH}$ = 7.4 Hz, 2 H, Ph *p*-H), 6.60 (d, $^3J_{HH}$ = 7.4 Hz, 4 H, Ph *o*-H), 1.84 (s, 2H, LaCH$_2$). For resonances of the anion, see the data for **4a′**. Anal. Calcd for $C_{79}H_{95}LaB_2O_6$ (mol wt 1301.15): C, 72.93; H, 7.36. Found: C, 72.42; H, 6.95.

Reaction of 1b with 1 Equiv of [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]. Solid **1b** (34 mg, 50.0 μmol) and [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] (40 mg, 50.0 μmol) were mixed, and THF-d_8 (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(CH$_2$Ph-4-Me)$_2$(THF-d_8)$_n$][B(C$_6$F$_5$)$_4$] (**4b**), 1 equiv of *p*-xylene, and free PhNMe$_2$. ^{1}H NMR (300 MHz, THF-d_8, 20 °C): **4b**, δ 6.72 (d, $^3J_{HH}$ = 7.7 Hz, 4 H, Ar *m*-H), 6.12 (d, $^3J_{HH}$ = 7.7 Hz, 2 H, Ar *o*-H), 2.09 (s, 6 H, Me), 1.63 (s, 4 H, LaCH$_2$); *p*-C$_8$H$_{10}$, δ 6.93 (s, 4 H, Ar H), 2.18 (s, 6 H, Me). ^{13}C NMR (75.4 MHz, THF-d_8, 20 °C): **4b**, δ 149.2 (Ar C$_{ipso}$), 132.4 (d, $^1J_{CH}$ = 151.3 Hz, Ar *m*-CH), 129.2 (Ar *C*-Me), 123.5 (d, $^1J_{CH}$ = 152.7 Hz, Ar *o*-CH), 70.6 (t, $^1J_{CH}$ = 134.0 Hz, LaCH$_2$), 21.5 (q, $^1J_{CH}$ = 125.0 Hz, Me); *p*-C$_8$H$_{10}$, 136.2 (Ar C), 130.6 (d, $^1J_{CH}$ = 155.5 Hz, Ar CH), 22.1 (q, $^1J_{CH}$ = 125.7 Hz, Me).

Reaction of 1b with 2 Equiv of [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]. Solid **1b** (34.0 mg, 50.0 μmol) and [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] (80.0 mg, 100.0 μmol) were mixed, and THF-d_8 (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 $[La(CH_2Ph\text{-}4\text{-}Me)(THF\text{-}d_8)_n][B(C_6F_5)_4]_2$ (**5b**), 2 equiv of *p*-xylene, and free $PhNMe_2$. ^1H NMR (300 MHz, THF-d_8, 20 °C): δ 7.14 (d, $^3J_{HH}$ = 7.5 Hz, 2 H, Ar *m*-H), 6.57 (d, $^3J_{HH}$ = 7.5 Hz, 2 H, Ar *o*-H), 2.20 (s, 3 H, Ar *p*-H), 1.79 (s, 4 H, $LaCH_2$). ^{13}C NMR (75.4 MHz, THF-d_8, 20 °C): δ 149.2 (Ar C_{ipso}), 134.3 (d, $^1J_{CH}$ = 151.4 Hz, Ar *m*-CH), 125.6 (d, $^1J_{CH}$ = 151.3 Hz, Ar *o*-CH), 132.8 (Ar *C*-Me), 78.0 (t, $^1J_{CH}$ = 129.7 Hz, $LaCH_2$), 21.1 (q, $^1J_{CH}$ = 126.6 Hz, Me).

Synthesis of $[La(CH_2Ph\text{-}4\text{-}Me)_2(THF)_4][B(C_6H_5)_4]\cdot THF$ (4b′). THF (0.5 mL) was added to a mixture of 67 mg (100 μmol) of **1b** and 44 mg (100 μmol) of $[HNMe_2Ph][BPh_4]$. The resulting light yellow solution was cooled to −30 °C for 3 days, producing yellowish crystals of **4b′** (74 mg, 72%). ^1H NMR (300 MHz, THF-d_8, 20 °C): δ 6.87 (d, $^3J_{HH}$ = 7.5 Hz, 4 H, Ar *m*-H), 6.18 (d, $^3J_{HH}$ = 7.7 Hz, 2 H, Ar *o*-H), 2.14 (s, 6 H, Me), 1.59 (s, 4 H, $LaCH_2$). ^{13}C NMR (75.4 MHz, THF-d_8, 20 °C): δ 166.1 (q, $^1J_{CB}$ = 48.7 Hz, BPh_4 C_{ipso}), 148.5 (Ar C_{ipso}), 133.5 (d, $^1J_{CH}$ = 155.2 Hz, Ar *m*-CH), 128.9 (Ar *C*-Me), 124.0 (d, $^1J_{CH}$ = 153.0 Hz, Ar *o*-CH), 70.4 (t, $^1J_{CH}$ = 131.0 Hz, $LaCH_2$), 21.6 (q, $^1J_{CH}$ = 125.0 Hz, Me). Anal. Calcd for $C_{60}H_{78}BLaO_5$ (mol wt 1028.99): C, 70.04; H, 7.64. Found: C, 69.87; H, 7.54.

Synthesis of $[La(CH_2Ph\text{-}4\text{-}Me)(THF)_6][B(C_6H_5)_4]_2$ (5b′). THF (0.5 mL) was added to a mixture of 67 mg (100 μmol) of **1b** and 88 mg (200 μmol) of $[HNMe_2Ph][BPh_4]$. The resulting light yellow solution was cooled to −30 °C for 3 days, producing yellowish crystals of **5b′** (80 mg, 61%). ^1H NMR (300 MHz, THF-d_8, 20 °C): δ 76.90 (d, $^3J_{HH}$ = 7.3 Hz, 2 H, Ar *m*-H), 6.47 (d, $^3J_{HH}$ = 7.3 Hz, 2 H, Ar *o*-H), 2.09 (s, 6 H, Me), 1.77 (s, 2H, $LaCH_2$). Anal. Calcd for $C_{80}H_{97}B_2LaO_6$ (mol wt 1315.17): C, 73.06; H, 7.43. Found: C, 73.00; H, 7.48.

Reaction of 2 with $[HNMe_2Ph][B(C_6F_5)_4]$. A solution of **2** (42 mg, 50.0 μmol) in THF-d_8 (0.6 mL) was added to solid $[HNMe_2Ph][B(C_6F_5)_4]$ (40 mg, 50.0 μmol). The obtained solution was transferred to an NMR tube and analyzed by NMR spectroscopy, which showed full conversion to the ionic species $\{[PhC(N\text{-}2,6\text{-}Pr^i{}_2C_6H_3)_2]La(CH_2Ph)(THF\text{-}d_8)_n\}[B(C_6F_5)_4]$ (**6**), 1 equiv of toluene, and free $PhNMe_2$. ^1H NMR (500 MHz, THF-d_8, 20 °C): δ 7.13 (m, 2 H, Ar H), 7.00 (m, 5 H, Ph), 6.94 (m, 4 H, Ar H), 6.84 (t, $^3J_{HH}$ = 7.5 Hz, 4 H, Bz *m*-H), 6.65 (d, $^3J_{HH}$ = 7.5 Hz, 4 H, Bz *o*-H), 6.55 (t, $^3J_{HH}$ = 7.5 Hz, 2 H, Bz *p*-H), 3.25 (sept, $^3J_{HH}$ = 6.7 Hz, 4 H, C*H*Me_2), 1.90 (s, 4 H, $LaCH_2$), 1.22 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, Pr^i Me), 0.81 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, Pr^i Me). ^{13}C NMR (125.7 MHz, THF-d_8, 20 °C): δ 176.8 (N*C*N), 151.2 (Bz C_{ipso}), 146.0 (Ph C_{ipso}), 142.7 (Ar C_{ipso}), 133.1 (Ar C), 131.9 (d, $^1J_{CH}$ = 160.5 Hz, Bz CH), 131.4 (d, $^1J_{CH}$ = 156.5 Hz, Ar CH), 128.7 (d, $^1J_{CH}$ = 160.0 Hz, Ph CH), 127.0 (d, $^1J_{CH}$ = 160.5 Hz, Ph CH), 126.5 (d, $^1J_{CH}$ = 158.8 Hz, Ph CH), 125.7 (d, $^1J_{CH}$ = 154.1 Hz, Ar CH), 124.2 (d, $^1J_{CH}$ = 152.3 Hz, Bz CH), 120.5 (d, $^1J_{CH}$ = 160.7 Hz, Bz CH), 78.3 (t, $^1J_{CH}$ = 130.0 Hz, $LaCH_2$), 30.5 (d, $^1J_{CH}$ = 123.9 Hz, *C*HMe_2), 26.2 (q, $^1J_{CH}$ = 125.6 Hz, Pr^i Me), 24.8 (q, $^1J_{CH}$ = 125.6 Hz, Pr^i Me).

Procedure for Ethylene Polymerization. Polymerizations were performed in a 50 mL glass miniclave (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), $[HNMe_2Ph][B(C_6F_5)_4]$ (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 N_2-filled glovebox. Typically, an NMR tube equipped with a Teflon (Young) valve was charged with the (pre)catalyst (10 μmol), the activator $[PhNMe_2H][B(C_6F_5)_4]$ (10 μmol, where appropriate), ferrocene (as internal standard, 100 μmol), and the aminoalkene substrate 2,2-dimethyl-4-pentenylamine (1000 μmol) dissolved in C_6D_6 or C_6D_5Br (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.

Procedure for the Isomerization of 2,2-Dimethyl-4-pentenylamine. Samples were prepared and examined as described above for the hydroamination/cyclization procedure. Conversions were determined by ^1H NMR following the decrease of the olefinic resonances of the substrate. The product was characterized as (*E*)-2,2-dimethyl-3-pentylamine by ^1H and ^{13}C NMR and GC-MS. Data for (*E*)-2,2-dimethyl-3-pentylamine are as follows. ^1H NMR (500 MHz, C_6D_5Br, 20 °C): δ 5.49 (dq, 1 H, $^3J_{HH}$ = 6.1 Hz, $^3J_{HH}$ = 15.4 Hz, MeC*H*=CH), 5.43 (d, 1 H, $^3J_{HH}$ = 15.4 Hz, MeCH=C*H*), 2.28 (s, 2 H, CH_2NH_2), 1.56 (d, $^3J_{HH}$ = 6.1 Hz, 3 H, *Me*CH=CH), 0.85 (s, 6 H, CMe_2), 0.73 (s, 2 H, NH_2). ^{13}C NMR (125.7 MHz, C_6D_5Br, 20 °C): δ 135.6 (d, $^1J_{CH}$ = 148.2 Hz, MeCH=*C*H), 118.7 (d, $^1J_{CH}$ = 151.0 Hz, Me*C*H=CH), 49.9 (t, $^1J_{CH}$ = 130.7 Hz, CH_2NH_2), 34.2 (s, *C*Me_2) 21.2 (q, $^1J_{CH}$ = 124.6 Hz, C*Me*$_2$), 14.7 (d, $^1J_{CH}$ = 125.0 Hz, *Me*CH=CH). GC-MS: *m*/*z* 113 [M^+].

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Supporting Information Available: CIF files giving crystallographic data for **1a**,**b**, **2**, **3**, **4a′**, and **5b′**, including atomic coordinates, full bond distances, and bond angles as well as anisotropic thermal parameters, and figures giving fits used for determination of rate constants and ^1H NMR spectra of neutral and cationic lanthanum complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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