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Zwitterionic Trivalent (Alkyl)Lanthanide Complexes in Ziegler-type Butadiene Polymerization

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Zwitterionic Trivalent (Alkyl)Lanthanide Complexes in Ziegler-type Butadiene Polymerization

Abstract
The organolanthanide complexes $\text{Ln}\{\text{C(SiMe}_2\text{H)}_3\}_3$ ($\text{Ln} = \text{La, Ce, Pr, Nd}$, 1a-c, 1d) react with one or two equiv. of $\text{B(C}_6\text{F}_5\text{)}_3$ to yield the well-defined zwitterionic species $\text{Ln}\{\text{C(SiMe}_2\text{H)}_3\}_2\text{HB(C}_6\text{F}_5\text{)}_3$ ($\text{Ln} = \text{La, Ce, Pr, Nd}$, 2a-d) or $\text{LnC(SiMe}_2\text{H)}_3\{\text{HB(C}_6\text{F}_5\text{)}_3\}_2$ ($\text{Ln} = \text{La, Ce, Pr, Nd}$, 3a-d), respectively. These complexes are shown to contain labile, bridging Si–H $\rightleftharpoons$ Ln and o-F $\rightarrow$ Ln interactions based upon the observation of low one-bond silicon-hydrogen coupling constants ($^{1}J_{\text{SiH}}$) in $^{1}\text{H}$ NMR spectra of 2a and 3a, the presence of only one set of $\text{C}_6\text{F}_5$ signals in the $^{19}\text{F}$ NMR spectra of 2a and 3a, the detection of only m-F and p-F resonances in $^{19}\text{F}$ NMR spectra of 2b-d and 3b-d, two $\nu_{\text{SiH}}$ bands in IR spectra of 2a-d, and X-ray crystallography analyses of 2b and 3d. In addition, a hexametertoluene molecule is coordinated to neodymium in 3d. Reactions of 1a and (AlMe$_3$)$_2$ yield labile adducts with an approximate stoichiometry of 1a·3AlMe$_3$. Exchange between free and bound AlMe$_3$ groups was observed in EXSY NMR experiments with greater than 3 equiv. of AlMe$_3$. Compounds 2a-d and 3a-d, in the presence of AlBu$_3$, are precatalysts for polymerization of butadiene. The neodymium alkyl 3d has the highest activity of the series, and its performance is consistent with chain transfer reactions with AlBu$_3$.

Keywords
polybutadiene, neodymium alkyl, polymerization, Ziegler catalyst, rare earth

Disciplines
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Abstract. The organolanthanide complexes $\text{Ln}\{\text{C(SiHMe}_2\text{)}_3\}_3$ ($\text{Ln} = \text{La}, \text{1a}; \text{Ce}, \text{1b}; \text{Pr}, \text{1c}; \text{Nd}, \text{1d}$) react with one or two equiv. of $\text{B(C}_6\text{F}_5\text{)}_3$ to yield the well-defined zwitterionic species $\text{Ln}\{\text{C(SiHMe}_2\text{)}_3\}_2\text{HB(C}_6\text{F}_5\text{)}_3$ ($\text{Ln} = \text{La}, \text{2a}; \text{Ce}, \text{2b}; \text{Pr}, \text{2c}; \text{Nd}, \text{2d}$) or $\text{LnC(SiHMe}_2\text{)}_3\{\text{HB(C}_6\text{F}_5\text{)}_3\}_2$ ($\text{Ln} = \text{La}, \text{3a}; \text{Ce}, \text{3b}; \text{Pr}, \text{3c}; \text{Nd}, \text{3d}$), respectively. These complexes are shown to contain labile, bridging Si–H→Ln and o-F→Ln interactions based upon the observation of low one-bond silicon-hydrogen coupling constants ($^1J_{\text{SiH}}$) in $^1\text{H}$ NMR spectra of $\text{2a}$ and $\text{3a}$, the presence of one set of $\text{C}_6\text{F}_5$ signals in the $^{19}\text{F}$ NMR spectra of $\text{2a}$ and $\text{3a}$, the detection of only m-F and p-F resonances in $^{19}\text{F}$ NMR spectra of $\text{2b-d}$ and $\text{3b-d}$, two $v_{\text{SiH}}$ bands in IR spectra of $\text{2a-d}$, and X-ray crystallography analyses of $\text{2b}$ and $\text{3d}$. In addition, a hexahapto-
toluene molecule is coordinated to neodymium in 3d. Reactions of 1a and (AlMe3)2 yield labile adducts with an approximate stoichiometry of 1a·3AlMe3. Exchange between free and bound AlMe3 groups was observed in EXSY NMR experiments with greater than 3 equiv. of AlMe3. Compounds 2a-d and 3a-d, in the presence of Al/iBu3, are precatalysts for polymerization of butadiene. The neodymium alkyl 3d has the highest activity of the series, and its performance is consistent with chain transfer reactions with Al/iBu3.

KEYWORDS. polybutadiene, neodymium alkyl, polymerization, Ziegler catalyst, rare earth

Introduction

Rare-earth metal-based Ziegler-type catalysts are highly active for insertion polymerizations, including the synthesis of polybutadiene with high 1,4-cis content used in high-performance tires.1-3 These catalysts, composed of neodymium salts, alkylating agents, and chloride sources of varying proportions, are typically evaluated on the basis of polymerization outcomes (activity, molecular weight, dispersity, and microstructure). The complex precatalyst mixtures form active species through multistep, and often ambiguous pathways to give highly active, yet poorly defined, species. Despite these complications, several trends have emerged from polymerization studies, and the interpretation of data suggest superior catalysts are monomeric, containing a single, positively charged neodymium center that is coordinated by a reactive chain via multi-hapto interactions involving allyl and olefin moieties. For example, a monomeric neodymium carboxylate precatalyst, formed as a carboxylic acid adduct and mixed with Et2AlCl, iBu2AlH, and Al/iBu3, has significantly enhanced butadiene polymerization activity compared to oligomeric neodymium carboxylates or other salts.4 Second, coordinating ligands such as THF reduce activity and selectivity for cis-1,4-microstructure in butadiene polymerizations catalyzed
by the neodymium versatate/iBu₂AlH/iBuCl mixture, for example. Likewise, competitive coordination between diene and arenes has been proposed on the basis of the influence of aromatic solvents on polymerization activity and polymer microstructure, with higher activity and higher cis-selectivity given by the combination of Nd{N(SiMe₃)₂}₃, [HNMe₂Ph][B(C₆F₅)₄] and Al/iBu₃ for butadiene polymerization in heptane (86% cis-1,4) compared with toluene (70%). Typically, a chloride source is needed to achieve high selectivity for cis-1,4 butadiene enchainment. The formation of multiple sites with inequivalent activities, from neodymium salts, are also proposed on the basis of kinetic studies and multimodal polymer distributions. In addition, the growing polymer chain may transfer from the active site to aluminum, and back to neodymium.

Active Ziegler-type catalytic species may also be accessed from structurally-characterized neodymium tetraalkylaluminate or neodymium allyl compounds, which have metal-carbon bonds and compositions closer to those associated with plausible catalytic structures. For example, the combination of Nd(AlMe₃)₃ and Et₂AlCl provides highly 1,4-cis-selective isoprene polymerization catalysts, postulated to be [MeNdCl₂] or [Me₂NdCl]ₙ and proposed to resemble Ziegler catalysts from Nd(O₂CR)₃/Et₂AlCl/iBu₂AlH/Al/iBu₃ mixtures. In these systems, the presence of Et₂AlCl, as a source of chloride, appears necessary for high cis selectivity. Still, Al/iBu₃ and AlMe₃ present in the Ziegler and model systems, respectively, interact with metal centers with distinct coordination modes that likely influence the species present and catalytic mechanism. For example, dimeric species may be produced from bridging bimetallic alkylaluminates, such as in {Cp*₂La(μ-Et₂AlEt₂)}₂ formed in the substitution reaction of La(AlEt₃)₃ and Cp*H (Cp* = C₅Me₅) to complicate the catalyst activation process. In addition, cationic and dicationic lanthanide allyl species resembles the proposed propagating species,
still require trialkylaluminum to achieve polymerization activity. In this regard, allyl or aluminate moieties present in the precatalyst are difficult to distinguish from end groups resulting from chain-transfer to organoaluminum species and do not clarify the nature of the initiating species.

Homoleptic alkyl compounds, such as Ln(CH₂SiMe₃)₃THF₃, Li₃[LnMe₆], and Ln(AlMe₄)₃, react with Brønsted acids or Lewis acids such as B(C₆F₅)₃ in the presence of ethers to form R₂Ln(L)₄⁺ or RLn(L)₅⁺.15,16 Weaker Lewis acids such as BPh₃ or Al(CH₂SiMe₃)₃, are also sufficiently reactive to abstract alkyl groups in the presence of coordinating ether groups.17 These cationic organolanthanides also catalyze the polymerization of dienes, with dicationic precatalysts having higher activity than monocationic species.11,18 Alternatively, the monomeric, cationic, and donor-solvent-free alkyl lanthanide complex Cp*La{CH(SiMe₃)₂}BPh₄ has been generated by the reaction of Cp*La{CH(SiMe₃)₂}₃ and [PhNMe₂H]BPh₄,19 where BPh₄ is tightly coordinated to the La center. New, well-defined alkyl lanthanide precatalysts and their activation to cationic alkyl species could further advance polymerization chemistry.

The recently described tris(alkyl) complexes of the early lanthanides Ln{C(SiHMe₂)₃}₃ (Ln = La, Ce, Pr, Nd)20 and group 3 (Ln = Y)21 provide a possible entry-point into well-defined zwitterionic organometallic species. The Ln{C(SiHMe₂)₃}₃ compounds are stabilized by non-classical β-Si–H→Ln interactions and are easily synthesized free from coordinating ethereal donor solvents or alkali metal-containing salts. Moreover, these complexes are isostructural across the series, containing similar and small one-bond silicon-hydrogen coupling constants (¹J_SiH), low frequencies for Si–H stretching modes (ν_SiH), and nearly identical solid-state structures determined by X-ray diffraction. The zwitterionic cerium species Ce{C(SiHMe₂)₃}₂HB(C₆F₅)₃, formed by reaction of Ce{C(SiHMe₂)₃}₃ and B(C₆F₅)₃, is isolable.
as an ether-free species.\textsuperscript{22} Related reactions of other Ln\{C(SiHMe\textsubscript{2})\textsubscript{3}\}\textsubscript{3} and B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} could provide well-defined, solvent-free catalysts for olefin or diene polymerization, and the resulting series of cationic, dicationic, or zwitterionic derivatives could provide trends to compare with the trends of Ziegler-type catalyst systems. Here, we report the synthesis and characterization of mono- and dicationic alkyl hydridoborate lanthanide complexes, examine the components needed to access catalysts for polymerization of 1,3-butadiene, and study the features of the most active precatalyst, NdC(SiHMe\textsubscript{2})\textsubscript{3}\{HB(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}\}\textsubscript{2}.

Results and Discussion

Synthesis and characterization of zwitterionic lanthanide dialkyl and monoalkyl species.

Reactions of Ln\{C(SiHMe\textsubscript{2})\textsubscript{3}\}\textsubscript{3} (Ln = La, 1\textsuperscript{a}; Ce, 1\textsuperscript{b}; Pr, 1\textsuperscript{c}; Nd, 1\textsuperscript{d}) and one equiv. of B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} in benzene afford zwitterionic dialkyl species Ln\{C(SiHMe\textsubscript{2})\textsubscript{3}\}\textsubscript{2}HB(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} (2\textsuperscript{a-d}) and 0.5 equiv. of disilacyclobutane \{Me\textsubscript{2}Si–C(SiHMe\textsubscript{2})\textsubscript{2}\}\textsubscript{2} within 30 min. (eq. 1). These products contain a new B–H bond as part of the HB(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} moiety and the head-to-tail dimer of two Me\textsubscript{2}Si=C(SiHMe\textsubscript{2})\textsubscript{2}. Together, these groups represent parts of a C(SiHMe\textsubscript{2})\textsubscript{3} ligand, and their formation is consistent with abstraction of a hydride from a β-SiH rather than alkyl group abstraction that would form [(Me\textsubscript{2}HSi)\textsubscript{3}C–B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}]\textsuperscript{−}. The zwitterionic species 2\textsuperscript{a-d} are isolated in good yields by evaporating the volatile components and washing 2 with pentane.
The $^1$H NMR spectrum of a micromolar scale reaction of $1a$ and B(C$_6$F$_5$)$_3$ in benzene-$d_6$ indicated quantitative conversion to $2a$ in < 5 min. New signals at 4.45 (6 H, SiH, $^1J_{	ext{SiH}} = 135$ Hz) and 0.21 ppm (36 H, SiMe$_2$, $^3J_{	ext{HH}} = 3.4$ Hz) were assigned to $2a$, and peaks at 4.68, 0.56 and 0.18 ppm matched reported assignments for disilacyclobutane.$^{23}$ The SiHMe$_2$ signals of $2a$ and disilacyclobutane integrated in a 3:1 ratio and suggested that two alkyl groups remained bonded to the lanthanum center. The $^1$H NMR spectrum of isolated $2a$ in benzene-$d_6$ contained alkyl signals equivalent to those from in situ generation. The $^1J_{	ext{SiH}}$ of 135 Hz for $2a$ is similar to that of $1a$ (135 vs 137 Hz). In $1a$, the process exchanging bridging and terminal SiH groups becomes slower than the NMR timescale below 220 K, giving two signals for the SiH and three signals for the SiMe$_2$. In contrast, the SiHMe$_2$ of $2a$ appeared equivalent by NMR even at 190 K. The $^{29}$Si{${^1}$H} NMR signal of $2a$ at −11.2 ppm was only slightly lower frequency than in $1a$ (−13.1 ppm). The $^{11}$B NMR spectrum in benzene-$d_6$ of $2a$ revealed a doublet at −18 ppm ($^1J_{	ext{BH}} = 68$ Hz), confirmed the presence of the hydridoborate moiety, and suggested a bridging Ln–H–B interactions. For comparison, the $^{11}$B NMR signal for an outer-sphere hydridoborate in [Cp$_2$ZrN(SiHMe$_2$)$_2$][HB(C$_6$F$_5$)$_3$] appeared at −24.8 ppm ($^1J_{	ext{BH}} = 91$ Hz).$^{24}$ Three $^{19}$F signals were observed at −133.6 ppm (6 F, o-C$_6$F$_5$), −156.0 ppm (3 F, p-C$_6$F$_5$), and −161.0 ppm (6 F, m-C$_6$F$_5$). The observed $\Delta\delta$ between $m$-F and $p$-F signals $>3$ ppm also provides support for the coordination of the hydridoborato ligand to the lanthanide center.$^{25}$

The $^1$H NMR spectra for paramagnetic $2b$-$d$ each contained a single, broad peak for the SiMe$_2$ group (Table 1). Possible $^1$H NMR signals for the SiH group, as well as peaks in the $^{29}$Si{${^1}$H} NMR spectra, were not detected in these paramagnetic complexes. In contrast, $^1$H NMR spectra of paramagnetic tris(alkyl) lanthanides $1b$-$d$ (at room temperature) revealed peaks both for SiMe$_2$ and SiH. The difference between $1b$-$d$ and $2b$-$d$, in terms of SiH signals, is likely related
to the rate of exchange between bridging LnOH-Si and non-bridging H-Si groups. These two moieties are present in both 1 and 2, with similar average $J_{\text{SiH}}$ (for 1a and 2a, see above); however, distinct signals for bridging and terminal SiHMe$_2$ groups were detected for 1a in low temperature $^1$H NMR spectra, whereas exchange in 2a cannot be resolved. $^{11}$B NMR signals were broad and the chemical shifts appeared outside the expected region for HB(C$_6$F$_5$)$_3$ in a diamagnetic environment. The $^{19}$F NMR spectra of 2b-d each showed two signals, assigned to $m$-F and $p$-F, with similar chemical shifts as in the spectrum of diamagnetic 2a. The $^{19}$F NMR (and the $^1$H and $^{11}$B NMR) signals present in the spectra of 2a, but not for 2b-d, suggest the C$_6$F$_5$, BH, and SiH moieties have significant interactions with the paramagnetic center. This idea is also consistent with the spectroscopic data for 2a, as well as the IR spectra and solid-state structure of 2b (below).

Table 1. NMR chemical shifts of 1b-d, 2b-d, and 3b-d acquired in benzene-$d_6$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^1$H NMR SiMe</th>
<th>$^{11}$B NMR</th>
<th>$^{19}$F NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>m-F</td>
<td>p-F</td>
</tr>
<tr>
<td>Ce{C(SiHMe$_2$)$_3$}$_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ce{C(SiHMe$_2$)$_3$}$_2$HB(C$_6$F$_5$)$_3$</td>
<td>1b</td>
<td>1.0</td>
<td>--</td>
</tr>
<tr>
<td>CeC(SiHMe$_2$)$_3${HB(C$_6$F$_5$)$_3$}$_2$</td>
<td>2b</td>
<td>3.99</td>
<td>$-45$</td>
</tr>
<tr>
<td>Pr{C(SiHMe$_2$)$_3$}$_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pr{C(SiHMe$_2$)$_3$}$_2$HB(C$_6$F$_5$)$_3$</td>
<td>1c</td>
<td>2.2</td>
<td>--</td>
</tr>
<tr>
<td>PrC(SiHMe$_2$)$_3${HB(C$_6$F$_5$)$_3$}$_2$</td>
<td>2c</td>
<td>10.11</td>
<td>$-68$</td>
</tr>
<tr>
<td>Nd{C(SiHMe$_2$)$_3$}$_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd{C(SiHMe$_2$)$_3$}$_2$HB(C$_6$F$_5$)$_3$</td>
<td>1d</td>
<td>1.8</td>
<td>--</td>
</tr>
<tr>
<td>NdC(SiHMe$_2$)$_3${HB(C$_6$F$_5$)$_3$}$_2$</td>
<td>2d</td>
<td>5.63</td>
<td>$-4$</td>
</tr>
<tr>
<td>3b-d</td>
<td>3d</td>
<td>8.29</td>
<td>25</td>
</tr>
</tbody>
</table>

$^a$From references 20 and 22.

Infrared spectroscopy is also helpful for characterization and for comparing diamagnetic and paramagnetic compounds (Table 2). The IR spectra (KBr) of 2a-d contained bands in the ranges of 2109–2117 cm$^{-1}$ and 1787–1795 cm$^{-1}$, assigned to stretching modes of classical Si–H and non-classical Si–H$\rightarrow$Ln interactions, respectively. The latter bands appeared at lower energy than
those in the neutral starting materials 1a-d. In addition, 2255–2268 cm\(^{-1}\) bands in the IR spectra of 2a-d were assigned to B-H stretching modes. These assignments were supported by IR spectra of the labeled isotopologues Ln\{C(SiDMe\(_2\))\}_3DB(C\(_6\)F\(_5\))\(_3\) (2-d\(_7\)), which were synthesized by reaction of Ln\{C(SiDMe\(_2\))\}_3 (1-d\(_9\)) and B(C\(_6\)F\(_5\))\(_3\) and which lacked bands at \(~2110, 1790,\) and 2260 cm\(^{-1}\). In the spectra of the labeled species, signals at \(~1530, ~1310,\) and 1100 cm\(^{-1}\) were tentatively assigned to \(\nu_{B-D}\) and \(\nu_{Si-D}\) from classical Si–D and non-classical Ln\(\leftrightarrow\)D–Si; these signals were not present in the spectra of 2. In general, the similar spectra for 2a-d, acquired in the solid state, suggest that the four zwitterionic species adopt closely related structures. Comparisons with NMR spectroscopy indicate that Si–H\(\leftrightarrow\)Ln interactions persist in both solid state and in solution, and that exchange between classical Si–H and non-classical Si–H\(\leftrightarrow\)Ln is slow on the IR timescale but rapid on the \(^1\)H NMR timescale.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Classical (\nu_{SiH}) (cm(^{-1}))</th>
<th>Non-classical (\nu_{SiH}) (cm(^{-1}))</th>
<th>(\nu_{BH}) (cm(^{-1}))</th>
<th>(\delta_{SiH}) (ppm)</th>
<th>(^1J_{SiH}) (Hz)</th>
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<tr>
<td>La</td>
<td>2108</td>
<td>1829</td>
<td>2263</td>
<td>4.26</td>
<td>137</td>
</tr>
<tr>
<td></td>
<td>2109</td>
<td>1787</td>
<td>2252</td>
<td>4.45</td>
<td>135</td>
</tr>
<tr>
<td></td>
<td>2106</td>
<td>--</td>
<td>2252</td>
<td>4.28</td>
<td>135</td>
</tr>
<tr>
<td>Ce</td>
<td>2107</td>
<td>1829</td>
<td>2268</td>
<td>5</td>
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</tr>
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</tr>
<tr>
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<td>2117</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Pr</td>
<td>2108</td>
<td>1829</td>
<td>2255</td>
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<tr>
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<td>2114</td>
<td>1792</td>
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<td>2111</td>
<td>--</td>
<td>2257</td>
<td>--</td>
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<td>Nd</td>
<td>2108</td>
<td>1829</td>
<td>2258</td>
<td>28</td>
<td>--</td>
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<tr>
<td></td>
<td>2113</td>
<td>1795</td>
<td>2257</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

These interpretations of the spectroscopic data, particularly the presence of Si–H\(\leftrightarrow\)Ln, the formation of HB(C\(_6\)F\(_5\))\(_3\), and the 2:1 ratio of C(SiHMe\(_2\))\(_3\):HB(C\(_6\)F\(_5\))\(_3\), are supported by a single
crystal X-ray diffraction study of \(2b\) (CCDC: 1507398, previously communicated).\(^{22}\) The crystallographic analysis further indicates that four of the six SiHMe\(_2\) groups form Si–H→Ce interactions, and two of the three perfluorophenyl groups coordinate through \(\sigma\)-F→Ce interactions \(\text{Ce1–F1}, 2.610(1); \text{Ce1–F6}, 2.584(1) \text{Å}\). The H1b is also pointed toward the cerium center, as suggested by the \(^{11}\)B NMR spectrum of \(2a\), to create a tripodal \(\mu\)-H,F,F-ligand.

Reactions of \(1a\text{-}d\) and two equiv. of B(C\(_6\)F\(_5\))\(_3\) in benzene form the mono(alkyl) species \(\text{LnC(SiHMe}_2)_3\{\text{HB(C}_6\text{F}_5)_3\}_2\) (3a-d) and one equiv. of disilacyclobutane, as indicated by integration of \(^1\)H NMR spectrum of the crude reaction mixture for diamagnetic 3a (eq. 2).

\[
\begin{align*}
\text{Ln} &= \text{La 1a} \\
& \quad \text{Ce 1b} \\
& \quad \text{Pr 1c} \\
& \quad \text{Nd 1d} \\
\text{Me}_2\text{HSi} &+ 2 \text{B(C}_6\text{F}_5)_3 \\
\text{benzene} &\xrightarrow{\text{r.t., 30 min}} \\
\text{Me}_2\text{HSi} &+ \text{Me}_2\text{Si} \\
& \quad \text{Ln} = \text{La 3a (91%)} \\
& \quad \text{Ce 3b (62%)} \\
& \quad \text{Pr 3c (76%)} \\
& \quad \text{Nd 3d (85%)}
\end{align*}
\]

The \(^1\)H NMR spectrum of isolated 3a contained two signals. A multiplet at 4.28 ppm (3 H, \(^1J_{\text{SiH}} = 135 \text{ Hz}\)) and a doublet at –0.04 ppm (18 H, \(^3J_{\text{HH}} = 3.6 \text{ Hz}\)) were assigned to the SiH and SiMe\(_2\) groups, respectively. During isolation, prolonged drying of the sample to remove benzene or pentane leads to minor decomposition to unidentified species (which are not the hydrolysis product HC(SiHMe\(_2\))\(_3\)). The \(^{29}\)Si NMR chemical shift of –10.3 ppm, determined through a \(^1\)H-\(^{29}\)Si HMBC experiment, was slightly upfield from those of 2a (–11.2 ppm) and 1a (–13.1 ppm). The \(^{11}\)B NMR spectrum showed an intense doublet at –17.7 ppm, and the one-bond boron–hydrogen coupling constant \(^1J_{\text{BH}} = 58.4 \text{ Hz}\) was 10 Hz lower than the observed H-B coupling in 2a. The \(^{19}\)F NMR spectrum contained three broad signals at –136.2 ppm (12 F, \(\sigma\)-C\(_6\)F\(_5\)), –
160.0 ppm (6 F, \( p\)-C\(_6\)F\(_5\)), and –164.3 ppm (12 F, \( m\)-C\(_6\)F\(_5\)), which suggested that all C\(_6\)F\(_5\) groups are exchanging rapidly at room temperature. As in 2a, the >3 ppm \( \Delta\delta \) between \( m\)-F and \( p\)-F signals was consistent with coordination of the hydridoborate ligand to the lanthanide center.\(^{25}\)

The \(^1\)H NMR spectra of the paramagnetic complexes 3b-d each showed one broad peak assigned to the SiMe\(_2\) group (Table 1). As for 2b-d, SiH signals were not detected in \(^1\)H NMR spectra of 3b-d. The \(^{11}\)B NMR spectra of 3b and 3d revealed paramagnetically shifted, broad singlets that are ~35 ppm downfield of the corresponding signal in 2b and 2d (a \(^{11}\)B NMR signal for praseodymium analogue 3c was not detected). The \(^{19}\)F NMR spectra of 3b-d each contained two peaks assigned to \( m\)-F and \( p\)-F groups. These signals are downfield of the corresponding signals in 2b-d, by 1 ppm (\( m\)-F) and 3 ppm (\( p\)-F) and in the same range as in the \(^{19}\)F NMR spectrum of diamagnetic 3a. The observation of \( o\)-F by \(^{19}\)F NMR in 3a and the absence of this signal for 3b-d could also be explained by fluxional \( o\)-F\( \rightarrow \)Ln interactions, similar to 2b-d. These \(^{11}\)B and \(^{19}\)F NMR studies also suggested that HB(C\(_6\)F\(_5\))\(_3\) was associated with the lanthanide center in toluene-\( d_8\) or benzene-\( d_6\) (see below). Interestingly, the IR spectra for 3a-d each contained only one band between 2100-2120 cm\(^{-1}\) for SiH stretching mode and one band between 2252-2263 cm\(^{-1}\) assigned to B-H stretching mode. The lower frequency SiH band observed in 1a-d and 2a-d was not detected in 3a-d.

A single crystal X-ray diffraction study of 3d reveals neodymium coordinated by one C(SiHMe\(_2\))\(_3\), two HB(C\(_6\)F\(_5\))\(_3\), and one toluene ligand (Figure 1). The tris(dimethylsilyl)methyl ligand bonds to Nd through the C1, and two secondary Si–H\( \rightarrow \)Nd interactions are suggested by the conformation of the ligand and short Nd\( \cdots\)Si interatomic distances. The Nd1–C1 distance of 2.514(9) Å in 3d is 0.11 Å shorter than that of the average Nd–C distance (2.639(5) Å) in 1d. The two Si–H\( \rightarrow \)Nd agostic-like interactions were determined by the short Nd\( \cdots\)Si interatomic
distances, Nd1···Si1 (3.135(3) Å) and Nd1···Si2 (3.102(3) Å), which are slightly shorter than the average Nd···Si distance of the six Si–H→Ln in neutral 1d (3.152 ± 0.01 Å, ranging from 3.1349(9) to 3.1727(8) Å). In addition, the ∠Nd1–C1–Si1 and ∠Nd1–C1–Si2 are 87.6(1) and 89.1(1)°, respectively, in 3d for bridging Si–H→Nd groups and are similar to those in 1d (average ∠Nd–C–Si, 88.2 ± 0.5°). Note that although these geometric parameters only indirectly suggest Si–H→Nd interactions, this approach is needed for the analysis because SiH were placed in calculated positions. However, similar parameters have been observed in crystal structures where bridging H are objectively located (subject to the uncertainties locating a H atom in the vicinity of a heavy element center by X-ray crystallography) and supported by NMR and IR spectroscopy. One of the HB(C₆F₅)₃ is coordinated to Nd in a H,F,F-tridentate manner, while the second hydroborate binds via a bidentate H,F mode. The first HB(C₆F₅)₃ coordinates with Nd1–F24 and Nd1–F30 distances of 2.857(6) and 2.616(6) Å, respectively, while the second binds with the Nd1–F60 internuclear separation of 2.600(7) Å. Considering the effect of the lanthanide contraction (the ionic radius of Nd(III) is ~0.034 Å smaller than Ce(III)), these distances are effectively longer than Ce–F distances for 2b.22

The distances between Nd1 and the aromatic carbons of the toluene ligand (C70 to C75) range between 2.954(1) and 3.026(1) Å (Nd-C_{ave} = 2.90 Å) indicating hexahapto coordination. Only one toluene molecule is coordinated to Nd1. While additional toluene ligands do not displace the HB(C₆F₅)₃ to generate solvent-separated ion pairs, one HB(C₆F₅)₃ coordinates in the bidentate mode noted above. A few classes of trivalent rare earth arene compounds have been reported, including tetrachloroaluminates first prepared by Cotton and later expanded to include a range of lanthanide and arene combinations, such as (η⁶-C₆H₆)Nd(AlCl₄)₃ (Nd-C_{ave} = 2.90 Å).31 Arene compounds containing alkyltrichloroaluminates, such as (η⁶-C₆H₆)Nd(AlMeCl₃)₃ (Nd-C_{ave}
= 2.96 Å), are also effective precatalysts for butadiene polymerization (upon activation with diisobutylaluminum hydride or dibutylmagnesium) that give comparable activities to the neodymium carboxylates.\(^{32}\) Crystallographically characterized rare earth compounds containing an alkyl and a coordinated arene are rare, and the \textit{cis}-disposed toluene and alkyl ligands in compound 3d provide likely models of coordination sites for monomers and the growing

\textbf{Figure 1.} Thermal ellipsoid plot of NdC(SiMe$_2$)$_3$\{HB(C$_6$F$_5$)$_3$\}$_2$·C$_6$H$_5$Me (3d·C$_6$H$_5$Me) at 25% probability. The H atoms included in the image are bonded to either Si or B and were objectively
located in the Fourier difference map. All other H atoms and non-bridging F atoms were omitted for clarity. Dotted lines highlight short Nd–H distances.

polymer chain. In this context, we note that the silyl groups in the -C(SiHMe₂)₃ ligand are oriented to create space for the toluene ligand. For comparison, a cationic scandium methyl compound, supported by a β-diketiminato ligand and a precatalyst for ethylene polymerization, coordinates bromobenzene via a hexahapto interaction in a site adjacent to the methyl ligand, while a few cationic group 4 and thorium organometallic arene compounds have been reported. Attempts to isolate 1,3-diene-coordinated analogues of 3d have not yet been successful, and for now, toluene is considered a surrogate for coordinated diene in the active catalyst.

Neutral arene compounds of the type (η⁴-C₆H₅Me)Ln{N(C₆F₅)₂}₃ (Ln = Ce, Nd), also contain Ln←F, but in contrast, involve unsymmetrical coordination of toluene. For example, the Nd–C distances range from 2.98(2) to 3.17(1) Å for the bonding carbon, while the other two Nd–C distances are longer (3.31(1) and 3.32(1) Å).

Attempts to make tris(hydridoborate)-lanthanide species via the addition of a third equiv. of B(C₆F₅)₃ to 1a-d yield 3a-d and one equiv. of unreacted B(C₆F₅)₃. Thus, the remaining alkyl is inert toward β-SiH abstraction and displacement by this strong Lewis acid.

**Butadiene Polymerization.** Compounds 2a-d and 3a-d, generated from in situ reactions of 1a-d and 1 or 2 equiv. of B(C₆F₅)₃, respectively, form precatalysts for the polymerization of butadiene upon addition of triisobutylaluminum (eq. 3, Table 3). Mixtures of neutral 1a-d and butadiene (20 psi) heated at 60 °C for 15 min., with or without Al/iBu₃, do not yield polybutadiene. Reactions of 2a-d or 3a-d and butadiene under conditions without Al/iBu₃ also do not afford isolable polybutadiene. This behavior is similar to that of other cationic or dicationic
organometallic precatalysts such as \([\text{Ln}(\eta^3-\text{C}_3\text{H}_5)_2\text{THF}_3][\text{B}(\text{C}_6\text{F}_5)_3]\) (Ln = Y, La, Nd).\(^{11}\) The species, 3d, shows an activity (defined here as the mass of isolated polybutadiene per mol Nd per hour) of \(2.1 \times 10^5\) g polybutadiene·(mol Nd·h)\(^{-1}\), in a similar range as the industrial Ziegler-type neodymium versatate (NdV\(_3\)) precatalyst (ca. \(2 - 3 \times 10^5\) g polybutadiene·(mol Nd·h)\(^{-1}\)). Compound 3d is less active than monomeric versatic acid adduct NdV\(_3\)·HV.\(^4\)

\[
\begin{align*}
\text{20 psi} & \quad \text{Ln(C(SiMe3)3)}_3 + a \text{ B(C6F5)}_3 + 10 \text{ AlBu3} \\
\text{60 \degree C, toluene, 15 or 30 min.} & \quad \text{1,4-cis} \quad \text{1,4-trans} \quad \text{1,2-vinyl} \\
\text{Ln} & = \text{La, Ce, Pr, or Nd} \\
a & = 1 \text{ or 2 equiv.}
\end{align*}
\]

Table 3. Polymerization of 1,3-Butadiene\(^{[a]}\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Complex</th>
<th>Yield(^{[b]})</th>
<th>Activity(^{[c]})</th>
<th>Microstructure(^{[d]})</th>
<th>(M_n)</th>
<th>(M_w)</th>
<th>(M_w/M_n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2a</td>
<td>0.81</td>
<td>1220(^{[g]})</td>
<td>67.9/27.9/4.2</td>
<td>114.5</td>
<td>201.5</td>
<td>1.76</td>
</tr>
<tr>
<td>2</td>
<td>2b</td>
<td>0.63</td>
<td>1920</td>
<td>50.0/47.1/2.9</td>
<td>41.5</td>
<td>68.1</td>
<td>1.64</td>
</tr>
<tr>
<td>3</td>
<td>2c</td>
<td>0.99</td>
<td>1500(^{[g]})</td>
<td>47.2/50.0/2.8</td>
<td>28.1</td>
<td>44.7</td>
<td>1.59</td>
</tr>
<tr>
<td>4</td>
<td>2d</td>
<td>0.99</td>
<td>2990</td>
<td>47.7/49.3/3.0</td>
<td>81.5</td>
<td>123.0</td>
<td>1.51</td>
</tr>
<tr>
<td>5</td>
<td>3a</td>
<td>0.59</td>
<td>900(^{[g]})</td>
<td>65.2/30.7/4.1</td>
<td>68.5</td>
<td>108.2</td>
<td>1.58</td>
</tr>
<tr>
<td>6</td>
<td>3b</td>
<td>0.95</td>
<td>2880</td>
<td>60.7/36.0/3.3</td>
<td>66.2</td>
<td>126.4</td>
<td>1.91</td>
</tr>
<tr>
<td>7</td>
<td>3c</td>
<td>1.01</td>
<td>1540(^{[g]})</td>
<td>52.3/44.1/3.6</td>
<td>93.5</td>
<td>180.5</td>
<td>1.93</td>
</tr>
<tr>
<td>8</td>
<td>3d</td>
<td>1.16</td>
<td>3520</td>
<td>61.0/35.9/3.1</td>
<td>142.1</td>
<td>268.6</td>
<td>1.89</td>
</tr>
</tbody>
</table>

\(^{[a]}\) Conditions: 0.022 mmol 1a-d and 1 or 2 equiv. of B(C\(_6\)F\(_5\))\(_3\), 0.22 mmol AlBu\(_3\), 12 mL toluene, 20 psi butadiene (maintained by addition of gas every 3 min.), 60 \degree C, 15 min. \(^{[b]}\) Isolated polymer (in g). \(^{[c]}\) (g polybutadiene)·(mole Ln)\(^{-1}\)·min\(^{-1}\). \(^{[d]}\) 1,4-cis:1,4-trans:1,2-vinyl ratio, determined by IR analysis. \(^{[e]}\) \(\times 10^3\) g·mol\(^{-1}\). \(^{[f]}\) Determined by GPC vs PS standards. \(^{[g]}\) 30 min.
A few general observations come from the data in Table 3. First, the trend in activity is Nd > Ce >> Pr > La for both 2a-d and 3a-d series of catalysts. The significantly higher activity of Nd and Ce catalysts compared to La and Pr species is reflected in doubled reaction times (15 vs 30 min.) needed to acquire similar quantities of polybutadiene product. The lower activity of the praseodymium-based catalysts contrasts its typical higher performance than cerium in Ziegler-type systems. Overall, variation of the lanthanide affects the catalytic performance (in terms of activity) more than switching between dialkyl or monoalkyl precatalyst for a particular lanthanide ion; however, GPC data clearly indicate that precatalysts 2 and 3 provide distinct active species (see below). For the less active lanthanum- and praseodymium-based catalysts, the activities of monocationic species are similar or higher to that of the dicationic analogue 3a or 3c. The cerium and neodymium-based dicationic catalysts 3b-d, in contrast, are significantly more active under these conditions than their corresponding monocationic 2b-d species. For comparison, cationic diallyl lanthanum and neodymium compounds [Ln(η3-C3H5)2THF]2[B(C6F5)4] are only slightly less active than the dicationic species formed by addition of [HNPhMe2][B(C6F5)4]. Alternatively, the catalyst Nd(AlMe4)3 and one equiv. of [HNPhMe2][B(C6F5)4] doubles the yield of polyisoprene compared with the catalyst generated with two equiv. of anilinium perfluorophenylborate.

These polymerizations were performed with approximately constant pressure and concentration of butadiene to maintain steady-state conditions in order to standardize comparisons between the metal centers and dialkyl and monoalkyl species, mitigate side reactions favored at lower butadiene concentrations in more active catalysts, and mimic large excesses of butadiene at the early stages in commercial polymerizations. In addition, butadiene is added as a gas to the pre-heated catalyst mixture so that initiation will be fast. A downside of this
approach is that conversion of monomer, as well as the ratio of monomer/catalyst, cannot be determined, thus preventing estimation of number of chains per lanthanide site. Under these conditions, high activity and high $M_n$ together suggest a larger number of fast growing chains (e.g., catalyst 3d), whereas low activity and high $M_n$ suggest fewer reactive sites and/or slow chain transfer or termination relative to propagation (e.g., catalyst 2a). Both cerium catalysts 2b and 3b provide relatively low $M_n$ and high activity, which is consistent with fast insertions and fast chain transfer. Thus, rates (and possibly mechanisms) and relative rates of initiation, propagation, and termination vary between catalysts 2a-d and 3a-d.

The GPC data reveal monomodal distributions with good molecular weight dispersity ($D$ or $M_w/M_n$) ranging from 1.5 to 2 for all dialkyl and monoalkyl lanthanide precatalysts, and all the polymers produced under these conditions were soluble (no gel formation). The lowest dispersity (1.51) is obtained under these conditions with dialkyl neodymium 2d, which also reacts with reasonably high activity; thus, extended reaction times might produce higher molecular weight polybutadiene with low $D$. Higher molecular weight polymer is obtained from 3d, accompanied by higher $D$.

Although there are no overall trends relating the catalyst’s activity, polymer microstructure, molecular weight, and dispersity, we noticed a few features of the polymerizations. First, the more active species for each lanthanide (either monoalkyl or dialkyl) provides polybutadiene with slightly higher dispersity and slightly improved 1,4-cis selectivity. In general, 1,4-based insertions dominate the microstructure, and lower 1,4-cis stereochemistry accompanies higher 1,4-trans content. The (low) vinyl content is similar for polybutadiene produced in reactions catalyzed by 2b-d and 3b-d (~3%), whereas lanthanum-based 2a and 3a react with slightly higher amount of 1,2-insertion (4%). Both 2a and 3a also afford polybutadiene with the highest
1,4-cis content, praseodymium-based 2c and 3c both give polymer with a low percentage of 1,4-cis groups, while the monoalkyl cerium 3b and neodymium 3d catalysts give ca. 10% higher 1,4-cis selectivity than their dialkyl analogues.

Of the series of dialkyl and monoalkyl early lanthanides in combination with 10 equiv. of \( \text{Al}i\text{Bu}_3 \), the neodymium monoalkyl 3d provides the most active catalyst for polymerization of butadiene. Further experiments probe the reactivity of 3d, using lower concentrations of catalyst to give better reproducibility and less gel formation at longer reaction times. We attribute gel formation to ultra-high molecular weight polybutadiene. This assignment is based in part on the appearance of gels at later stages of the polymerization and on similarity of solid-state \(^{13}\text{C}\) NMR spectra under magic angle spinning (MAS) of the insoluble gels and soluble (but precipitated) polybutadiene rubbers obtained from 3d-catalyzed polymerizations (see Figure S55 for solid-state \(^{13}\text{C}\) NMR spectra). In this context, we note that the rates of likely steps involved in these polymerizations (insertion, isomerization, chain transfer) change as a function of reactant concentrations to affect activity, molecular weight and dispersity of the polymer product, and microstructure. Thus, direct comparisons of reaction outcomes are most meaningful between experiments with nearly identical polymerization conditions.

First, a series of polymerization experiments quenched at 5, 10, 15, 20, and 30 min. show that the molecular weight (\( M_n \)) increases in a nearly linear fashion over this time period (Table 4, Figure 2). Although the rate (activity) is lower under these diluted conditions with 10 equiv. of \( \text{Al}i\text{Bu}_3 \), the dispersity is close to 1. \( M_w/M_n \), however, is below 1.5 only during the first 20 min., and insoluble materials (gels) are formed at reaction times >30 mins. Even though the pressure of butadiene is kept constant in these experiments, its effective concentration at the active neodymium site likely decreases at longer reaction times due to the long chains and viscous
reaction media. The change in reaction media likely affect activity, polymer microstructure, and apparent molecular weight.

**Table 4.** Polymerization of 1,3-Butadiene by NdC(SiMe₂)₃{HB(C₆F₅)₃}₂ (3d)[a]

<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>5</td>
<td>0.155</td>
<td>2816</td>
<td>62/37/1</td>
<td>18.3</td>
<td>21.1</td>
<td>1.15</td>
</tr>
<tr>
<td>10</td>
<td>0.224</td>
<td>2034</td>
<td>49/50/1</td>
<td>61.2</td>
<td>69.1</td>
<td>1.13</td>
</tr>
<tr>
<td>15</td>
<td>0.233</td>
<td>1411</td>
<td>50/49/1</td>
<td>83.1</td>
<td>115</td>
<td>1.38</td>
</tr>
<tr>
<td>20</td>
<td>0.380</td>
<td>1725</td>
<td>58/41/1</td>
<td>120.2</td>
<td>135</td>
<td>1.12</td>
</tr>
<tr>
<td>30</td>
<td>0.637</td>
<td>1930</td>
<td>75/24/1</td>
<td>192.1</td>
<td>402</td>
<td>2.09</td>
</tr>
</tbody>
</table>

[a] Conditions: 0.011 mmol 1d; 0.022 mmol B(C₆F₅)₃, 0.11 mmol Al/Bu₃, 12 mL toluene, 15-20 psi butadiene (maintained by addition of gas every 3 min.), 60 °C. [b] Isolated polymer (in g). [c] (g polybutadiene)·(mole Ln)⁻¹·min⁻¹. [d] 1,4-cis:1,4-trans:1,2-vinyl ratio, determined by IR analysis. [e] × 10³ g·mol⁻¹. [f] Determined by GPC vs PS standards.
Figure 2. Plot of number averaged molecular weight ($M_n$) and dispersity ($M_w/M_n$) versus time for 3d-catalyzed butadiene polymerizations (10 equiv. of Al Bu₃).

Polymerization experiments with increased Al Bu₃ concentration result in decreased molecular weights of the polybutadiene product (Table 5, Figure 3), which is consistent with transfer of active chains from neodymium to aluminum, which serves as a chain transfer agent (CTA). In Ziegler-type systems (NdV₃/Al Bu₃/Et₃Al₂Cl₃), increasing
Al/iBu₃ reduces the polybutadiene molecular weight and the dispersity.⁴² Reversible exchange of chains between neodymium and aluminum, more generally known as coordinative chain transfer polymerization (CCTP),⁴³ is proposed to account for these trends.⁸,⁴² However, Landis and co-workers have pointed out that a hafnium-catalyzed α-olefin polymerization system, which includes a similar molecular weight regulation as in the Ziegler-type butadiene polymerization, is also effectively described by an irreversible chain transfer model (see below).⁴⁴,⁴⁵ In the present polybutadiene system, low D and a linear relationship between conversion and Mₙ is more consistent with reversible chain transfer; however, the higher D and gel formation at longer reaction times cannot rule out slower polymeryl transfer from active neodymium to dormant aluminum species with longer chains.

In addition, the dispersity decreases as the concentration of Al/iBu₃ increases (once full activity is achieved at [Al/iBu₃]/[3d] = 20). We postulate that the variation of activity and D with changing [Al/iBu₃] reflects competition between rates of insertion and chain transfer. In the experiment with 10 equiv. of Al/iBu₃ (Table 5, entry 2), per site insertion is much faster than chain transfer to give long chains and low D. The low concentration of Al/iBu₃ here and in entry 1 does not give maximum activity of 3d (with this lower 3d concentration, see below). With the higher concentration of Al/iBu₃ in entry 3, the D increases. We attribute this to the rate exchange of isobutyl for polybutadienyl bonded to neodymium competing with insertion, resulting in a broader molecular weight distribution. Alternatively, the rates of transfer of polymerylaluminum to active neodymium sites (i.e., back transfer) may compete with isobutylaluminum transfer to neodymium (i.e., chain transfer) at certain concentrations of polymerylAlX₂ and Al/iBu₃, and this
would also lead to broader $D$. The $D$ decreases in experiments with even higher concentration of alkylaluminum species, which is consistent with either (or both) of these mechanistic models.

Table 5. Effect of Al/iBu$_3$ co-catalyst concentration on 3d-catalyzed butadiene polymerization.$^{[a]}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>[Al]/[Nd]</th>
<th>Yield$^{[b]}$</th>
<th>Activity$^{[c]}$</th>
<th>Microstructure$^{[d]}$</th>
<th>$M_n^{[e],[f]}$</th>
<th>$M_w^{[e],[f]}$</th>
<th>$M_w/M_n^{[f]}$</th>
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<tr>
<td>1</td>
<td>5</td>
<td>0.020</td>
<td>104</td>
<td>16/79/5</td>
<td>&lt;1.0$^{[g]}$</td>
<td>&lt;1.0$^{[g]}$</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>0.233</td>
<td>1411</td>
<td>50/49/1</td>
<td>82.2</td>
<td>115</td>
<td>1.38</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>0.530</td>
<td>3212</td>
<td>56/42/2</td>
<td>31.2</td>
<td>89.4</td>
<td>2.86</td>
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<tr>
<td>4</td>
<td>50</td>
<td>0.527</td>
<td>3195</td>
<td>60/38/2</td>
<td>12.8</td>
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<td>5</td>
<td>100</td>
<td>0.534</td>
<td>3236</td>
<td>55/42/3</td>
<td>5.74</td>
<td>9.57</td>
<td>1.67</td>
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</table>

[a] Conditions: 0.011 mmol 1d, 0.022 mmol B(C$_6$F$_5$)$_3$, $n$ equiv. Al/iBu$_3$, 12 mL toluene, 15-20 psi butadiene (maintained by addition of gas every 3 min), 60 °C, 15 min. [b] Isolated polymer (in g). [c] (g polybutadiene)/(mol Nd)$^{-1}$·min$^{-1}$. [d] 1,4-cis:1,4-trans:1,2-vinyl ratio, determined by IR analysis. [e] × 10$^3$ g·mol$^{-1}$. [f] Determined by GPC vs PS standards. [g] Oligomer formation with $M_w$ below detection limit.

In these experiments, the 1,4-cis-content of the polybutadiene microstructure varies from ca. 40% to 75%, whereas Ziegler-type carboxylate catalysts give greater than 90% selectivity in the presence of a chloride source, such as iBu$_2$AlCl or Al$_2$Et$_3$Cl,$^8$ or using the NdCl$_3$ precatalyst.$^{40}$ Unfortunately, 3d is not an active catalyst for butadiene polymerization with 10 or 50 equiv. of iBu$_2$AlCl, or with a 9:1 mixture of Al/iBu$_3$:iBu$_2$AlCl, and this chloride-addition approach is not effective for accessing polybutadiene with high 1,4-cis content with 3d. Combination of 3d and iBu$_2$AlH (50 equiv.) affords only oligomers after 15 mins. Butadiene polymerizations using 3d
and methylaluminoxine (MAO) provide slightly higher *cis* content (80%), but the activity (~1100 g PBD·(mol 3d)⁻¹·min⁻¹) is on the low side and the dispersity is high (3.28).

Instead, we noted that toluene is coordinated in the solid-state structure of 3d (see above). Thus, toluene as the reaction solvent also provides a ligand for the neodymium center that may compete with butadiene and the polymeryl chain to affect activity, stereoselectivity, and molecular weight. An aromatic solvent-free polymerization might alter these outcomes. The

![Graph](image)

**Figure 3.** Butadiene polymerization by 1d + 2 B(C₆F₅)₃ with varying equivalents of Al/iBu₃ for entries 3 and 6-9 in Table 3.
reactions of 1d and 2 equiv. of B(C₆F₅)₃ in cyclohexane or heptane generate a pale green suspension, which dissolves upon addition of Al/iBu₃ to form a homogeneous, teal solution that is active for butadiene polymerization. These polymerization experiments were performed at higher catalyst concentrations to minimize the effects of [Al/iBu₃] on the polymerization activity. Interestingly, the microstructure of the polymer changes from near 50:50 mixture of 1,4-cis:1,4-trans units in reactions performed in toluene or cyclohexane to 90% 1,4-cis units in polymerizations performed in heptane (Table 6). These results are remarkable, in that >90% 1,4-cis content is obtained for a neodymium catalyst without a chloride-cocatalyst. For comparison, catalysts derived from Nd{N(SiMe₃)₂}₃ and one equiv. of [HNMe₂Ph][B(C₆F₅)₄], [Ph₃C][B(C₆F₅)₄], B(C₆F₅)₃, or MAO provide 10-15% higher 1,4-cis content (up to 87%) in heptane than in toluene, although the activity also changed in those systems.

Table 6. Solvent effects in 3d-catalyzed butadiene polymerization[a]

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<td>Heptane</td>
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<td>3330</td>
<td>91/6/3</td>
<td>54.1</td>
<td>80.0</td>
<td>1.48</td>
</tr>
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[a] Conditions: 0.028 mmol 1d, 0.056 mmol B(C₆F₅)₃, 0.28 mmol Al/iBu₃, 20 mL solvent, 15-20 psi butadiene (maintained by addition of gas every 3 min), 60 °C, 15 min. [b] Isolated polymer (in g). [c] (g polybutadiene)(mol Nd)⁻¹·min⁻¹. [d] 1,4-cis:1,4-trans:1,2-vinyl ratio, determined by IR analysis. [e] × 10³ g·mol⁻¹. [f] Determined by GPC vs PS standards.

Organolanthanide and alkylaluminum exchange reactions. The butadiene polymerization catalysis above features an inverse relationship between molecular weight and equivalents of Al/iBu₃, which is attributed to chain transfer from active lanthanide centers to dormant aluminum centers concurrent with iBu transfer to the active site to initiate a new chain. The polymerization
is also characterized by a linear increase in molecular weight in proportion to reaction time while the dispersity remains consistently low (below 2). As noted above, these two contradictory observations may be rationalized by re-activation of aluminum-bonded chains by their transfer back to active neodymium sites. The use of C(SiHMe$_2$)$_3$ as an initiating group, which is distinct from the isobutyl (or other organo groups) on aluminum, could be useful for studying alkyl group exchange, tracking initiating lanthanide sites, and investigating chain transfer between active and dormant sites, as well as potentially providing a strategy for end group functionalization. In addition, the strong Lewis acid B(C$_6$F$_3$)$_3$ reacts with 1a-d or 2a-d, and we were curious about the interactions of these organolanthanides with weaker organoaluminum Lewis acids, such as AlMe$_3$ and Al$i$Bu$_3$.

First, the reaction of 1a and 2 equiv. of AlMe$_3$ in toluene-$d_8$ results in the complete disappearance of $^1$H and $^{29}$Si NMR signals attributed to 1a ($^1$J$_{SiH}$ = 136 Hz, 298 K). Two new intense peaks appear at 4.21 ($^1$J$_{SiH}$ = 168 Hz) and 4.59 ppm ($^1$J$_{SiH}$ = 135 Hz) in a 2:1 integrated ratio, that we assign to SiH groups. Note that the $^1$H NMR chemical shifts of 1a overlap with the signal at 4.21 ppm, however these species are clearly distinguished by a $^1$H-$^{29}$Si HSQC experiment that shows unique $^1$J$_{SiH}$ and $^{29}$Si NMR chemical shift values for the adduct with AlMe$_3$ (see Figure 4, and SI for all 2D NMR experiments). On the basis of the similarity between signal ratio and reactant ratio, as well as the higher $^1$J$_{SiH}$ at 4.21 ppm, we suggest that interaction of a C(SiHMe$_2$)$_3$ group and AlMe$_3$ results in the disruption of Ln$\rightarrow$H-Si bonding in that ligand. A plausible structure might involve bridging Ln-Me-Al and Al-H-Si interactions. These interactions are further characterized by their $^1$J$_{SiH}$ values. Compound 1a gives average $^1$J$_{SiH}$ = 136 Hz, while bridging (2 H, $^1$J$_{SiH}$ = 114 Hz) and terminal SiH (1 H, 186 Hz) signals are resolved at 180 K.$^{20}$ The weighted average of the low temperature values matches the $^1$J$_{SiH}$ of 1a
measured at room temperature (fast exchange); therefore, averaging of these values can be used to estimate the number of bridging SiH groups in a C(SiHMe₂)₃ ligand. In 1a·2AlMe₃ in particular, the J_{SiH} of 168 Hz corresponds to weighted average of 1 bridging and 2 terminal SiH groups, while the 135 Hz coupling constant corresponds to 2 bridging and 1 terminal SiH groups. We assign the former signals to ligands containing Al-H-Si interactions, whereas the latter are assigned to La-C(SiHMe₂)₃ containing two La-H-Si (Figure 4).

**Figure 4.** ¹H-²⁹Si HSQC of the reaction of 1a and 2 equiv. of AlMe₃, measured at 273 K in toluene-­d₈. The 1D ¹H NMR spectrum is overlaid above the 2D spectrum. The HSQC spectrum was acquired without ²⁹Si decoupling during acquisition to observe ¹J_{SiH} splittings.
These interactions are likely labile, given that evaporation of the reaction mixture returns AlMe$_3$-free 1a. Further support for labile 1a-AlMe$_3$ interactions is provided by a $^1$H-$^1$H ROESY NMR experiment, in which small quantities of free AlMe$_3$ show exchange crosspeaks to the complexed AlMe$_3$ signals (Figure S59). In addition, ROESY crosspeaks indicate short through-space distances between complexed AlMe$_3$ and all SiMe$_2$ groups, suggesting that AlMe$_3$ is intimately associated with the lanthanum center to be in close proximity to all C(SiHMe$_2$)$_3$ ligands. Finally, a number of weaker crosspeaks in the $^1$H-$^{29}$Si HSQC spectrum, with a range of $^1$J$_{SiH}$ values of 135, 165, 135 and 182 Hz, suggest that a few 1a·(AlMe$_3$)$_n$ adducts of varying stoichiometry are also present.

Multiple signals assigned to methylaluminum, methylsilyl, and hydridosilyl groups change in relative intensity as the amount of AlMe$_3$ is increased above 3 equivalents. Mixtures of 1a and 5 equiv. of AlMe$_3$ persist at room temperature for 48 h or at 60 °C for 2 h; however, attempts to isolate adducts by crystallization were unsuccessful. The $^1$H NMR spectrum contains a strong signal at 4.15 ppm ($^1$J$_{SiH}$ = 164 Hz), corresponding to an average of one Al–H-Si interaction per C(SiHMe$_2$)$_3$ ligand. Free AlMe$_3$ is observed, and the stoichiometry and integrated ratio of SiH and complexed AlMe$_3$ suggest that the maximum ratio of 1a:AlMe$_3$ is 1:3. The $^1$H-$^1$H ROESY spectrum again indicates that free and complexed AlMe$_3$ are in exchange (Figure S62).

In these experiments with 1a and AlMe$_3$, the C(SiHMe$_2$)$_3$ groups appear to remain bonded to the lanthanide center, based on $^1$H NMR spectra of mixtures of paramagnetic 1d and (AlMe$_3$)$_2$, in which signals for SiHMe$_2$ were paramagnetically shifted and not detected in the diamagnetic region. In contrast to the reactions of 1 and B(C$_6$F$_5$)$_3$, disilacyclobutane was not detected in the $^1$H NMR spectra of any of the reactions. Also, unlike the selective, irreversible reactions with the
borane Lewis acid, the AlMe₃ reactions are reversible and give exchanging species. Both B(C₆F₅)₃ and AlMe₃ Lewis acids interact with 1 via the SiH groups.

Next, reactions of monoalkyl species 3 and excess (AlMe₃)₂ (10 equiv.) result in alkyl group transfer from the lanthanide to aluminum, as evidenced by similar diamagnetic signals associated with SiH (4.44 ppm) and SiMe (0.25 ppm) groups in spectra for reactions of diamagnetic 3a and paramagnetic 3d. A B(C₆F₅)₃-derived borate is likely coordinated to the lanthanide, as evidenced by a ¹¹B NMR signal at –17.4 ppm in the reaction of 3a and AlMe₃ that is absent in the corresponding reaction of paramagnetic 3d. A small, yet sharp ¹¹B NMR peak was observed at 86 ppm in the reactions of both 3a and 3b with AlMe₃, likely associated with some B–C₆F₅/Al–Me exchange to give non-coordinated BMe₃.⁴⁶ The ¹⁹F NMR spectra of 3a or 3d and (AlMe₃)₂ also contained common signals at –122.1, –153 (para), and –162 ppm (meta) from C₆F₅ groups. The downfield signal is from a group likely bonded to aluminum, whereas the upfield signals are assigned to Ln{HB(C₆F₅)₃} moieties. An additional signal at –130 ppm was only present in the reaction mixture of 3a and AlMe₃, and supported the idea that perfluorophenylborate group(s) remained associated with the lanthanide center under polymerization conditions of toluene and excess AlR₃. In fact, mixtures of 3 and Al/iBu₃ also provide ¹H, ¹¹B, and ¹⁹F spectra that lead to the same conclusions.

The possibility of C(SiHMe₂)₃ being incorporated as a polybutadiene endgroup would rely on faster insertion of butadiene than transfer to aluminum, and this was tested by quenching a polymerization after a short reaction time to generate oligomeric species. Promisingly, signals of SiHMe₂ moieties were observed in the resulting crude material, and the chemical shifts were not consistent with formation of HC(SiHMe₂)₃ (from protonolysis of Nd-C(SiHMe₂)₃ or Al-C(SiHMe₂)₃ during the quench). However, these SiMe signals are removed by washing the
oligomeric solid product with methanol, and C(SiHMe₂)₃ groups are not likely to be end groups of the bulk polybutadiene. Thus, the rare earth species obtained from the combination of 3 and AlMe₃ contain HB(C₆F₅)₃ and likely methyl groups, perhaps as tetramethylaluminates.

**Conclusion**

The tris(alkyl) Ln{C(SiHMe₂)₃}₃ (Ln = La, Ce, Pr, and Nd) react with 1 or 2 equiv. of the strong Lewis acid B(C₆F₅)₃ to afford isolable and well-defined zwitterionic hydridoborate di(alkyl) or mono(alkyl) complexes, respectively. In contrast, the reactions of Ln{C(SiHMe₂)₃}₃ with weaker Lewis acids AlMe₃ result in adduct formation. A third, distinct reactivity pattern is observed in interactions of alkylaluminum compounds with the zwitterionic lanthanide precatalysts for butadiene polymerization, which involves the rapid transfer of alkyl groups from the lanthanide center, presumably to form tris(dimethylsilyl)methylaluminum species. In addition, organoboranes are formed in these reaction mixtures. Possible reactions that balance the change in charge that accompanies the conversion of anionic [HB(C₆F₅)]⁻ to neutral BR₃ species could involve formation of aluminate counterions or transfer of an anionic group to the lanthanide center to reduce its formal charge. Unfortunately, these reaction mixtures are sufficiently complex that those steps cannot be conclusively identified, and we are currently exploring alternative counterions that could reduce the complexity of these exchange reactions. Regardless, it is noteworthy that the zwitterionic compounds that undergo facile R-group exchange with trialkylaluminums are also those which provide catalytically active species. The features are either similar for organolanthanides that catalyze butadiene polymerization and those that undergo alkyl group exchange with organoaluminums, or alkyl group exchange of tris(dimethylsilyl)methyl groups is an essential requirement for polymerization activity. In this
context, we note that diene polymerization activity requires trialkylaluminum cocatalysts for
cationic allyl lanthanides\textsuperscript{11} and chloroaluminum cocatalysts for lanthanide tetraalkylaluminates.\textsuperscript{12} 

Any of the eight compounds of the series, combined with triisobutylaluminum, provide active 
butadiene polymerization catalysts. Some of the general features of the polymerization parallel 
those observed with Ziegler-type lanthanide halide, alkoxide, and carboxylate precatalysts, such 
as the higher activity of neodymium-derived catalysts compared to the other organolanthanide 
catalysts studied under equivalent conditions. Under a single set of equivalent conditions with 
constant butadiene pressure, the complexes follow the trend Nd > Ce >> Pr > La with the 
mono(alkyl) species being more reactive than the corresponding bis(alkyl) in all cases except for 
La. The outcomes used to evaluate the polymerization efficacy, including activity (polymer yield 
per catalyst per unit time) and molecular weight vary considerably over the series for a single set 
of polymerization conditions.

Detailed studies of butadiene polymerization with NdC(SiHMe\textsubscript{2})\textsubscript{3}\{HB(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}\}_2 (3\textbf{d}) show that 
these polymerization outcomes also vary considerably depending on catalyst concentration, ratio 
of neodymium to triisobutylaluminum, reaction time, and solvent. Alternatively, the apparent 
activity of neodymium sites varies with the concentration of 3\textbf{d} and concentration of Al/\textsubscript{Bu\textsubscript{3}}, 
with lower concentrations (at 1:10 molar ratios) giving lower activity per site while higher 
centration give higher activity. Independent experiments in which [Al/\textsubscript{Bu\textsubscript{3}}] is varied while 
[3\textbf{d}] is held constant show that this activity trend tracks with aluminum concentration until the 
maximum activity is obtained. This concentration effect is unlikely to be related to the catalyst 
activation step involving [Nd]–C(SiHMe\textsubscript{2})\textsubscript{3}/Al/\textsubscript{Bu\textsubscript{3}} exchange because even 5 equiv. of Al/\textsubscript{Bu\textsubscript{3}} 
appears to give effective transfer of the C(SiHMe\textsubscript{2})\textsubscript{3} group from neodymium, even though that 
quantity of co-catalyst does not achieve maximum activity. Likely, Al/\textsubscript{Bu\textsubscript{3}} is required for a
number of functions during the polymerization process that affect the activity of the polymerization site.

A summary of observations associated with the polymerization mechanism follow. First, $M_n$ increases linearly with time (at constant butadiene concentration), and $M_w/M_n \sim 1.15$ over this time. These two observations are characteristics associated with living polymerizations. In contrast, $M_n$ decreases as $[\text{Al/Bu}_3]$ increases. At longer times, $M_w$ and $M_w/M_n$ increase, indicating that some chains are growing faster than others (which are likely not growing at all). These two observations are inconsistent with living polymerization character. Our interpretation of this data is that chain transfer between Nd and Al is reversible until a point where the polymeryil chains are too long. At that point, the aluminum chains cannot exchange with Nd to grow. Once the polymer chains on Nd and on Al become sufficiently long or Al/Bu$_3$ is entirely consumed, the exchange process(es) are slowed, and the chains bonded to neodymium grow (leading to gelation) while the length of the chains bonded to aluminum do not further increase.

Moreover, many of the polymerization outcomes are dependent on competing rates of insertion and chain transfer steps, which may also vary considerably based on the lanthanide ion, the number of alkyl groups bonded to the active center and its formal charge, and the composition and concentration of the alkylaluminum cocatalyst(s). Thus, the optimal conditions for bis(alkyl) lanthanum for example, are unlikely to be equivalent even to those of other similarly structured alkyllanthanides. Although the typical comparison of catalysts under identical conditions appears to be the most straightforward means of identifying the “best” catalyst, this approach may in fact limit catalyst discovery. In this context, decoupling precatalyst generation (i.e., construction of Ln–C bonds) and formation of cationic or zwitterionic species from catalyst initiation, diene
insertion for chain propagation, and chain transfer steps is a valuable strategy for characterizing intrinsic catalytic properties in these complex sites.

**Experimental.**

**General Procedures.** All reactions were performed under a dry argon or nitrogen atmosphere using standard Schlenk techniques or under nitrogen atmosphere in a glovebox, unless indicated. Dry, oxygen-free solvents were used throughout. Benzene, toluene, pentane, and tetrahydrofuran were degassed by sparging with nitrogen, filtered through activated alumina columns, and stored under nitrogen. Heptane and cyclohexane were stirred with H$_2$SO$_4$, washed with aqueous Na$_2$CO$_3$, distilled from CaH$_2$ under nitrogen, and stored in a nitrogen-filled glovebox. Benzene-$d_6$ and toluene-$d_8$ were heated at reflux over Na/K alloy, vacuum-transferred, and stored over 4 Å molecular sieves in a nitrogen-filled glovebox. Ln\{(SiHMe$_2$)$_3$\}_3 (Ln = La, Ce, Pr, Nd), Ce\{(SiHMe$_2$)$_3$\}_2HB(C$_6$F$_5$)$_3$, and B(C$_6$F$_5$)$_3$ were prepared following literature procedure.$^{47}$ AliBu$_3$, iBu$_2$AlH, iBu$_2$AlCl, MAO, and butadiene were all purchased from Sigma-Aldrich and used as received. Butadiene is a flammable toxic gas and should be used in a well-ventilated fume hood, and alkylaluminum reagents are pyrophoric and should be handled with caution.

$^1$H, $^{11}$B, $^{13}$C\{$^1$H}, $^{19}$F NMR spectra were collected on Bruker DRX-400 and Bruker Avance III 600 spectrometers. $^{29}$Si NMR chemical shifts were determined by $^1$H-$^{29}$Si HMBC experiments on a Bruker Avance III 600 NMR spectrometer. Solid-state NMR experiments were performed on the polybutadiene samples on a 9.4 T Avance III HD NMR spectrometer with a Bruker 4.0 mm HX MAS probe. Infrared spectra were recorded on a Bruker Vertex 80 spectrometer. GPC analysis was conducted using a Viscotek GPCmax VE 2001 at 0.8 mL/min. in tetrahydrofuran and referenced to polystyrene standards. Elemental analyses were performed using a PerkinElmer 2400 Series II CHN/S analyzer at the Iowa State Chemical Instrumentation Facility.
\text{La}[\text{C}(\text{SiMe}_2)\text{H}_3]_2\text{HB}(\text{C}_6\text{F}_5)_3 \ (2a) \ as \ a \ representative \ example \ of \ Ln[C(\text{SiMe}_2)\text{H}_3]_2\text{HB}(\text{C}_6\text{F}_5)_3 \ (2). \ La[C(\text{SiMe}_2)\text{H}_3]_3 \ (0.095 \ \text{g}, 0.134 \ \text{mmol}) \ was \ dissolved \ in \ benzene \ (4 \ \text{mL}). \ In \ a \ separate \ vessel, \ B(\text{C}_6\text{F}_5)_3 \ (0.068 \ \text{g}, 0.134 \ \text{mmol}) \ was \ dissolved \ in \ benzene \ (1.5 \ \text{mL}), \ and \ this \ solution \ was \ added \ in \ a \ dropwise \ fashion \ to \ the \ La[C(\text{SiMe}_2)\text{H}_3]_3. \ The \ reaction \ mixture \ was \ stirred \ for \ 30 \ \text{min.,} \ and \ then \ the \ volatiles \ materials \ were \ removed \ under \ reduced \ pressure \ to \ give \ a \ yellow \ semi-solid. \ This \ residue \ was \ washed \ with \ pentane \ (3 \times 5 \ \text{mL}) \ and \ then \ dried \ in \ vacuo \ to \ yield \ La[C(\text{SiMe}_2)\text{H}_3]_2\text{HB}(\text{C}_6\text{F}_5)_3 \ (0.115 \ \text{g}, 0.112 \ \text{mmol}, 83\%) \ as \ a \ yellow-orange \ solid. \ \text{1}^H \ \text{NMR} \ (\text{benzene}-d_6, 600 \ \text{MHz}, 25 \ ^\circ\text{C}): \ \delta \ 4.45 \ (\text{m}, \ ^1J_{\text{SiH}} = 135.2 \ \text{Hz}, 6 \ \text{H}, \ \text{SiH}), \ 0.21 \ (\text{d}, \ ^3J_{\text{HH}} = 3.4 \ \text{Hz}, 36 \ \text{H}, \ \text{SiMe}_2). \ \text{11}B \ \text{NMR} \ (\text{benzene}-d_6, 192 \ \text{MHz}, 25 \ ^\circ\text{C}): \ \delta \ -17.5 \ (\text{d}, \ ^{1}J_{\text{BH}} = 68.9 \ \text{Hz}). \ \text{13}C\{^1\text{H}\} \ \text{NMR} \ (\text{benzene}-d_6, 150 \ \text{MHz}, 25 \ ^\circ\text{C}): \ \delta \ 150.2 \ (\text{br}, \ \text{C}_6\text{F}_5), \ 148.4 \ (\text{br}, \ \text{C}_6\text{F}_5), \ 139.3 \ (\text{br}, \ \text{C}_6\text{F}_5), \ 137.0 \ (\text{br}, \ \text{C}_6\text{F}_5), \ 2.2 \ (\text{SiMe}_2). \ \text{19}F \ \text{NMR} \ (\text{benzene}-d_6, 564 \ \text{MHz}, 25 \ ^\circ\text{C}): \ \delta \ -133.6 \ (3 \ \text{F}, \ \text{ortho-}\text{C}_6\text{F}_5), \ -156.0 \ (3 \ \text{F}, \ \text{para-}\text{C}_6\text{F}_5), \ -161.0 \ (3 \ \text{F}, \ \text{meta-}\text{C}_6\text{F}_5). \ \text{29}Si\{^1\text{H}\} \ \text{NMR} \ (\text{benzene}-d_6, 119 \ \text{MHz}, 25 \ ^\circ\text{C}): \ \delta \ -11.2 \ (\text{SiHMe}_2). \ \text{IR} \ (\text{KBr}, \ \text{cm}^{-1}): \ 2958 \ (\text{m}), \ 2904 \ (\text{w}), \ 2263 \ (\text{br}, \ \text{SiH}), \ 1787 \ (\text{br}, \ \text{SiH}), \ 1646 \ (\text{m}), \ 1603 \ (\text{w}), \ 1516 \ (\text{s}), \ 1467 \ (\text{br}, \ s) 1372 \ (\text{m}), \ 1283 \ (\text{s}), \ 1258 \ (\text{s}), \ 1110 \ (\text{br}, \ s), \ 1079 \ (\text{br}, \ s), \ 959 \ (\text{br}, \ s), \ 896 \ (\text{br}, \ s), \ 837 \ (\text{br}, \ s), \ 786 \ (\text{s}), \ 673 \ (\text{m}). \ \text{Anal.} \ \text{Calcd} \ for \ \text{BC}_{32}\text{F}_{15}\text{H}_{43}\text{Si}_{3}\text{La}: \ C, 37.28; \ H, 4.20. \ \text{Found}: \ C, 37.81; \ H, 4.00. \ \text{Mp}, 171 \ ^\circ\text{C} \ (\text{dec}).

\text{LaC}(\text{SiMe}_2)\text{H}_3\{\text{HB}(\text{C}_6\text{F}_5)_3\}_2 \ (3a) \ as \ a \ representative \ example \ of \ LnC(\text{SiMe}_2)\text{H}_3\{\text{HB}(\text{C}_6\text{F}_5)_3\}_2 \ (3). \ A \ similar \ procedure \ as \ given \ for \ 2a, \ in \ which \ B(\text{C}_6\text{F}_5)_3 \ (0.193 \ \text{g}, 0.377 \ \text{mmol}) \ and \ La[C(\text{SiMe}_2)\text{H}_3]_3 \ (0.130 \ \text{g}, 0.184 \ \text{mmol}) \ were \ allowed \ to \ react \ for \ 1 \ \text{h} \ afforded \ LaC(\text{SiMe}_2)\text{H}_3\{\text{HB}(\text{C}_6\text{F}_5)_3\}_2 \ (0.226 \ \text{g}, 0.167 \ \text{mmol}, 91\%) \ as \ a \ green \ solid. \ The \ solid \ product \ is \ washed \ with \ pentane \ and \ dried \ for \ ~1 \ \text{h}. \ Exhaustive \ drying \ leads \ to \ decomposition. \ \text{1}^H \ \text{NMR} \ (\text{benzene}-d_6, 600 \ \text{MHz}, 25 \ ^\circ\text{C}): \ \delta \ 4.28 \ (\text{m}, \ ^1J_{\text{SiH}} = 134.7 \ \text{Hz}, 3 \ \text{H}, \ \text{SiH}), -0.04 \ (\text{d}, \ ^3J_{\text{HH}} = 3.6
$^{11}$B NMR (benzene-$d_6$, 192 MHz, 25 °C): $\delta$ –17.5 (d, $J_{BH} = 58.4$ Hz).

$^{13}$C\{\textsuperscript{1}H\} NMR (benzene-$d_6$, 150 MHz, 25 °C): $\delta$ 149.9 (br, C$_6$F$_5$), 148.4 (br, C$_6$F$_5$), 141.2 (br, C$_6$F$_5$), 139.5 (br, C$_6$F$_5$), 138.8 (br, C$_6$F$_5$), 137.2 (br, C$_6$F$_5$), –1.2 (SiMe$_2$).

$^{19}$F NMR (benzene-$d_6$, 564 MHz, 25 °C): $\delta$ –136.2 (6 F, ortho-C$_6$F$_5$), –160.0 (6 F, para-C$_6$F$_5$), –164.3 (6 F, meta-C$_6$F$_5$).

$^{29}$Si\{\textsuperscript{1}H\} NMR (benzene-$d_6$, 119 MHz, 25 °C): $\delta$ –10.3 (SiHMe$_2$). IR (KBr, cm$^{-1}$): 2963 (m), 2252 (br, $\nu_{BH}$), 2106 (br $\nu_{SiH}$), 1649 (m), 1606 (w), 1518 (s), 1468 (br, s) 1375 (m), 1283 (s), 1267 (s), 1117 (br, s), 1081 (br, s), 974 (br, s), 953 (s), 896 (br, s), 842 (br, s), 790 (m), 672 (m).

Anal. Calcd for B$_2$C$_{48}$F$_{30}$H$_{35}$Si$_3$La: C, 40.41; H, 2.47. Found: C, 40.84; H, 2.59. Mp, 170-173 °C.

**Representative example of butadiene polymerization provided material characterized by**

**Table 3, entry 8.** Stock solutions of Nd\{C(SiHMe$_2$)$_3$\}$_3$ (1.0 mL; 22 mM in toluene, 0.022 mmol) and B(C$_6$F$_5$)$_3$ (1.0 mL, 44 mM in toluene, 0.044 mmol) were mixed in a test tube for 3-5 minutes to yield a teal solution. Al$\textit{t}$Bu$_3$ (0.044 g, 0.22 mmol) was placed in a 10 mL volumetric flask and toluene was added to give a 22 mM solution. Combination of the two solutions in a glass reactor containing a magnetic stir bar afforded a pale green solution. The reactor was sealed, placed in an oil bath preheated to 60 °C, and stirred for 5 min. The reactor was pressurized with butadiene gas (~20 psi). Upon addition of butadiene, the solution turned pale yellow and fumes arose from the surface of the stirring solution. The reactor pressure was maintained between 15-20 psi throughout the reaction, as monitored by a gauge on the reactor, through the addition of butadiene gas (3×). Methanol (2 mL) was added after 15 min. to quench the reaction, giving a colorless solution and a small amount of precipitate. The reaction mixture was then added to an acidic MeOH solution (10 mL of 10% 3M HCl in MeOH) to precipitate the polybutadiene. The supernatant was decanted, and the polybutadiene solid was washed with MeOH (5 × 5 mL), transferred to a pre-tared vial, and dried until the mass (1.16 g) remained constant.
Supporting Information.

The following files are available free of charge.

Synthesis of compounds 2, 2-d7 and 3, additional spectroscopic data, and polymer characterization (PDF).


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Ln = La 1a
Ce 1b
Pr 1c
Nd 1d

+ B(C₆F₅)₃
r.t., 30 min

Ln = La 2a (83%)
Ce 2b (71%)
Pr 2c (68%)
Nd 2d (85%)

186x56mm (600 x 600 DPI)
Ln = La 1a  
Ce 1b  
Pr 1c  
Nd 1d  

Ln = La 3a (91%)  
Ce 3b (62%)  
Pr 3c (76%)  
Nd 3d (85%)  

+ 2 B(C₆F₅)₃  

r.t., 30 min  

186x64mm (600 x 600 DPI)
\[ \text{Ln}([\text{SiHMe}_2]_3) + a \text{ B(C}_6\text{F}_5)_3 + 10 \text{ Al} / \text{Bu}_3 \]

\[ \rightarrow \]

20 psi

\[ \text{60 °C, toluene, 15 or 30 min.} \]

Ln = La, Ce, Pr, or Nd

a = 1 or 2 equiv.

1,4-cis 1,4-trans 1,2-vinyl

159x31mm (600 x 600 DPI)
$M_n$, $M_w/M_n$
equivalents of AliBu$_3$

Activity (g PBD/mol min)
La\{C(SiHMe_2)_3\}_3 + 2 AlMe_3

\textsuperscript{1}H - \textsuperscript{29}Si HSQC NMR without \textsuperscript{29}Si decoupling at 273 K

- Averaged Signals
  \textsuperscript{1}H: 4.21 \& 0.38 ppm
  \textsuperscript{29}Si: -13.4 ppm

- Averaged Signals
  \textsuperscript{1}H: 4.59 \& 0.28 ppm
  \textsuperscript{29}Si: -12.2 ppm

- Free AlMe_3

- Tol-d_8

- 1H Spectrum

- 29Si Projection

- 1H: 4.21 \& 0.38 ppm
- 29Si: -13.4 ppm

- 1H: 4.59 \& 0.28 ppm
- 29Si: -12.2 ppm

- 1H: 0.19 ppm