CHEMISTRY
A European Journal

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## Accepted Article

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**To be cited as:** *Chem. Eur. J.* 10.1002/chem.202000325

**Link to VoR:** http://dx.doi.org/10.1002/chem.202000325

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# Rare Earth Catalyzed C–H Bond Alumination of Terminal Alkynes

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**Abstract:** Organoaluminum reagents' application in catalytic C–H bond functionalization is limited by competitive side reactions, such as carboalumination and hydroalumination. Here, we demonstrate that rare-earth tetramethylaluminate complexes catalyze the exclusive C–H bond metalation of terminal alkynes with the commodity reagents trimethyl-, triethyl-, and triisobutylaluminum. Kinetic experiments probing alkyl group exchange between rare earth aluminates and trialkylaluminum, C–H bond metalation of alkynes, and catalytic conversions reveal distinct pathways of catalytic aluminations with triethylaluminum vs. trimethylaluminum. Most significantly, kinetic data point to reversible formation of a unique [Ln]($AlR_4$)$_2$·$AlR_3$ adduct, followed by turnover-limiting alkyne metalation. That is, C–H bond activation occurs from a more associated organometallic species, rather than the expected coordinatively unsaturated species. These mechanistic conclusions allude to a new general strategy for catalytic C–H bond alumination that make use of highly electrophilic metal catalysts.

## Introduction

Organoaluminum compounds are versatile and sustainable reagents finding utility in synthetic organic, organometallic, and polymer chemistry for more than fifty years. The high elemental abundance of aluminum in the earth's crust (8%) and relatively low toxicity combined with straightforward, atom-economical and scaleable preparation from aluminum, hydrogen, and alkenes have resulted in commercial applications of trialkylaluminum reagents.[1] Moreover, organoaluminums combine nucleophilicity and Lewis acidity to offer reactivity, such as conjugate addition and facile transmetalation, that is complementary to other useful reagents, including organo-magnesium, -zinc, -copper and -lithium compounds. Unfortunately, syntheses of complex organoaluminum compounds instead typically involve salt metathesis reactions that rely upon other alkylating agents and corrosive aluminum halides. Ideally, direct metalation of C–H bonds by inexpensive trialkylaluminums could greatly increase the availability of functional-group containing organoaluminum compounds, but C–H bond alumination is underdeveloped compared to other catalytic C–H bond functionalization methods such as borylation[2-7] or silylation.[8-10]

Instead, most C–H bond alumination reactions rely on the inherent reactivity of organoaluminum species. Intramolecular activations, pioneered by Eisch and coworkers, convert mixed arylaluminum compounds into benzaluminoles.[11] Stoichiometric aluminations of aryl and heteroaryl compounds are accomplished with heterobimetallic aluminate complexes.[12] Another heterobimetallic, the niobium aluminate $Cp_2Nb(\mu\text{-}H)_2AlEt_2$, mediates metalation of one equiv. of benzene by triethylaluminum to generate diethylphenylaluminum.[13] Interestingly, alumination of unactivated aryl C–H bonds, making use of diketiminate aluminum hydride, is catalyzed by palladium at room temperature.[14, 15]

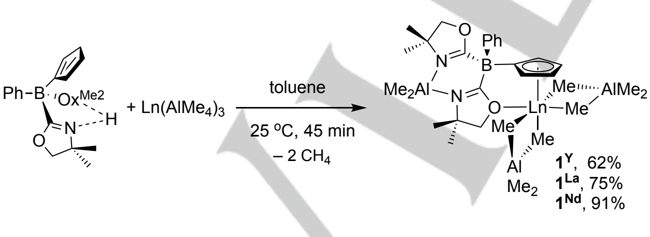
The more common transition-metal-catalyzed reaction pathways of alkylaluminums and unsaturated organic compounds, namely hydroaluminations and carboaluminations involving the addition of organoaluminum compounds to alkenes and alkynes,[16] limit the direct metalation chemistry. Instead, these reactions provide valuable organic nucleophiles for synthesis and are industrially important in Ziegler-type polymerizations.[17-20] In reactions between terminal alkynes and alkylaluminum compounds, organometal-catalyzed routes to alkynylaluminum species were unknown, prior to the present work. The latter species, which are useful alkynyl transfer agents,[21] complement the reactivity of lithium and copper acetylides in carbon-alkyne bond forming reactions and have even been utilized in the synthesis of valuable biomolecules, such as prostaglandins.[22] Alkynyldialkylaluminums are conventionally generated in situ, via salt elimination reactions of lithium acetylides with dialkylaluminum halides, along with solid waste byproducts that may further influence reactivity.[23, 24] Few aliphatic alkynylaluminum species have been isolated and characterized by modern spectroscopic techniques. Catalytic routes to alkynylaluminums could facilitate their isolation and characterization, as well as provide easier access to these useful nucleophiles.

Metalation of arylalkynes by triphenylaluminum gives alkynyldiphenylaluminum, but this approach is limited by the availability of $AlPh_3$ and the fact that aluminum phenyl and alkynyl groups in alkynyldiphenylaluminum are both highly reactive in subsequent group transfer reactions.[25] On the other hand, uncatalyzed reactions of trialkylaluminums and terminal aliphatic alkynes typically generate mixtures of carboalumination, hydroalumination, and metalation products.[26] This poor intrinsic selectivity improves in the presence of amines, either in stoichiometric or catalytic quantities. Binger originally showed that tertiary amine-coordinated adducts $R_2AlH\cdot NR_3$ selectively metalate 1-alkynes, giving alkynylaluminum compounds and dihydrogen as a byproduct.[27] More recently, Micouin and coworkers developed Lewis base-catalyzed methane eliminations from the combination of trimethylaluminum and terminal alkynes.[28] Although competing H atom transfer reactions of higher alkylaluminums containing β-hydrogen limit this approach to trimethylaluminum, these studies suggest that four-coordinate aluminum species favor metalation over addition or insertion to unsaturated organics. For example, highly electrophilic metal centers such as those of rare earth elements containing more tightly associated aluminate centers, that disfavor insertion, could catalyze alumination of terminal alkynes.

Lanthanide aluminates, upon activation, are typically catalyst precursors for alkene and diene polymerization and are also used to generate highly reactive species such as masked alkylidenes and cationic alkyls.[29-40] In the few reports of aluminum addition chemistry, piano-stool scandium compounds catalyze the carboalumination of ether-containing alkynes,[41] and bent-sandwich yttrium compounds catalyze hydroalumination,[42] together suggesting that the appropriate ancillary ligands also are required to promote alumination pathways. In the initial phase of this work, we communicated that a neodymium aluminate supported by a cyclopentadienylborate ligand, $\{Me_2Al(Ox^{Me2})_2BPh(C_5H_4)\}$-$Nd(AlMe_4)_2$ (**$1^{Nd}$**; $Ox^{Me2}$ = 4,4-dimethyl-2-oxazoline), is a catalyst for alumination of terminal alkynes.[43] The paramagnetic neodymium center, however, limited NMR spectroscopic studies and kinetic measurements that are needed to establish solution-phase structural dynamics and mechanistic features leading to selective C–H bond activation. Here we report a series of diamagnetic and paramagnetic zwitterionic rare earth complexes that provide trends in activity, access to mechanistic data that implicate pathways that vary with the trialkylaluminum reactant, and lead to superior catalysts that provide access to isolable alkynylaluminum compounds.

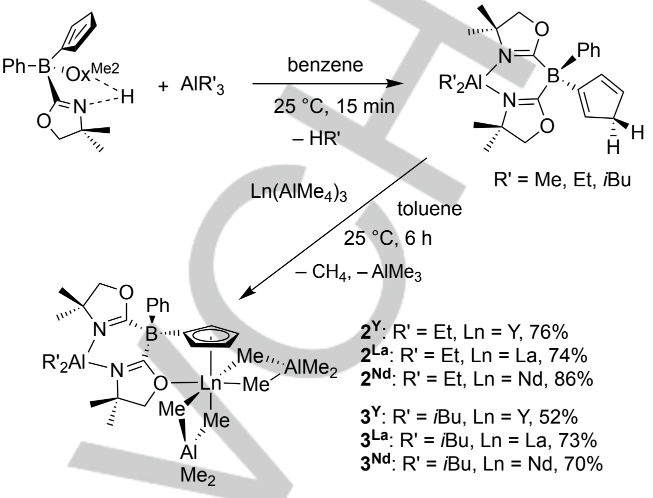
## Results and Discussion

**Zwitterionic Piano-stool Rare Earth Aluminate Catalysts.** The complexes $\{Me_2Al(Ox^{Me2})_2PhBCp\}Ln(AlMe_4)_2$ (Ln = Y, **$1^{Y}$**; Ln = La, **$1^{La}$**) are synthesized from $H\{PhB(Ox^{Me2})_2C_5H_5\}$ and $Ln(AlMe_4)_3$ in toluene at room temperature in respectable yields (Scheme 1), similar to our previously reported preparation of $\{Me_2Al(Ox^{Me2})_2PhBCp\}Nd(AlMe_4)_2$ (**$1^{Nd}$**).[43] All three aluminum atoms from the tris(tetramethylaluminate) precursors are incorporated into the heteroleptic products, which contains a bis(oxazoline)-coordinated dimethylaluminum and two $AlMe_4$ ligands. Methane, formed in the protonolysis steps, is the only byproduct detected in $^1H$ NMR spectra of micromole-scale reactions performed in benzene-$d_6$.



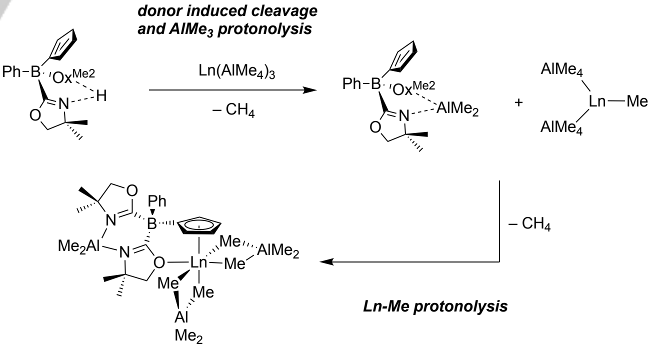
Scheme 1. Synthesis of heteroleptic heterobimetallic cyclopentadienylborato rare earth aluminates.

Compounds **$1^{Ln}$** can also be accessed via the reaction of $Ln(AlMe_4)_3$ and dimethylaluminum-coordinated bis(oxazolinyl)borate. κ$^2$-$Ph(C_5H_5)B(Ox^{Me2})_2AlMe_2$ itself is formed by treatment of $H\{PhB(Ox^{Me2})_2C_5H_5\}$ with 0.5 eq. of $(AlMe_3)_2$.[43] This preparation may be extended to triethyl- and triisobutylaluminum (Scheme 2), and the complexes $\{R'_2Al(Ox^{Me2})_2PhBCp\}Ln(AlMe_4)_2$ (**$2^{Y, La, Nd}$**, R' = Et; **$3^{Y, La, Nd}$**, R' = *i*Bu) are synthesized from the *in-situ* generated κ$^2$-$Ph(C_5H_5)B(Ox^{Me2})_2AlR'_2$ (R' = Et, *i*Bu).



Scheme 2. Synthesis of heteroleptic heterobimetallic cyclopentadienylborato rare earth aluminates with mixed alkylaluminum species.

The reaction of $Ln(AlMe_4)_3$ and $H\{PhB(Ox^{Me2})_2C_5H_5\}$ of Scheme 1 is significantly faster than the corresponding reaction with dialkylaluminum-bonded κ$^2$-$Ph(C_5H_5)B(Ox^{Me2})_2AlR'_2$ in Scheme 2. Based upon this observation, a likely pathway to **1**, shown in Scheme 3, involves oxazoline donor-induced cleavage of the lanthanide aluminate to form [Ln]–Me and oxazoline-coordinated trimethylaluminum.[44] The latter species eliminates methane to give the bis(4,4-dimethyl-2-oxazolinyl)borate aluminumdimethyl moiety. Then, $C_5H_5$ metalation by the $(AlMe_4)_2LnMe$ gives **$1^{Ln}$**.



Scheme 3. Proposed pathway to **$1^{Ln}$**.

NMR spectra of the half-sandwich compounds **$1^{Ln}$**, **$2^{Ln}$**, and **$3^{Ln}$** reveal a few common characteristics. First, similar $^1H$ NMR signals corresponding to the diastereotopic $AlR'_2$ were observed in related diamagnetic yttrium and lanthanum congeners. In general, peaks from methylaluminum or methylenealuminum in $B(Ox^{Me2})_2AlR'_2$ appeared at lower frequency than those from $AlR_3$ or $AlMe_4$ species. Second, NMR spectra were consistent with $C_s$-symmetric complexes, on the basis of a single set of diastereotopic methyl and methylene signals from the two oxazolines, two signals for diastereotopic dialkylalumino groups, and two signals assigned to $C_5H_4$. That is, the two oxazoline groups appear to be equivalent. The gas phase DFT-calculated model of $\mathbf{1}^{\mathbf{Y}}$ (see below) and crystal structure of $\mathbf{1}^{\mathbf{Nd}}$,[43] in contrast, reveals an oxygen from an oxazoline coordinating to the neodymium center, giving a static $C_1$ symmetric structure with inequivalent oxazolines. Likely, the Ln–$O_{\mathrm{oxazoline}}$ bond is highly labile, enabling exchange of oxazolines via rotation about the B–$Cp^{\mathrm{ipso}}$ bond.

The exchange of free and associated alkylaluminum species may be important for accessing catalytically active species, either coordinatively-unsaturated or highly associated intermediates. A single, broad resonance (24 H), assigned to $AlMe_4$ groups, was observed in the spectra for all the compounds (Y: –0.24 ppm; La: –0.17 to –0.19 ppm). The $AlMe_4$ signals of the paramagnetic neodymium species $\mathbf{2}^{\mathbf{Nd}}$ and $\mathbf{3}^{\mathbf{Nd}}$ manifested as broad peaks centered around ~6.5 ppm, similar to the spectrum of $\mathbf{1}^{\mathbf{Nd}}$. The $AlMe_4$ groups are highly fluxional, and bridging Ln-Me-Al and terminal Al-Me undergo rapidly exchange even at 193 K. In contrast, these groups are resolved in homoleptic analogues in spectra acquired at low temperature.[33]

Although bridging and terminal groups do not resolve at low temperature, the broad $AlMe_4$ resonance sharpens in a variable temperature $^1H$ NMR study of $\mathbf{1}^{\mathbf{Y}}$, and a doublet ($^2J_{YH}$ = 1.9 Hz) corresponding to averaged coupling of bridging and terminal methyls can be observed at 253 K (Figure 1). The dynamic behavior of aluminates $\mathbf{1\text{-}3}^{\mathbf{Ln}}$, which is apparent in $^1H$ NMR spectra at a distinctly lower temperature regime than those of homoleptic $Ln(AlMe_4)_3$ (Ln = Y, La), may also affect intermolecular exchange rates with $AlR_3$ which are key to the proposed catalytic mechanisms (see below).

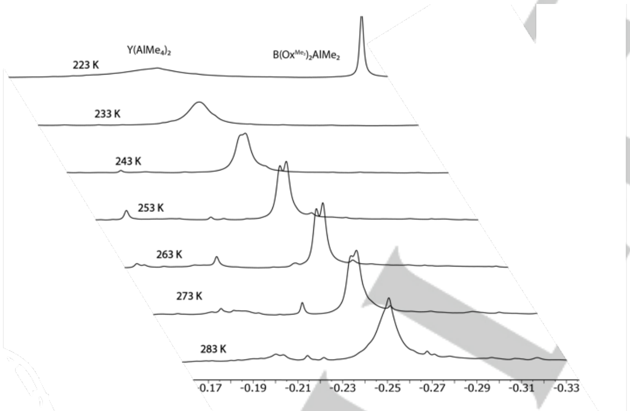


**Figure 1.** $^1H$ NMR spectra of $\{Me_2Al(Ox^{Me2})_2PhBC_5H_4\}Ln(AlMe_4)_2$ ($\mathbf{1}^{\mathbf{Y}}$), acquired in toluene-$d_8$ from 223-283 K.

In a 2D $^1H$ NOESY experiment on $\mathbf{2}^{\mathbf{La}}$, the signal assigned to $AlMe_4$ correlated with both signals of the $C_5H_4$ group and methylene and methyl groups of the oxazoline (Figures S22-23). Through-space interactions were also detected between $AlMe_4$ and the $B(Ox^{Me2})_2Al\underline{Et}_2$. Similarly, a NOESY experiment on $\mathbf{3}^{\mathbf{Y}}$ revealed close contacts between Al*i*Bu$_2$ groups and $AlMe_4$. In contrast, correlations between $AlMe_2$ and $AlMe_4$ groups in $\mathbf{1}^{\mathbf{Y}}$ were not detected. The spatial proximity of the $AlMe_4$ and $AlEt_2$ or Al*i*Bu$_2$ groups is likely responsible for the slower catalytic performances of $\mathbf{2}^{\mathbf{Ln}}$ and $\mathbf{3}^{\mathbf{Ln}}$ compared to $\mathbf{1}^{\mathbf{Ln}}$ (see below).

Yttrium chemical shifts for compounds $\mathbf{1}^{\mathbf{Y}}$, $\mathbf{2}^{\mathbf{Y}}$, and $\mathbf{3}^{\mathbf{Y}}$ (Figures 2A, S16, and S33), determined through $^1H$-$^{89}Y\{^1H\}$ HSQC experiments that revealed cross-peaks with signals from $AlMe_4$, were almost identical to $Y(AlMe_4)_3$ (394 ppm).[33] The IR spectra of the heteroleptic tetramethylaluminate complexes in the solid state revealed two distinct bands between 1530-1600 cm$^{-1}$ that were assigned to $\nu_{C=N}$ of two inequivalent oxazolines, owing to the likely coordination of only one to the lanthanide center via oxygen.

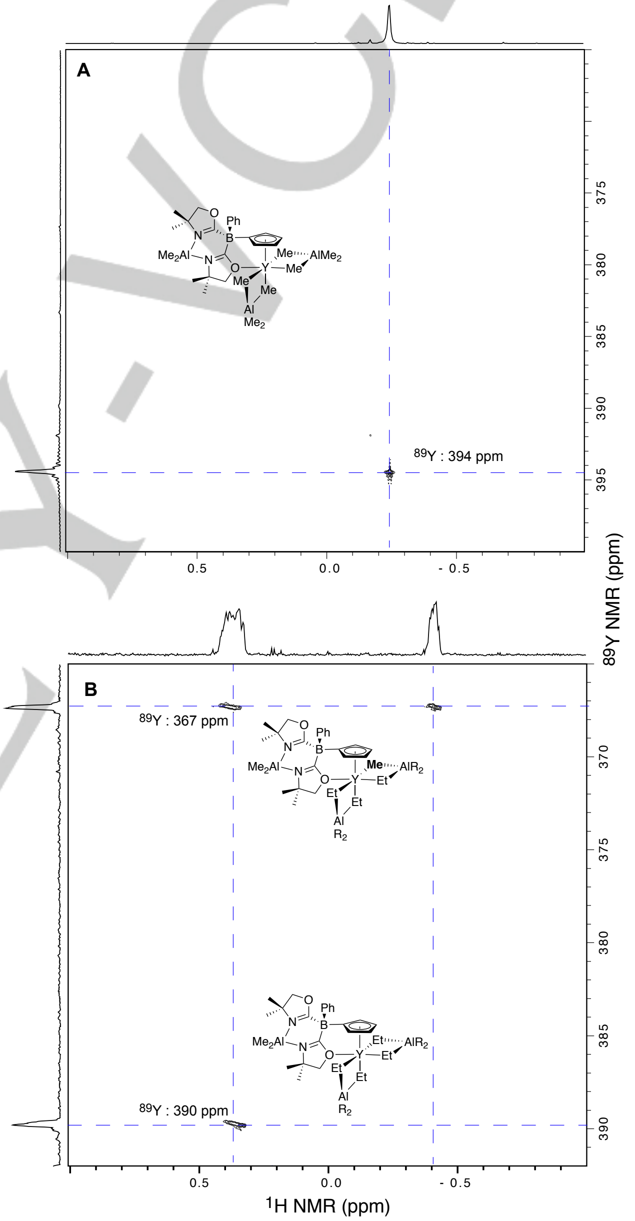


**Figure 2.** $^1H$-$^{89}Y\{^1H\}$ NMR spectra of (**A**) $\mathbf{1}^{\mathbf{Y}}$ and (**B**) $\mathbf{1}^{\mathbf{Y}}$ + 10 equiv. of triethylaluminum.

A gas-phase model $\mathbf{1}^{\mathbf{Y\text{-}CALC}}$ was optimized using DFT methods (LANL2DZ + ECP(Al, Y)/M06-2X-D3),[45-47] starting with an initial geometry based on the atomic coordinates of $\mathbf{1}^{\mathbf{Nd}}$ composed of O-coordinated oxazoline and two bidentate ($\mu$-Me)$_2$AlMe$_2$ units. Interestingly, the DFT-optimized geometry of

**1$^{\text{Y-CALC}}$** reveals inequivalent coordination modes of the AlMe$_4$ ligands, with one forming a bidentate (μ-Me)$_2$AlMe$_2$ structure and the second giving monodentate coordination (μ-Me)AlMe$_3$ (Figure 3). The former Y–C distances are calculated to be 2.723 and 2.626 Å, with a longer third distance (dashed bond in Figure 3) of 3.01 Å. The calculated Y–C distance in the monodentate tetramethylaluminate is 2.464 Å. The structure also features an oxazoline coordinating to yttrium through its oxygen. The calculated ν$_{CN}$ of this O-coordinated oxazoline, which is part of the bis(oxazolinyl)borate moiety coordinated to dimethylaluminum, is 1598 cm$^{-1}$, whereas the calculated ν$_{CN}$ of the other oxazoline, coordinated only to aluminum, is 1532 cm$^{-1}$. These calculated values are in reasonable agreement with experimental ν$_{CN}$ of 1594 and 1560 cm$^{-1}$.

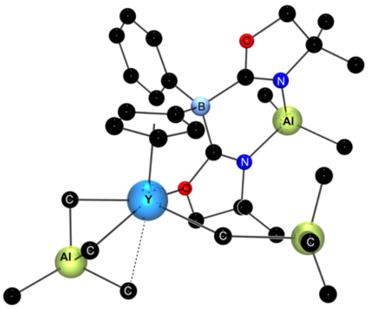


**Figure 3.** Optimized gas-phase geometry for **1$^{\text{Y-CALC}}$**.

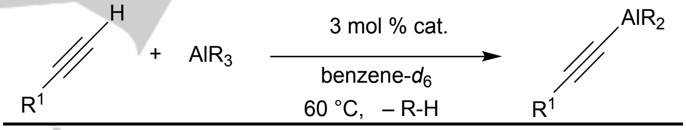
**Catalytic Alumination of Terminal Alkynes.** The compounds **1$^{\text{Ln}}$** are effective precatalysts for alumination reactions of terminal alkynes (R$^1$C≡CH) with AlR$_3$ (R = Me, Et, *i*Bu; R$^1$ = alkyl or aryl), giving dimeric alkynylaluminums (R$^1$C≡C–AlR$_2$)$_2$ and the alkane byproduct with high selectivity at 60 ° C (Table 1). A few important points are revealed by the present studies. First, **1$^{\text{Y}}$** and **1$^{\text{La}}$** afford significantly faster catalysts than our previously reported **1$^{\text{Nd}}$** in comparable alkynylalumination reactions.[43] Second, neither Y(AlMe$_4$)$_3$ nor La(AlMe$_4$)$_3$ provide active catalysts for the metalation of 1-hexyne with trimethylaluminum at 60 °C after 24 h (only starting materials are observed in $^1$H NMR spectra), in contrast to catalytically active Nd(AlMe$_4$)$_3$. Ln(AlMe$_4$)$_3$ is unselective and affords both ethylalumination and alkyne C–H alumination in reactions of triethylaluminum and 1-hexyne. That is, the cyclopentadienyl ligand enhances the catalytic properties of yttrium and lanthanum to a greater extent than those of neodymium, and catalytic rates for reaction of AlMe$_3$ increase following the trend: Ln(AlMe$_4$)$_3$ (Ln = Y, La) << Nd(AlMe$_4$)$_3$ < **1$^{\text{Nd}}$** < **1$^{\text{Ln}}$** (Ln = Y, La).

Interestingly, the peripheral dialkylaluminum groups coordinated to the bis(oxazolinyl)borate also have a significant effect on reaction rates, following the trend (**1$^{\text{Ln}}$** > **2$^{\text{Ln}}$** ~ **3$^{\text{Ln}}$**). For example, the rate of alumination of 3,3-dimethyl-1-butyne by triethylaluminum is much faster with the dimethylalumino bis(oxazolinyl)borate ligand in **1$^{\text{Y}}$** than with diethylaluminum **2$^{\text{Y}}$** and diisobutylaluminum **3$^{\text{Y}}$** catalysts, based on time needed to achieve high conversion under equivalent conditions. The AlR'$_2$ groups in **2$^{\text{Ln}}$** or **3$^{\text{Ln}}$** do not undergo detectable chemical exchange with free trialkylaluminums or with lanthanide aluminates, as shown by an $^1$H-$^1$H EXSY experiment, or upon treatment of **1-3$^{\text{Ln}}$** with a different trialkylauminum. Although the aluminum-only ligand κ$^2$-Ph(C$_5$H$_5$)B(Ox$^{\text{Me2}}$)$_2$AlMe$_2$ is a catalyst for alkynylalumination, it is even slower than **1$^{\text{Nd}}$**.[43] Together, it seems unlikely that the trend in catalytic activity results from chemical reactions directly involving the dialkylaluminum-coordinated bis(oxazolinyl)borate. Instead, the steric effects from the bulkier dialkylaluminum, as suggested by nOe studies above, are most likely responsible for the change in catalytic performance.

Reactions catalyzed by **1$^{\text{Y}}$** and **1$^{\text{La}}$** also exhibit improved selectivity, with respect to side reactions involving higher alkylaluminum reactants, compared to **1$^{\text{Nd}}$**. For example, products of side carboalumination processes are not detected in **1$^{\text{Y}}$**-catalyzed reactions with triethylaluminum, as is observed with **1$^{\text{Nd}}$** or Ln(AlMe$_4$)$_3$ (Ln = Y, La) as catalysts. In addition, products of hydroalumination with triisobutylaluminum, which occurs via β-hydride transfer processes in the absence of a catalyst, are also not detected.

Trimethylaluminum reacts more sluggishly compared to the higher alkylaluminum analogues, as expected on the basis of previously observed trends for reactions of AlR$_3$ and phenylacetylene or benzophenone[25] and for **1$^{\text{Nd}}$**-catalyzed reactions.[43] The products *n*BuC≡C–AlEt$_2$ and *n*BuC≡C–Al*i*Bu$_2$ are formed within two hours in reactions of triethyl- or triisobutylaluminum with 1-hexyne catalyzed by **1$^{\text{Y}}$**, whereas reactions of trimethylaluminum under similar conditions are more than 3× longer.

**Table 1.** Comparisons of catalysts and reagents in the alumination of terminal alkynes

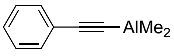
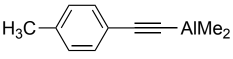
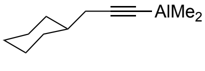
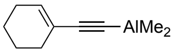
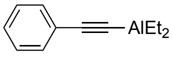
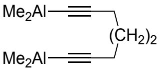


| R$^1$ | R | cat. | Time (h) | yield (%) |
|---|---|---|---|---|
| *n*Bu | Me | Y(AlMe$_4$)$_3$ | 24 | < 2 |
| *n*Bu | Me | La(AlMe$_4$)$_3$ | 24 | < 2 |
| *n*Bu | Me | Nd(AlMe$_4$)$_3$ | 24 | < 2 |
| *n*Bu | Me | **1$^{\text{Y}}$** | 6 | > 99 |
| *n*Bu | Me | **1$^{\text{La}}$** | 6 | > 99 |
| *n*Bu | Me | **1$^{\text{Nd}}$** | 18 | > 99 |
| *n*Bu | Et | **1$^{\text{Y}}$** | 2 | > 99 |
| *n*Bu | *i*Bu | **1$^{\text{Y}}$** | 1.5 | > 99 |
| *n*Bu | Et | Y(AlMe$_4$)$_3$ | 8 | 73 [a] |
| *t*Bu | Et | Ln(AlMe$_4$)$_3$<br>(Ln = Y, La) | < 1 | > 99 |
| *t*Bu | Et | **1$^{\text{Y}}$** | < 1 | > 99 |
| *t*Bu | Et | **2$^{\text{Y}}$** | 5 | > 99 |
| *t*Bu | Et | **3$^{\text{Y}}$** | 6 | > 99 |

[a] The remaining products (27%) are vinylaluminum species produced from ethylalumination.

A series of alkynylaluminum products R$^1$C≡C–AlR$_2$ were isolated from these reactions in good yield (Table 2). Terminal alkynes with either alkyl or aryl substituents react readily. As an example, bulky tert-butyl acetylene affords the alkynylaluminum product after short reaction times. An internal, conjugated alkene in cyclohexenyl acetylene is also tolerated in the reaction without addition to the double or triple bond. p-Tolylacetylene requires slightly longer reaction time than phenylacetylene under similar conditions; however, reaction rates are highly sensitive to trialkylaluminum and alkyne concentration (see below). These reactions have been performed on moderate scales, giving 0.25 g of hexynylaluminum and 0.3 g of phenylethynylaluminum, for example.

**Table 2.** Catalytic synthesis of alkynylaluminum compounds.

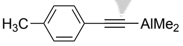
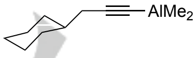
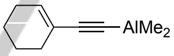
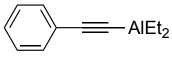
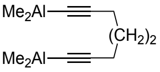
| Product[a] | Time (h) | Isolated yield (%) |
|---|---|---|
| $n$Bu–≡–AlMe$_2$ | 4 | 87 |
|  | 4 | 97 |
|  | 6 | 91 |
|  | 4 | 95 |
|  | 4 | 80 |
| $n$Bu–≡–AlEt$_2$ | 2 | 94 |
|  | 2 | 95 |
| $t$Bu–≡–AlEt$_2$ | 1 | 88 |
| $n$Bu–≡–AliBu$_2$ | 1 | 91 |
|  | 6 | 91 |

[a] Reaction conditions: 3 mol % **1$^Y$**, 60 °C, benzene.

Reaction of 1,7-octadiyne with an equivalent of trimethylaluminum in the presence of **1$^Y$** yields a mixture of $Me_2AlC{\equiv}C(CH_2)_4C{\equiv}CAlMe_2$, $Me_2AlC{\equiv}C(CH_2)_4C{\equiv}CH$ and starting materials. The monoaluminated alkyne was not isolated in this reaction; however, addition of a second equivalent of trimethylaluminum results in full conversion to new bis(dimethylaluminum)diyne $Me_2AlC{\equiv}C(CH_2)_4C{\equiv}CAlMe_2$, which is isolated as a brown-red solid (91%). In contrasting and complementary chemistry, polystyrene-supported methylpiperidine-catalyst mediates monoalumination of 1,7-octadiyne exclusively to $Me_2AlC{\equiv}C(CH_2)_4C{\equiv}CH$, and the bis(dimethylaluminum) product is not observed.[48]

The catalytic products, alkynyldialkylaluminum dimers, are isolable as analytically pure species and are fully characterized by NMR and IR spectroscopy. Many of these compounds were only previously generated and used in-situ, and their characterization was typically limited to titration of the alkynyl moiety present. In other cases, alkynylaluminums were quenched by reactions with carbonyl compounds in lieu of isolation. Here, we provide previously lacking spectroscopic data for this class of organoaluminums. The $^1$H and $^{13}$C{$^1$H} NMR chemical shifts of the AlMe$_2$ groups of the alkynylaluminum are higher frequency with respect to free trimethylaluminum (–0.39 and –7.1 ppm for $^1$H and $^{13}$C NMR, respectively). The $^{13}$C{$^1$H} NMR chemical shifts of *sp* hybridized alkynyl carbons are significantly higher in frequency than the alkyne starting materials, and the high frequency shift for the signal associated with the β-carbon is much larger than that of the α-carbon (Table 3). For example, the terminal and internal alkynyl carbons of 1-hexyne appeared at 68 and 85 ppm in the $^{13}$C{$^1$H} NMR spectrum, respectively. These values were 91 (and broadened due to $^{27}$Al) and 140 ppm for $n$BuC≡C–AlMe$_2$. In addition, intense bands in the IR spectra from 2050 to 2100 cm$^{-1}$ were assigned to $\nu_{C\equiv C}$, in contrast to the less intense and higher energy $\nu_{C\equiv C}$ of terminal alkynes.

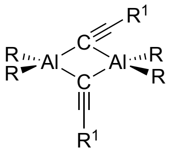
**Table 3.** $^{13}$C NMR spectroscopic data for isolated alkynylaluminum species

| Species | R$^1$C**C**AlR$_2$ $^{13}$C (ppm) | R$^1$**C**CAlR$_2$ $^{13}$C (ppm) | Δ(R$^1$**C**CAlR$_2$ – R$^1$**C**CH) $^{13}$C (ppm) |
|---|---|---|---|
| $n$Bu–≡–AlMe$_2$ | 90.09 | 139.97 | 53.97 |
|  | 97.11 | 120.25 | 36.25 |
|  | 96.76 | 117.33 | 33.33 |
|  | 90.61 | 139.79 | 56.19 |
|  | 94.03 | 138.12 | 55.12 |
| $n$Bu–≡–AlEt$_2$ | 85.86 | 140.91 | 54.91 |
|  | 93.33 | 120.39 | 36.39 |
| $t$Bu–≡–AlEt$_2$ | 81.92 | 149.88 | 55.88 |
| $n$Bu–≡–AliBu$_2$ | 87.22 | 142.25 | 56.25 |
|  | 90.64 | 138.83 | 54.83 |

Ground state geometries and IR frequencies of dimeric alkynylaluminum species **(R$^1$C≡CAlR$_2$)$_2$-calc** (R$^1$ = CyCH$_2$, $t$Bu, $n$Bu) were computed at the 6-31G$^{**}$/M06-2X-D3 level of theory.[46, 47, 49] The $C_2$-symmetric, acetylide-bridged dimeric starting geometries optimize to $C_1$ species that contained asymmetrically bridging alkynyl units, as expected on the basis of crystal structures of (R$^1$C≡CAlR$_2$)$_2$.[24, 50] As a result, two $^{13}$C NMR shifts for the alkynyl carbon and two $\nu_{C\equiv C}$ are calculated. Trends in the calculated $^{13}$C NMR chemical shifts (DFT-GIAO; 6-31G$^{**}$/B3LYP-

D3)[47, 49, 51, 52] were in good agreement with experimental observations, particularly the deshielded $R^1\mathbf{C{\equiv}C}AlR_2$.The $\nu_{C\equiv C}$ of $\mathbf{(R^1C{\equiv}CAlMe_2)_2}$**-calc** are ca. 50 $cm^{-1}$ lower than calculated values for $R^1C{\equiv}CH$-calc, accurately matching the experimental trend (Table 4).

**Table 4.** Calculated NMR and IR spectroscopic properties of gas-phase dimeric alkynylaluminum species.

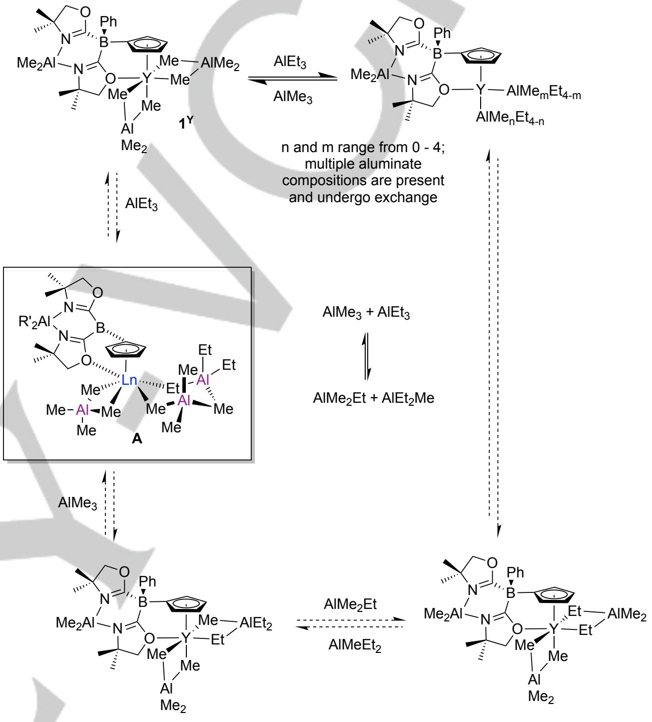


| $R^1$ | Calculated $R^1C\underline{\mathbf{C}}AlR_2$ $^{13}C$ (ppm) | Calculated $R^1\underline{\mathbf{C}}CAlR_2$ $^{13}C$ (ppm) | Calculated $R^1CCAlR_2$ $\nu_{CC}$ ($cm^{-1}$) | Calculated $R^1CCH$ $\nu_{CC}$ ($cm^{-1}$) |
|---|---|---|---|---|
| $CH_2Cy$ | 81.95, 95.19 | 122.07, 139.60 | 2140, 2148 | 2188 |
| *t*Bu | 76.87, 92.16 | 132.32, 147.40 | 2130, 2138 | 2181 |
| *n*Bu | 84.96, 93.63 | 128.31, 137.39 | 2141, 2144 | 2189 |

**Mechanistic Studies.** Possible intermediates in rare-earth-catalyzed alumination reactions of terminal alkynes $R^1C{\equiv}CH$ and $AlR_3$ to give $R^1C{\equiv}C–AlR_2$ include the mixed alkylaluminate $\{R'_2Al(Ox^{Me2})_2PhBCp\}Ln(AlR_nMe_{4-n})_2$, lanthanide acetylide species $[Ln]–C{\equiv}CR^1$, lanthanide alkyls derived from $AlR_3$, and $R^1C{\equiv}C–AlMe_2$. The viability of such species, in terms of their formation and reactivity, are discussed here.

The reaction of $\mathbf{1^Y}$ and triethylaluminum at room temperature leads to the highly fluxional mixed-alkyl aluminate species collectively assigned as $\{Me_2Al(Ox^{Me2})_2PhBCp\}Y(AlMe_nEt_{4-n})_2$. These species and free alkylaluminum compounds $(AlMe_{3-n}Et_n)_2$ exchange rapidly (Scheme 4), with species populations affected by the relative initial concentrations of $\mathbf{1^Y}$ and triethylaluminum. For example, a $^1H$-$^{89}Y\{^1H\}$ HSQC experiment on mixtures of $\mathbf{1^Y}$ and 10 equiv. of triethylaluminum revealed two distinct yttrium species. One compound contains only bridging Y-Et-Al, while the other has both Y-Me-Al and Y-Et-Al moieties (Figure 2B above). The alkylaluminum and lanthanide alkylaluminate species undergo chemical exchange, confirmed by crosspeaks in a 2D $^1H$ EXSY experiment between ethyl groups (methylene and methyl) in the two moieties.

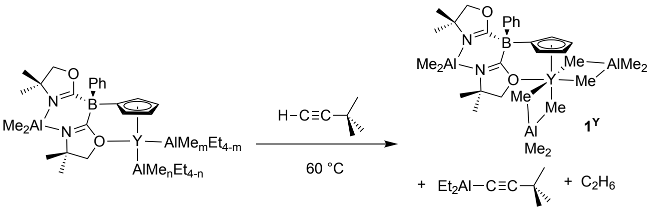
The rate of chemical exchange occurring in the mixture obtained from reaction of $\mathbf{1^Y}$ and one equiv. of triethylaluminum in benzene-$d_6$ ($k_{on}+k_{off}$; $k_{on}$ = 2.08 $M^{-1}s^{-1}$, corresponding to transfer of ethyl from $AlEt_nMe_{3-n}$ to $[Y](AlMe_nEt_{4-n})_2$ and $k_{off}$ = 3.60 $M^{-1}s^{-1}$, the reverse process) was extracted from $^1H$ EXSY NMR experiments performed with varying mixing times (see Figure S74).[53] Note that trialkylaluminum species are rapidly exchanging mixtures of monomers and dimers, with the dimer/monomer equilibrium constants $K_{eq} = [AlR_3]^2/[Al_2R_6]$ varying with temperature and alkyl group. For example at 60 °C, $K_{eq}^{Me} = 4.75 \times 10^{-7}$ M, $K_{eq}^{Et} = 8.47 \times 10^{-5}$ M, and $K_{eq}^{iBu}$ = 20.47 M for $AlMe_3$, $AlEt_3$ and Al*i*$Bu_3$, respectively.[54-56] The lowest energy configuration of trimethyl- and triethylaluminum is the dimer, but the exchange involves monomers because the $[AlR_4]$ moiety contains only one aluminum, which correspond to half-order rate dependence on $[Al_2R_6]$ or first-order dependence on $[AlR_3]$. The rate of an exchange process that is directly proportional to monomer concentration $[AlR_3]$ will be also directly proportional to the square root of dimer concentration, scaled by the equilibrium constant: rate ~ $[Al_2R_6]^{1/2} = ([AlR_3])^2/K_{eq})^{1/2}$. Because these experiments have mixtures of methyl and ethyl aluminum groups with unknown equilibrium constants, and because the rate will be directly proportional to $[AlR_3]_{total}$ and only scaled by unknown $(K_{eq})^{1/2}$, the rate constants are given with respect to total trialkylaluminum concentration.



**Scheme 4.** Plausible steps in aluminate/alkylaluminum exchange. Variable temperature EXSY experiments implicate an associative exchange of trialkylaluminum and lanthanide bis(aluminate), via proposed intermediate **A**.

Repeating similar EXSY experiments at several temperatures (298-333 K) provides activation parameters $\Delta S^‡$ (–43±1 $cal{\cdot}mol^{-1}{\cdot}K^{-1}$) and $\Delta H^‡$ (4.1±0.4 $kcal{\cdot}mol^{-1}$; Figure S75) for ethyl group exchange between $[Ln](AlR_3Et)$ and $R_2AlEt$. The relatively large and negative activation entropy for alkyl exchange at the lanthanide center suggests a strongly associated transition state while ruling out a terminal alkyllanthanide intermediate such as [Ln]–Et. On the basis of this associative exchange and the readily accessible monodentate aluminate from DFT calculations, we propose the mechanism for alkyl group exchange depicted in Scheme 4, with exchange of methyl and ethyl groups occurring via intermediate **A**. For comparison, terminal and bridging methyls in cationic $[Cp_2Zr(AlMe_4)]^+$ exchange by dissociation of $AlMe_3$.[57] In a remarkable contrast with zirconium, $[Cp_2Hf(AlMe_4)]^+$ and $AlMe_3$ exchange by an associative process.[58]

Addition of 1 equiv. of *t*BuC≡CH to this mixture at room temperature does not generate detectable quantities of the aluminated product *t*BuC≡CAlEt2 or the alkynylaluminate.[59] Instead, heating the reaction mixture to 60 °C affords *t*BuC≡C–AlEt2 and ethane and reforms $\mathbf{1^Y}$ (Scheme 5).



**Scheme 5.** Selective extrusion of ethane and formation of $tBuC{\equiv}CAlEt_2$.

It was not possible to determine the rate law for the reaction of Scheme 5 because the mixed alkylaluminum $\{Me_2Al(Ox^{Me2})_2PhBCp\}Y(AlMe_nEt_{4-n})_2$ is generated in the presence of excess $AlR_nMe_{3-n}$ and the exchange processes described above complicate NMR integration. The reaction of **1**$^{Y}$ and $tBuC{\equiv}CH$ at 60 °C, however, follows a second-order rate law of equation (1), $k = 0.041\ M^{-1}s^{-1}$:

$$\frac{-d[\mathbf{1}^{Y}]}{dt} = k[\mathbf{1}^{Y}]^1[tBuC{\equiv}CH]^1 \quad (1)$$

In addition, the initial rates of reaction of $tBuC{\equiv}CH$ with **1**$^{Y}$ (alone) or with **1**$^{Y}$ in the presence of 10.4 equiv of $AlMe_3$ are equivalent within error. The rate of metalation is ca. two orders of magnitude slower than the trialkylaluminum/tetraalkylaluminate exchange. Together, the rapid alkylaluminum/aluminate exchange at room temperature and the requirement of elevated temperature for alumination and alkane formation provide compelling evidence that alkyne metalation is the turnover-limiting step during catalytic alumination.

The time-dependent concentrations of $tBuC{\equiv}CH$ and triethylaluminum starting materials and the $tBuC{\equiv}C{-}AlEt_2$ product were monitored in situ by $^1$H NMR spectroscopy for the alumination reaction catalyzed by **1**$^{Y}$ in benzene-$d_6$ heated at 60 °C. Non-linear least squares regression analysis of $[tBuC{\equiv}CH]$ versus time to the equation for a second-order rate law, namely equation (2), reveals first-order dependence on both $[AlEt_3]$ and $[tBuC{\equiv}CH]$, where $\Delta_o = [AlEt_3]_o - [tBuC{\equiv}CH]_o$, determined prior to heating the reaction mixture.

$$[tBuC{\equiv}CH] = \frac{\Delta_o[tBuC{\equiv}CH]_o}{[AlEt_3]_o e^{\Delta_o k_{obs} t} - [tBuC{\equiv}CH]_o} \quad (2)$$

A plot of $k_{obs}$ vs $[\mathbf{1}^{Y}]$ is linear (Figure S77), indicating first-order dependence on catalyst concentration and providing the third-order experimental rate law of equation (3). Because a termolecular elementary step is highly unlikely, this rate law is better interpreted following the Michaelis-Menten-type model, modified for a ternary (two-substrate) reaction shown in the rate expression of equation (4), in which the catalyst and first substrate reversible form an adduct that subsequently reacts with the second substrate.[60] Thus, the experimental ternary-order rate constant ($k'$) corresponds to a composite of the product of forward rate constants divided by the sum of the rates of individual steps, which are dependent on $[AlEt_3]$ and $[tBuC{\equiv}CH]$.

$$\frac{-d[tBuC{\equiv}CH]}{dt} = k'[\mathbf{1}^{Y}]^1[tBuC{\equiv}CH]^1[AlEt_3]^1 \quad (3)$$

$$\frac{-d[tBuC{\equiv}CH]}{dt} = \frac{k_1k_2[\mathbf{1}^{Y}]^1[tBuC{\equiv}CH]^1[AlEt_3]^1}{k_1[AlEt_3] + k_{-1} + k_2[tBuC{\equiv}CH]} \quad (4)$$

The rate constant $k_2$ may be determined by fitting saturation curves obtained from initial rate measurements. The initial rates of product formation were measured over a series of experiments in which triethylaluminum concentration was varied. The initial rate increases as $[AlEt_3]$ increases in a nonlinear manner toward saturation (Figure 4). This data is fit to the equation $d[tBuC{\equiv}CAlEt_2]/dt = A[AlEt_3]/\{[AlEt_3] + B\}$ using nonlinear least-squares regression analysis, where $A = k_2[\mathbf{1}^{Y}][tBuC{\equiv}CH]$ and $B = \{k_{-1} + k_2[tBuC{\equiv}CH]\}/k_1$. From this fit, $k_2$ is calculated to be $0.34 \pm 0.03\ M^{-1}s^{-1}$ at 60 °C. A rough estimate of $k_2$ can also be calculated by substituting experimental values for initial rate at a particular concentration into eq 6, which affords $k_2 = 0.45\ M^{-1}s^{-1}$ at 60 °C in good agreement with the result from the $[AlEt_3]$ saturation experiments.

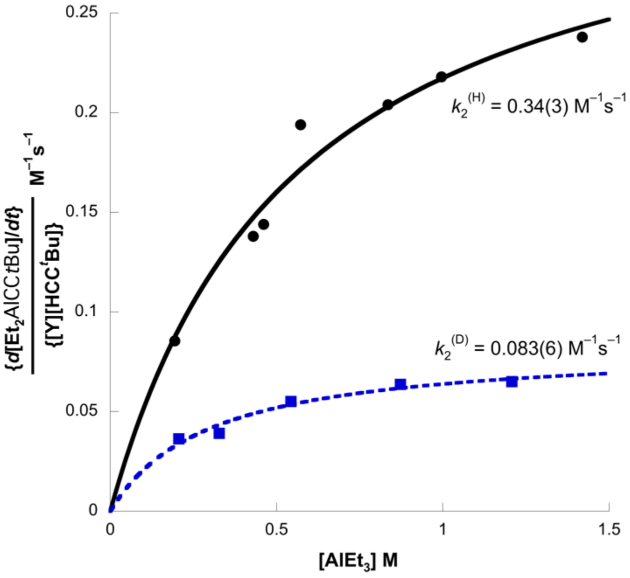
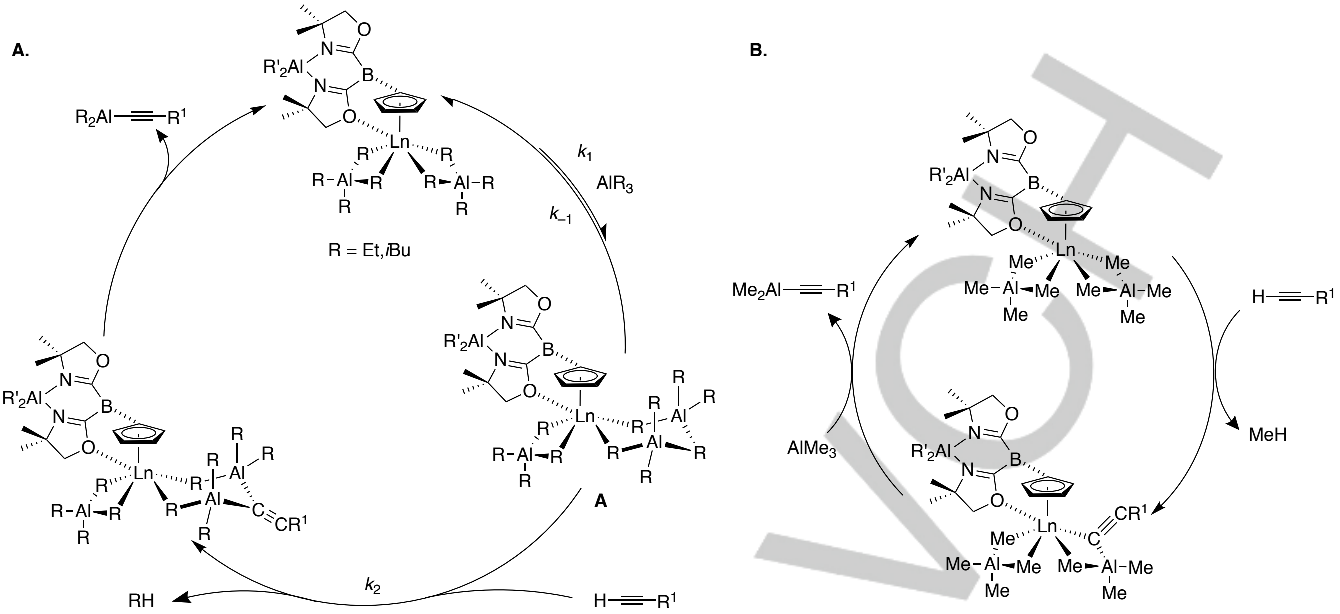


**Figure 4.** Plots of initial rate of product formation vs. $[AlEt_3]$ concentration for **1**$^{Y}$-catalyzed reactions of $tBuC{\equiv}CH$ or $tBuC{\equiv}CD$ at 60 °C, showing rate saturation in $[AlEt_3]$. The curve represents a nonlinear least-squares fit to the equation $d[tBuC{\equiv}CAlEt_2]/dt = A[AlEt_3]/\{[AlEt_3] + B\}$, where $A = k_2[\mathbf{1}^{Y}][tBuC{\equiv}CH]$ and $B = (k_{-1} + k_2[tBuC{\equiv}CH])/k_1$. $[AlEt_3] = 0.194\text{-}1.419$ M; $[tBuC{\equiv}CH] = 0.096$ M; $[\mathbf{1}^{Y}] = 0.012$ M.

The rates for **1**$^{Y}$-catalyzed alkynylalumination, determined for the isotopically labelled $tBuC{\equiv}CD$, show the expected saturation at higher $[AlEt_3]$. Nonlinear least-squares regression analysis provides $k_2^{(D)}$ (Figure 4), and $k_2^{(H)}/k_2^{(D)} = 4.1 \pm 0.4$. This large primary isotope effect further indicates that C–H bond is broken during the turnover-limiting step.

A catalytic cycle that is consistent with these data involves a reversible addition of rare earth tetraalkylaluminate catalyst and trialkylaluminum to form transient mixed-alkyl heterobimetallic **A** containing *four* aluminums. Three aluminums come from Et/Me-exchanged **1**$^{Y}$ and one comes from $AlR_3$. This adduct reacts by an irreversible and turnover-limiting alkyne metalation at an aluminum ethyl to yield a monoalkynyl



**Scheme 6. A.** Proposed catalytic cycle for alumination of *t*BuC≡CH with AlEt$_3$, by ethyl-exchanged $\mathbf{1}^{\mathrm{Y}}$. R may be a methyl group from $\mathbf{1}^{\mathrm{Y}}$, but ethyl groups preferentially react with alkyne. **B.** Proposed catalytic cycle for the alumination of R$^1$C≡CH with trimethylaluminum by $\mathbf{1}^{\mathrm{Y}}$.

aluminate species and ethane, which subsequently extrudes the product (Scheme 6A).

The evidence in support of this mechanism includes (*i*) a ternary rate law showing first order-concentration dependences on $\mathbf{1}^{\mathrm{Y}}$, *t*BuC≡CH, and AlEt$_3$, (*ii*) saturation upon addition of excess AlEt$_3$, and (*iii*) a large, primary kinetic isotope effect on $k_2$ in the catalytic C–H (or C–D) bond cleavage step. In this mechanism, the proposed resting state is the mixed rare earth bis(tetraalkylaluminate), which undergoes fast exchange with the trialkylaluminum species present in the reaction mixture. This exchange process is associative (Scheme 4), and the intermediate species in this exchange is also postulated to be the intermediate **A** that metalates alkyne during catalytic alkynylalumination. Note that $k_1$ and $k_{\mathrm{on}}$ are identically associated with the formation of transient adduct **A** (the precise values of $k_1$ and $k_{\mathrm{on}}$ may vary depending on R); in contrast, $k_{\mathrm{off}}$ and $k_{-1}$ are each associated with unique processes. $k_{\mathrm{off}}$ corresponds to the exchange of ethyl from [Ln](AlMe$_n$Et$_{4-n}$) and R$_2$AlEt while $k_{-1}$ involves dissociation of AlR$_3$ from [Ln](AlMe$_n$Et$_{4-n}$)·AlR$_3$ (**A**). Because **A** is transient, $k_{-1}$ is much larger than than $k_{\mathrm{off}}$ and $k_1$. Interestingly, the base-catalyzed alumination of alkynes is fastest at ca. 50 mol % NEt$_3$ and slower at 100 mol %, implying that the central Me$_3$Al·NEt$_3$ adduct is further promoted by the presence of AlMe$_3$,[61] and there may be some mechanistic analogy between the two systems.

A few other mechanisms are ruled out by these data. First, comparisons of rate constants for alkylaluminum/aluminate exchange and alkyne metalation establish the sequence as reversible trialkylaluminum association followed by alkyne metalation rather than reversible alkyne coordination prior to metalation by trialkylaluminum. Second, mechanisms involving alkylaluminum dissociation prior to alkyne metalation are eliminated by the first-order dependence on [AlR$_3$]. In this context, we note that the rate law for this C–H bond alumination contrasts that of carboalumination and polymerization (in the presence of alkylaluminums). The rates of the carboalumination processes have inverse dependence on [AlR$_3$], implying that trialkylaluminum must dissociate prior to insertion.[62] In addition, as noted above, exchange of bridging and terminal methyls in zirconium tetramethylaluminate is dissociative and suggests a zirconium methyl intermediate.[57]

A third mechanism, also ruled out by these data specifically for reactions of AlEt$_3$, and likely eliminated for Al*i*Bu$_3$, but plausible for AlMe$_3$, involves reaction of terminal alkyne and bis(tetraalkylaluminate) rather than the adduct **A** (ethyl-exchange $\mathbf{1}^{\mathrm{Y}}$ and AlR$_3$). Such a mechanism, shown in Scheme 6B, appears plausible for AlMe$_3$ on the basis of the observed stoichiometric reaction of $\mathbf{1}^{\mathrm{Y}}$ and *t*BuC≡CH. In fact, reactions of $\mathbf{1}^{\mathrm{Y}}$ and *t*BuC≡CH produce methane and new yttrium alkynylaluminate species. The catalytic product *t*BuC≡C–AlMe$_2$ is formed only upon addition of AlMe$_3$ to this yttrium alkynylaluminate; however, this displacement of *t*BuC≡C–AlMe$_2$ by AlMe$_3$ is rapid at room temperature.

In the case of the pathway of Scheme 6B when R = Et, *i*Bu, the resting state would be an alkynylated rare earth aluminate, and exchange between this species and {Me$_2$Al(Ox$^{\mathrm{Me2}}$)$_2$PhBCp}Y(AlMe$_n$Et$_{4-n}$)$_2$ would have to be responsible for catalytic rate law showing a first-order dependence on [AlEt$_3$]. This idea is somewhat ruled out by the immediate and irreversible extrusion of *t*BuC≡CAlEt$_2$ upon reaction of $\mathbf{1}^{\mathrm{Y}}$, AlEt$_3$, and *t*BuC≡CH, which indicates that the pair of species [Y](AlR$_4$) + R$_2$AlC≡CR is not in equilibrium with [Y](R$_3$AlC≡CR) + AlR$_3$.

Most significantly, the reaction of $\mathbf{1}^{\mathrm{Y}}$ and *t*BuC≡CH is not kinetically competent for the catalytic reactions involving AlEt$_3$. The rate constant for metalation of *t*BuC≡CH by $\mathbf{1}^{\mathrm{Y}}$ is 8-11× smaller than the rate constant ($k_2$) for metalation during $\mathbf{1}^{\mathrm{Y}}$-

catalyzed reaction of *t*BuC≡CH and $AlEt_3$ (at 60 °C, saturated in $AlEt_3$). This difference matches the approximate 10-fold difference in catalytic rates of alkynyl alumination (–*d*[*t*BuC≡CH]/*d*t) for $AlMe_3$ and $AlEt_3$, normalized for catalyst, alkyne, and trialkylaluminum concentrations. One possibility is that these differences are simply a function of inequivalent rates of alkyne metalation by aluminum-methyl compared to aluminum-ethyl species. Unfortunately, we are not able to measure the experimental rate law or determine $k_2$ for catalytic metalations using $AlMe_3$ due to overlapping signals in the broad $^1H$ NMR spectra of reaction mixtures. Instead, we measured initial rates for the reaction of **1$^{Y}$** and *t*BuC≡CH, which are equivalent in the presence or absence of additional equivalents of $AlMe_3$, indicating zero-order dependence on [$AlMe_3$]. That is, *there is no rate enhancement of metalation by formation of* **1$^{Y}$**$\cdot AlMe_3$ suggesting that this metalation does not require the excess trimethylaluminum under catalytic conditions. Thus, the catalyst for metalation is **1$^{Y}$** rather than **1$^{Y}$**$\cdot AlMe_3$, and the rate laws and mechanisms for catalytic alumination with $AlMe_3$ (Scheme 6B) and $AlEt_3$ (Scheme 6A) are distinct. Likely, the faster catalytic chemistry of $AlEt_3$ and Al*i*Bu$_3$ is related to the much higher reactivity of trialkylaluminum adduct **A** in comparison to the tetraalkylaluminate resting state. Although the proposed structure of transient **A** is currently based only on its kinetically-determined composition, we speculate that its enhanced reactivity could results from a unique bridging Al–R–Al moiety not present in **1** or the catalytic resting state.

## Conclusion

The catalytic properties of compounds **1-3$^{Ln}$** contrast the typical behavior of transition metals in reactions of alkylaluminums and unsaturated organic compounds, which generally result in formal insertion into aluminum-carbon bonds. Carboalumination, the Aufbaureaktion,[63] and olefin polymerization (especially coordinative chain transfer polymerization)[64] all involve generation of transition-metal alkyls from interaction with alkylaluminum species, a series of one or many alkene insertions, followed by exchange with a new alkyl aluminum. The highly electrophilic lanthanide catalysts here do not access coordinatively unsaturated species, and metalation is observed rather than insertion. Because aluminum alkyls are known to react via three pathways with alkynes (carboalumination, hydroalumination, and C–H metalation), the selective C–H bond functionalization here represents an important breakthrough. Moreover, given the propensity of multimetallic species to mediate metalations of nonpolar C–H bonds,[65] the present chemistry with rare earth aluminates suggests strategies for catalytic alumination of less polar C–H bonds.

The products of this catalysis, monoalkynylaluminums, are now readily accessible for higher alkylaluminums. The alkylaluminum starting materials are directly synthesized from aluminum, hydrogen, and alkenes. Thus, this catalytic development may facilitate the applications of $R^1C≡C–AlR_2$ in new chemical transformations. Already, spectroscopic characterization of isolated $R^1C≡CAlR_2$ reveal an increase in the allowedness of $ν_{C≡C}$ and a generally smaller HOMO-LUMO gap of $R^1$**C**≡C–$AlR_2$ for alkynylated C≡C bonds compared to $R^1C≡CH$. We are currently working to apply this insight and the versatile catalytic preparation of $R^1C≡CAlR_2$ to develop their reactions with electrophiles, in carboalumination, and in polymerizations. In this context, comparisons with carboalumination catalysts and mechanism become even more important to enable the design of new transformations involving aluminum-carbon bond formations.

## Experimental Section

**General.** All manipulations were carried out under inert conditions, either using Schlenk techniques or in gloveboxes under a nitrogen atmosphere, unless stated otherwise. Dry and degassed solvents were used throughout. Benzene and toluene were sparged with nitrogen, passed through activated alumina columns, and stored under nitrogen. Deuterated benzene and toluene were degassed via three consecutive freeze-pump-thaw cycles, dried over Na/K alloy, vacuum transferred, and stored over molecular sieves under nitrogen. $H[PhB(Ox^{Me2})_2C_5H_5]$,[66] $Ln(AlMe_4)_3$ (Ln = Y, La, Nd),[33] and **1$^{Nd}$** [43] were synthesized according to corresponding literature procedures. Trimethylaluminum, triethylaluminum, and triisobutylaluminum were purchased from Aldrich and were used as received. Terminal alkynes were obtained from Aldrich, dried over anhydrous $MgSO_4$, distilled, and stored over molecular sieves in the glovebox.

$^1H$, $^{13}C\{^1H\}$ and $^{11}B$ NMR spectra were obtained on a Brucker Avance III 600 MHz spectrometer. $^{15}N$ chemical shifts obtained via $^{15}N$-$^1H$ HMBC experiments, originally referenced to liquid $NH_3$, were re-referenced to $CH_3NO_2$ by subtracting 381.9 ppm. $^{89}Y$ chemical shifts were obtained via $^{89}Y\{^1H\}$-$^1H$ HSQC experiments and were referenced internally to tetramethylsilane (TMS) to give the $^1H$ NMR frequency, and the yttrium chemical shift is calibrated on the basis of the known relationship of $^1H$ to $^{89}Y$ frequencies.

**$\{Me_2Al(Ox^{Me2})_2PhBCp\}Y(AlMe_4)_2$ (1$^{Y}$).** Toluene was added to a mixture of $H[PhB(Ox^{Me2})_2(C_5H_5)]$ (0.150 g, 0.428 mmol) and $Y(AlMe_4)_3$ (0.150 g, 0.428 mol), leading to immediate evolution of methane and a yellow solution. The solution was stirred vigorously for 45 min. All volatiles were removed in vacuo, and the solid residue was washed with pentane and dried to afford $\{Me_2Al(Ox^{Me2})_2PhBCp\}Y(AlMe_4)_2$ as a highly air- and moisture-sensitive pale yellow powder (0.177 g, 0.266 mmol, 62%). The room temperature spectra of isolated materials are broad. Therefore, NMR data is given for *in-situ* generated **1$^{Y}$**. $^1H$ NMR (benzene-$d_6$): δ 7.40 (vq, *J* = 8.5 Hz, 2 H, m-$C_6H_5$), 7.32 (vt, *J* = 7.3 Hz, 2 H, o-$C_6H_5$), 7.18 (vt, *J* = 6.6 Hz, 1 H, p-$C_6H_5$,), 6.33 (br s, 2 H $C_5H_4$), 6.21 (br s, 2 H, $C_5H_4$), 3.75 (d, $^2J_{HH}$ = 8.6 Hz, 2 H, $CNCMe_2CH_2O$), 3.30 (d, $^2J_{HH}$ = 8.6 Hz, 2 H, $CNCMe_2CH_2O$), 0.92 (s, 6 H, $CNCMe_2CH_2O$), 0.82 (s, 6 H, $CNCMe_2CH_2O$), –0.24 (br s, 24 H, $AlMe_4$), –0.45 (s, 3 H, $AlMe_2$), –0.69 (s, 3 H, $AlMe_2$). $^{13}C\{^1H\}$ NMR (benzene-$d_6$, 150 MHz): δ 133.51 (m-$C_6H_5$), 133.19 (ipso-$C_5H_4$), 128.92 (o-$C_6H_5$), 127.48 (p-$C_6H_5$), 121.76 ($C_5H_4$), 117.11 ($C_5H_4$), 81.41 ($CNCMe_2CH_2O$), 66.64 ($CNCMe_2CH_2O$), 27.92 ($CNCMe_2CH_2O$), 25.99 ($CNCMe_2CH_2O$), 1.53 (br, $AlMe_4$), –6.01 ($AlMe_2$), –6.80 ($AlMe_2$). $^{11}B$ NMR (benzene-$d_6$, 192 MHz): δ –16.7. $^{15}N\{^1H\}$ NMR (benzene-$d_6$, 60 MHz): δ –177.7 ($CNCMe_2CH_2O$). $^{89}Y\{^1H\}$ NMR (benzene-$d_6$, 29 MHz): δ 394. IR (KBr, cm$^{-1}$): 3069 w, 3047 w, 2926 s, 2827 m, 1594 m (C=N), 1560 m (C=N),1465 m, 1432 w, 1394 w, 1373 m, 1291 w, 1262 m, 1192 s, 1052 s, 974 m, 804 m, 697 s, 518 w, 419 w, 397 w.. Anal. Calcd for $C_{31}H_{55}BN_2O_2Al_3Y$: C, 55.71; H, 8.23; N, 4.19. Found: C, 55.93; H, 7.94; N, 4.01. Mp: 93-96 °C, dec.

**$\{Me_2Al(Ox^{Me2})_2PhBCp\}La(AlMe_4)_2$ (1$^{La}$).** Toluene was added to a mixture of $H[PhB(Ox^{Me2})_2C_5H_5]$ (0.150 g, 0.429 mmol) and $La(AlMe_4)_3$ (0.172 g, 0.429 mmol), leading to immediate evolution of methane and a yellow solution. The solution was stirred vigorously for 45 min. All volatiles were removed in vacuo, and the solid residue was washed with pentane and dried to afford $\{Me_2Al(Ox^{Me2})_2PhBCp\}La(AlMe_4)_2$ as a highly air and moisture sensitive yellow powder (0.228 g, 0.317 mmol, 74%). NMR data for the *in-situ* generated compound is presented; isolated material gives spectra with identical chemical shifts but broad signals. $^1$H NMR (benzene-$d_6$): δ 7.39 (m, 2 H, m-$\mathrm{C_6H_5}$), 7.36 (vt, $J$ = 7.0 Hz, 2 H, o-$\mathrm{C_6H_5}$), 7.20 (vt, $J$ = 6.3 Hz, 1 H, p-$\mathrm{C_6H_5}$), 6.38 (br s, 2 H $\mathrm{C_5H_4}$), 6.25 (br s, 2 H, $\mathrm{C_5H_4}$), 3.56 (d, $^2J_{\mathrm{HH}}$ = 8.4 Hz, 2 H, $\mathrm{CNCMe_2}\mathit{CH}_2\mathrm{O}$), 3.31 (d, $^2J_{\mathrm{HH}}$ = 8.4 Hz, 2 H, $\mathrm{CNCMe_2}\mathit{CH}_2\mathrm{O}$), 0.89 (s, 6 H, $\mathrm{CNC}\mathit{Me}_2\mathrm{CH_2O}$), 0.82 (s, 6 H, $\mathrm{CNC}\mathit{Me}_2\mathrm{CH_2O}$), –0.19 (br s, 24 H, $\mathrm{Al}\mathit{Me}_4$), –0.43 (s, 3 H, $\mathrm{Al}\mathit{Me}_2$), –0.77 (s, 3 H, $\mathrm{Al}\mathit{Me}_2$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (benzene-$d_6$, 150 MHz): δ 133.30 (m-$\mathrm{C_6H_5}$), 128.92 (o-$\mathrm{C_6H_5}$), 127.44 (p-$\mathrm{C_6H_5}$), 124.41 ($\mathrm{C_5H_4}$), 119.13 ($\mathrm{C_5H_4}$), 80.96 ($\mathrm{CNCMe_2}\mathit{C}\mathrm{H_2O}$), 70.48 ($\mathrm{CNCMe_2}\mathit{C}\mathrm{H_2O}$), 66.75 ($\mathrm{CN}\mathit{C}\mathrm{Me_2CH_2O}$), 27.96 ($\mathrm{CNC}\mathit{Me}_2\mathrm{CH_2O}$), 26.04 ($\mathrm{CNC}\mathit{Me}_2\mathrm{CH_2O}$), 2.55 ($\mathrm{Al}\mathit{Me}_4$), –6.09 ($\mathrm{Al}\mathit{Me}_2$), –6.99 ($\mathrm{Al}\mathit{Me}_2$). $^{11}$B NMR (benzene-$d_6$, 192 MHz): δ –16.57. $^{15}\mathrm{N}\{^1\mathrm{H}\}$ NMR (benzene-$d_6$, 60 MHz): δ –177.9 ($\mathrm{C}\mathit{N}\mathrm{CMe_2CH_2O}$). IR (KBr, cm$^{-1}$): 3070 w, 3049 w, 2969 m, 2929 s, 2827 w, 1594 s (C=N), 1557 m (C=N), 1489 w, 1464 m, 1433 w, 1394 w, 1373 m, 1291 m, 1260 m, 1197 s, 1052 m, 1037 m, 970 m, 939 w, 889 w, 845 w, 775 w, 698 s, 626 w, 579 m, 520 w, 419 w. Anal. Calcd for $\mathrm{C_{31}H_{55}BN_2O_2Al_3La}$: C, 51.83; H, 7.66; N, 3.90. Found: C, 49.67; H, 7.87; N, 3.78. Mp: 95-100 °C, dec.

**$\{\mathrm{Et_2Al(Ox^{Me2})_2PhBCp}\}\mathrm{Y(AlMe_4)_2}$ ($\mathbf{2^Y}$).** In the glovebox, $\mathrm{(AlEt_3)_2}$ (39.2 µL, 0.143 mmol) was added via syringe to a toluene solution (5 mL) of $\mathrm{H[PhB(Ox^{Me2})C_5H_5]}$ (0.100 g, 0.286 mmol). This solution was stirred for 15 min. A toluene solution (5 mL) of $\mathrm{Y(AlMe_4)_3}$ (0.100 g, 0.286 mmol) was slowly added to the first solution. The resulting solution was stirred vigorously for 6 h, and then all volatiles were removed in vacuo. The residue was washed with pentane and dried to obtain $\{\mathrm{Et_2Al(Ox^{Me2})_2PhBCp}\}\mathrm{Y(AlMe_4)_2}$ as a pale yellow powder (0.151 g, 0.217 mmol, 76%). $^1$H NMR (benzene-$d_6$): δ 7.41 (vd, $J$ = 7.3 Hz, 2 H, m-$\mathrm{C_6H_5}$), 7.32 (vt, $J$ = 7.5 Hz, 2 H, o-$\mathrm{C_6H_5}$), 7.18 (vt, $J$ = 7.5 Hz, 1 H, p-$\mathrm{C_6H_5}$), 6.32 (br s, 2 H, $\mathrm{C_5H}$), 6.19 (br s, 2 H, $\mathrm{C_5H_4}$), 3.75 (d, $^2J_{\mathrm{HH}}$ = 8.6 Hz, 2 H, $\mathrm{CNCMe_2}\mathit{CH}_2\mathrm{O}$), 3.31 (d, $^2J_{\mathrm{HH}}$ = 8.6 Hz, 2 H, $\mathrm{CNCMe_2}\mathit{CH}_2\mathrm{O}$), 1.24 (t, $^3J_{\mathrm{HH}}$ = 8.0 Hz, 3 H, $\mathrm{AlCH_2}\mathit{CH}_3$), 0.97 (s, 6 H, $\mathrm{CNC}\mathit{Me}_2\mathrm{CH_2O}$), 0.95 (t, $^3J_{\mathrm{HH}}$ = 8.0 Hz, 3 H, $\mathrm{AlCH_2}\mathit{CH}_3$), 0.88 (s, 6 H, $\mathrm{CNC}\mathit{Me}_2\mathrm{CH_2O}$), 0.12 (q, $^3J_{\mathrm{HH}}$ = 8.0 Hz, 2 H, $\mathrm{Al}\mathit{CH}_2\mathrm{CH_3}$), –0.10 (q, $^3J_{\mathrm{HH}}$ = 8.0 Hz, 2 H, $\mathrm{Al}\mathit{CH}_2\mathrm{CH_3}$), –0.24 (br s, 24 H, $\mathrm{Al}\mathit{Me}_4$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (benzene-$d_6$, 150 MHz): δ 133.55 (m-$\mathrm{C_6H_5}$), 133.15 (ipso-$\mathrm{C_5H_4}$), 127.46 (o-$\mathrm{C_6H_5}$), 127.21 (p-$\mathrm{C_6H_5}$), 121.63 ($\mathrm{C_5H_4}$), 117.11 ($\mathrm{C_5H_4}$), 81.26 ($\mathrm{CNCMe_2}\mathit{C}\mathrm{H_2O}$), 66.84 ($\mathrm{CN}\mathit{C}\mathrm{Me_2CH_2O}$), 27.56 ($\mathrm{CNC}\mathit{Me}_2\mathrm{CH_2O}$), 26.02 ($\mathrm{CNC}\mathit{Me}_2\mathrm{CH_2O}$), 9.90 ($\mathrm{AlCH_2}\mathit{C}\mathrm{H_3}$), 9.75 ($\mathrm{AlCH_2}\mathit{C}\mathrm{H_3}$), 2.61 (br, $\mathrm{Al}\mathit{C}\mathrm{H_2CH_3}$), 2.14 (br, $\mathrm{Al}\mathit{C}\mathrm{H_2CH_3}$), 1.57 (br, $\mathrm{Al}\mathit{Me}_4$). $^{11}$B NMR (benzene-$d_6$, 192 MHz): δ –16.71. $^{15}\mathrm{N}\{^1\mathrm{H}\}$ NMR (benzene-$d_6$, 60 MHz): δ –179.1 ($\mathrm{C}\mathit{N}\mathrm{CMe_2CH_2O}$). $^{89}\mathrm{Y}\{^1\mathrm{H}\}$ NMR (benzene-$d_6$, 29 MHz): δ 395. IR (KBr, cm$^{-1}$): 3071 w, 3049 w, 2932 s, 2927 s, 2867 s, 1591 s (C=N), 1552 m (C=N), 1464 m, 1433 w, 1411 w, 1374 m, 1292 m, 1260 m, 1195 s, 1052 m, 1038 s, 987 m, 970 s, 891 w, 845 w, 794 m, 702 s, 643 m, 593 w, 466 w. Anal. Calcd for $\mathrm{C_{33}H_{59}BN_2O_2Al_3Y}$: C, 56.92; H, 8.48; N, 4.02. Found: C, 57.32; H, 8.64; N, 3.99. Mp: 102-105 °C, dec.

**$\{\mathrm{Et_2Al(Ox^{Me2})_2PhBCp}\}\mathrm{La(AlMe_4)_2}$ ($\mathbf{2^{La}}$).** $\mathrm{(AlEt_3)_2}$ (39.2 µL, 0.143 mmol) was added via syringe to a toluene solution (5 mL) of $\mathrm{H[PhB(Ox^{Me2})C_5H_5]}$ (0.100 g, 0.286 mmol), and the solution was stirred for 15 min. A toluene solution (5 mL) of $\mathrm{La(AlMe_4)_3}$ (0.115 g, 0.286 mmol) was slowly added to the first solution. The resulting solution was stirred vigorously for 6 h, and then all volatiles were removed in vacuo. The solid residue was washed with pentane and dried to obtain $\{\mathrm{Et_2Al(Ox^{Me2})_2PhBCp}\}\mathrm{La(AlMe_4)_2}$ as a yellow powder (0.158 g, 0.212 mmol, 74%). $^1$H NMR (benzene-$d_6$): δ 7.41 (vd, $J$ = 7.1 Hz, 2 H, o-$\mathrm{C_6H_5}$), 7.37 (t, $J$ = 7.4 Hz, 2 H, m-$\mathrm{C_6H_5}$), 7.20 (t, $J$ = 7.4 Hz, 1 H, p-$\mathrm{C_6H_5}$), 6.37 (br s, 2 H, $\mathrm{C_5H_4}$), 6.24 (br s, 2 H, $\mathrm{C_5H_4}$), 3.56 (d, $^2J_{\mathrm{HH}}$ = 8.4 Hz, 2 H, $\mathrm{CNCMe_2C}\mathit{H}_2\mathrm{O}$), 3.30 (d, $^2J_{\mathrm{HH}}$ = 8.4 Hz, 2 H, $\mathrm{CNCMe_2C}\mathit{H}_2\mathrm{O}$), 1.23 (t, $^3J_{\mathrm{HH}}$ = 8.1 Hz, 3 H, $\mathrm{AlCH_2C}\mathit{H}_3$), 0.93 (s, 6 H, $\mathrm{CNC}\mathit{Me}_2\mathrm{CH_2O}$), 0.87 (m, 9 H, $\mathrm{CNC}\mathit{Me}_2\mathrm{CH_2O}$, $\mathrm{AlCH_2C}\mathit{H}_3$), 0.12 (q, $^3J_{\mathrm{HH}}$ = 8.1 Hz, 2 H, $\mathrm{AlC}\mathit{H}_2\mathrm{CH_3}$), –0.19 (br m, 26 H, $\mathrm{AlC}\mathit{H}_2\mathrm{CH_3}$, $\mathrm{Al}\mathit{Me}_4$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (benzene-$d_6$, 150 MHz): δ 133.21 (o-$\mathrm{C_6H_5}$), 128.68 (m-$\mathrm{C_6H_5}$), 127.47 (p-$\mathrm{C_6H_5}$), 124.26 ($\mathrm{C_5H_4}$), 119.16 ($\mathrm{C_5H_4}$), 80.79 ($\mathrm{CNCMe_2}\mathit{C}\mathrm{H_2O}$), 66.94 ($\mathrm{CN}\mathit{C}\mathrm{Me_2CH_2O}$), 27.53 ($\mathrm{CNC}\mathit{Me}_2\mathrm{CH_2O}$), 26.01 ($\mathrm{CNC}\mathit{Me}_2\mathrm{CH_2O}$), 9.87 ($\mathrm{AlCH_2}\mathit{C}\mathrm{H_3}$), 9.60 ($\mathrm{AlCH_2}\mathit{C}\mathrm{H_3}$), 2.83 (br, $\mathrm{Al}\mathit{Me}_4$), 2.55 (br, $\mathrm{Al}\mathit{C}\mathrm{H_2CH_3}$), 2.05 (br, $\mathrm{Al}\mathit{C}\mathrm{H_2CH_3}$). $^{11}$B NMR (benzene-$d_6$, 192 MHz): δ –16.7. $^{15}\mathrm{N}\{^1\mathrm{H}\}$ NMR (benzene-$d_6$, 60 MHz): δ –179.4 ($\mathrm{C}\mathit{N}\mathrm{CMe_2CH_2O}$). IR (KBr, cm$^{-1}$): 3072 w, 3047 w, 2929 s, 2729 w, 1594 s (C=N), 1542 m (C=N), 1464 m, 1433 w, 1412 w, 1373 m, 1293 m, 1261 m, 1194 s, 1134 w, 1050 m, 1037 m, 966 s, 933 m, 888 w, 845 m, 794 m, 700 s, 644 m, 591 m, 538 w, 499 w, 419 w. Anal. Calcd for $\mathrm{C_{33}H_{59}BN_2O_2Al_3La}$: C, 53.10; H, 7.91; N, 3.75. Found: C, 53.04; H, 8.46; N, 3.56. Mp: 97-100 °C, dec.

**$\{\mathrm{Et_2Al(Ox^{Me2})_2PhBCp}\}\mathrm{Nd(AlMe_4)_2}$ ($\mathbf{2^{Nd}}$).** $\mathrm{(AlEt_3)_2}$ (39.2 µL, 0.143 mmol) and $\mathrm{H[PhB(Ox^{Me2})C_5H_5]}$ (0.100 g, 0.286 mmol) were mixed in toluene (5 mL) and allowed to stir for 15 min. A toluene solution (5 mL) of $\mathrm{Nd(AlMe_4)_3}$ (0.116 g, 0.286 mmol) was slowly added to the reaction mixture, and the resulting solution was stirred vigorously for 6 h. All volatiles were removed in vacuo, and the residue was washed with pentane and dried to obtain $\{\mathrm{Et_2Al(Ox^{Me2})_2PhBCp}\}\mathrm{La(AlMe_4)_2}$ as a pale green powder (0.185 g, 0.246 mmol, 86%). $^1$H NMR (benzene-$d_6$): δ 13.15 (br s, 2 H, $\mathrm{C_5H_4}$), 6.46 (br s, 24 H, $\mathrm{Al}\mathit{Me}_4$), 4.48 (s, 1 H, p-$\mathrm{C_6H_5}$), 3.68 (br s, 2 H, $\mathrm{C_5H_4}$), 1.34 (br s, 2 H, $\mathrm{CNCMe_2C}\mathit{H}_2\mathrm{O}$), 0.05 (br s, 3 H, $\mathrm{AlCH_2C}\mathit{H}_3$), –0.08 (s, 2 H, $\mathrm{C_6H_5}$), –0.26 (s, 2 H, $\mathrm{C_6H_5}$), –1.67 (br s, 2 H, $\mathrm{AlC}\mathit{H}_2\mathrm{CH_3}$), –1.75 (s, 6 H, $\mathrm{CNC}\mathit{Me}_2\mathrm{CH_2O}$), –1.88 (s, 6 H, $\mathrm{CNC}\mathit{Me}_2\mathrm{CH_2O}$), –1.94 (br s, 3 H, $\mathrm{AlCH_2C}\mathit{H}_3$), –2.84 (br s, 2 H, $\mathrm{CNCMe_2C}\mathit{H}_2\mathrm{O}$), –3.09 (s, 2 H, $\mathrm{AlC}\mathit{H}_2\mathrm{CH_3}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (benzene-$d_6$, 150 MHz): δ 125.43 (p-$\mathrm{C_6H_5}$), 124.18 ($\mathrm{C_6H_5}$), 123.29 ($\mathrm{C_6H_5}$), 67.92 ($\mathrm{CN}\mathit{C}\mathrm{Me_2CH_2O}$), 63.71 ($\mathrm{CNCMe_2}\mathit{C}\mathrm{H_2O}$), 23.96 ($\mathrm{CNC}\mathit{Me}_2\mathrm{CH_2O}$), 22.95 ($\mathrm{CNC}\mathit{Me}_2\mathrm{CH_2O}$), 8.51 ($\mathrm{AlCH_2}\mathit{C}\mathrm{H_3}$), 6.76 ($\mathrm{AlCH_2}\mathit{C}\mathrm{H_3}$), 0.71 (br, $\mathrm{Al}\mathit{C}\mathrm{H_2CH_3}$), –1.33 ($\mathrm{Al}\mathit{C}\mathrm{H_2CH_3}$). $^{11}$B NMR (benzene-$d_6$, 192 MHz): δ –40.0. IR (KBr, cm$^{-1}$): 3071 w, 3050 w, 2929 s, 2868 s, 1595 s (C=N), 1539 m (C=N), 1492 w, 1463 m, 1434 w, 1411 w, 1373 m, 1291 m, 1261 m, 1194 s, 1132 w, 1053 m, 1038 m, 966 s, 936 w, 888 w, 869 w, 844 w, 802 m, 775 w, 703 s, 644 m, 592 m, 572 m, 499 w, 419 w, 398 w, 384 w. Anal. Calcd for $\mathrm{C_{33}H_{59}BN_2O_2Al_3Nd}$: C, 52.73; H, 7.85; N, 3.72. Found: C, 53.49; H, 8.35; N, 3.26. Mp: 110-115 °C, dec.

**$\{\mathit{i}\mathrm{Bu_2Al(Ox^{Me2})_2PhBCp}\}\mathrm{Y(AlMe_4)_2}$ ($\mathbf{3^Y}$).** $\mathrm{Al}\mathit{i}\mathrm{Bu_3}$ (72.2 µL, 0.286 mmol) and $\mathrm{H[PhB(Ox^{Me2})C_5H_5]}$ (0.100 g, 0.286 mmol) were mixed in toluene (5 mL) and stirred for 15 min. A toluene solution (5 mL) of $\mathrm{Y(AlMe_4)_3}$ (0.100 g, 0.286 mmol) was slowly added to this solution, and the resulting mixture was stirred vigorously for 6 h. All volatiles were removed in vacuo to obtain $\{\mathit{i}\mathrm{Bu_2Al(Ox^{Me2})_2PhBCp}\}\mathrm{Y(AlMe_4)_2}$ as a pale yellow solid (0.112 g, 0.149 mmol, 52%). $^1$H NMR (benzene-$d_6$): δ 7.39 (vt, $J$ = 7.4 Hz, 2 H, o-$\mathrm{C_6H_5}$), 7.32 (vt, $J$ = 7.4 Hz, 2 H, m-$\mathrm{C_6H_5}$), 7.19 (vt, $J$ = 7.3 Hz, 1 H, p-$\mathrm{C_6H_5}$), 6.31 (br s, 2 H, $\mathrm{C_5H_4}$), 6.11 (br s, 2 H, $\mathrm{C_5H_4}$), 3.80 (d, $^2J_{\mathrm{HH}}$ = 8.6 Hz, 2 H, $\mathrm{CNCMe_2}\mathit{CH}_2\mathrm{O}$), 3.26 (d, $^2J_{\mathrm{HH}}$ = 8.6 Hz, 2 H, $\mathrm{CNCMe_2}\mathit{CH}_2\mathrm{O}$), 1.95 (sept, $^3J_{\mathrm{HH}}$ = 6.5 Hz, 1 H, $\mathrm{AlCH_2C}\mathit{H}\mathrm{Me_2}$), 1.58 (sept, $^3J_{\mathrm{HH}}$ = 6.5 Hz, 1 H, $\mathrm{AlCH_2C}\mathit{H}\mathrm{Me_2}$), 1.17 (d, $^3J_{\mathrm{HH}}$ = 6.5 Hz, 6 H, $\mathrm{AlCH_2CH}\mathit{Me}_2$), 0.99 (s, 6 H, $\mathrm{CNC}\mathit{Me}_2\mathrm{CH_2O}$), 0.97 (s, 6 H, $\mathrm{CNC}\mathit{Me}_2\mathrm{CH_2O}$), 0.77 (d, $^3J_{\mathrm{HH}}$ = 6.4 Hz, 6 H, $\mathrm{AlCH_2CH}\mathit{Me}_2$), 0.18 (d, $^3J_{\mathrm{HH}}$ = 7.0 Hz, 2 H, $\mathrm{AlC}\mathit{H}_2\mathrm{CHMe_2}$), –0.04 (d, $^2J_{\mathrm{HH}}$ = 6.7 Hz, 2 H, $\mathrm{AlC}\mathit{H}_2\mathrm{CHMe_2}$), –0.24 (br s, 24 H, $\mathrm{Al}\mathit{Me}_4$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (benzene-$d_6$, 150 MHz): 133.72 (m-$\mathrm{C_6H_5}$), 133.27 (ipso-$\mathrm{C_5H_4}$), 127.38 (o-$\mathrm{C_6H_5}$), 127.16 (p-$\mathrm{C_6H_5}$), 121.50 ($\mathrm{C_5H_4}$), 117.07 ($\mathrm{C_5H_4}$), 81.24 ($\mathrm{CNCMe_2}\mathit{C}\mathrm{H_2O}$), 66.91 ($\mathrm{CN}\mathit{C}\mathrm{Me_2CH_2O}$), 28.94 ($\mathrm{AlCH_2CH}\mathit{Me}_2$), 28.71 ($\mathrm{AlCH_2CH}\mathit{Me}_2$), 27.99 ($\mathrm{AlCH_2CH}\mathit{Me}_2$), 27.05 ($\mathrm{AlCH_2}\mathit{C}\mathrm{HMe_2}$), 27.00 ($\mathrm{CNC}\mathit{Me}_2\mathrm{CH_2O}$), 26.29 ($\mathrm{AlCH_2}\mathit{C}\mathrm{HMe_2}$), 26.20 ($\mathrm{CNC}\mathit{Me}_2\mathrm{CH_2O}$), 25.42 ($\mathrm{AlCH_2CH}\mathit{Me}_2$), 24.89 ($\mathrm{Al}\mathit{C}\mathrm{H_2CHMe_2}$), 24.70 ($\mathrm{Al}\mathit{C}\mathrm{H_2CHMe_2}$), 1.75 ($\mathrm{Al}\mathit{Me}_4$). $^{11}$B NMR (benzene-$d_6$, 192 MHz): δ –16.74. $^{15}\mathrm{N}\{^1\mathrm{H}\}$ NMR (benzene-$d_6$, 60 MHz): δ –177.0 ($\mathrm{C}\mathit{N}\mathrm{CMe_2CH_2O}$). $^{89}\mathrm{Y}\{^1\mathrm{H}\ \}$ NMR (benzene-$d_6$, 29 MHz): δ 393. IR (KBr, cm$^{-1}$): 3071 w, 3048 w, 2948 s, 2886 s, 1588 m (C=N), 1551 m (C=N), 1534 m, 1464 m, 1433 w, 1397 w, 1374 m, 1362 m, 1317 w, 1293 m, 1258 w, 1194 s, 1137 w, 1052 s, 1038 s, 970 m, 889 w, 844 w, 797 m, 698 s, 593 m, 523 w, 439 w. Anal. Calcd for $\mathrm{C_{37}H_{67}BN_2O_2Al_3Y}$: C, 59.06; H, 8.91; N, 3.72. Found: C, 58.26; H, 8.82; N, 3.59. Mp: 93-95 °C, dec.

**$\{\mathit{i}\mathrm{Bu_2Al(Ox^{Me2})_2PhBCp}\}\mathrm{La(AlMe_4)_2}$ ($\mathbf{3^{La}}$).** $\mathrm{Al}\mathit{i}\mathrm{Bu_3}$ (72.2 µL, 0.286 mmol) was added via syringe to a toluene solution (5 mL) of $\mathrm{H[PhB(Ox^{Me2})C_5H_5]}$ (0.100 g, 0.286 mmol), and the reaction mixture was stirred for 15 min before a toluene solution (5 mL) of $\mathrm{La(AlMe_4)_3}$ (0.115 g, 0.286 mmol) was slowly added. The resulting solution was stirred vigorously for 6 h, and all volatiles were removed in vacuo, and the residue was washed with pentane and dried to obtain to obtain $\{\mathit{i}\mathrm{Bu_2Al(Ox^{Me2})_2PhBCp}\}\mathrm{La(AlMe_4)_2}$ as a pale yellow solid (0.167 g, 0.209 mmol, 73%). $^1$H NMR (benzene-$d_6$): δ 7.40-7.35 (m, 4 H, $\mathrm{C_6H_5}$), 7.20 (vt, *J* = 6.9 Hz, 1 H, p-C$_6$H$_5$), 6.36 (br s, 2 H, C$_5$H$_4$), 6.18 (br s, 2 H, C$_5$H$_4$), 3.59 (d, $^2J_{HH}$ = 7.9 Hz, 2 H, CNCMe$_2$C*H*$_2$O), 3.26 (d, $^2J_{HH}$ = 7.9 Hz, 2 H, CNCMe$_2$C*H*$_2$O), 1.94 (m, 1 H, AlCH$_2$C*H*Me$_2$), 1.49 (m, 1 H, AlCH$_2$C*H*Me$_2$), 1.16 (d, $^3J_{HH}$ = 6.3 Hz, 6 H, AlCH$_2$CH*Me*$_2$), 0.97 (s, 6 H, CNC*Me*$_2$CH$_2$O), 0.94 (s, 6 H, CNC*Me*$_2$CH$_2$O), 0.72 (d, $^3J_{HH}$ = 6.3 Hz, 6 H, AlCH$_2$CH*Me*$_2$), 0.17 (d, $^3J_{HH}$ = 6.8 Hz, 2 H, AlC*H*$_2$CHMe$_2$), –0.05 (d, $^3J_{HH}$ = 6.8 Hz, 2 H, AlC*H*$_2$CHMe$_2$), –0.17 (br s, 24 H, Al*Me*$_4$). $^{13}$C{$^1$H} NMR (benzene-*d*$_6$, 150 MHz): δ 133.21 (p-C$_6$H$_5$), 129.67 (ipso-C$_6$H$_5$), 128.89 (C$_6$H$_5$), 127.42 (C$_6$H$_5$), 126.03 (C$_5$H$_4$), 124.17 (C$_5$H$_4$), 119.10 (C$_5$H$_4$), 80.76 (CNCMe$_2$*C*H$_2$O), 70.48 (CN*C*Me$_2$CH$_2$O), 66.95 (CNCMe$_2$*C*H$_2$O), 29.08 (AlCH$_2$*C*HMe$_2$), 28.94 (CNCMe$_2$*C*H$_2$O), 28.70 (CNCMe$_2$*C*H$_2$O), 28.10 (AlCH$_2$*C*HMe$_2$), 27.90 (Al*C*H$_2$CHMe$_2$), 27.03 (CNC*Me*$_2$CH$_2$O), 26.14 (CNC*Me*$_2$CH$_2$O), 25.42 (Al*C*H$_2$CHMe$_2$), 3.13 (Al*Me*$_4$) $^{11}$B NMR (benzene-*d*$_6$, 192 MHz): δ –16.64. $^{15}$N{$^1$H} NMR (benzene-*d*$_6$, 60 MHz): δ –175.1 (C*N*CMe$_2$CH$_2$O). IR (KBr, cm$^{-1}$): 3071 w, 3049 w, 2948 s, 2922 s, 2866 s, 2864 s, 1591 s (C=N), 1535 m, 1463 m, 1374 m, 1362 w, 1317 w, 1292 w, 1258 w, 1185 s, 1132 w, 1052 m, 1037 w, 967 s, 938 w, 887 w, 842 w, 816 w, 797 w, 776 w, 702 s, 592 m, 441 w. Anal. Calcd for $C_{37}H_{67}BN_2O_2Al_3La$: C, 55.38; H, 8.35; N, 3.49. Found: C, 55.01; H, 7.95; N, 3.52. Mp: 105-110 °C, dec.

**{*i*Bu$_2$Al(Ox$^{Me2}$)$_2$PhBCp}Nd(AlMe$_4$)$_2$ (3$^{Nd}$).** Al*i*Bu$_3$ (72.2 µL, 0.286 mmol) was added via syringe to a toluene solution (5 mL) of H[PhB(Ox$^{Me2}$)C$_5$H$_5$] (0.100 g, 0.286 mmol), and the reaction mixture was stirred for 15 min before a toluene solution (5 mL) of Nd(AlMe$_4$)$_3$ (0.116 g, 0.286 mmol) was slowly added. The resulting solution was stirred vigorously for 6 h. All volatiles were removed in vacuo, and the residue was washed with pentane and dried to obtain to obtain {*i*Bu$_2$Al(Ox$^{Me2}$)$_2$PhBCp}Nd(AlMe$_4$)$_2$ as a light green solid (0.162 g, 0.200 mmol, 70%). $^1$H NMR (benzene-*d*$_6$): δ 13.49 (br s, 2 H, C$_5$H$_4$), 10.39 (br s, 2 H, C$_5$H$_4$), 6.52 (br s, 24 H, Al*Me*$_4$), 4.28 (s, 1 H, p-C$_6$H$_5$), 3.71 (s, 2 H, C$_6$H$_5$), 2.26 (s, 2 H, AlC*H*$_2$CHMe$_2$), 1.34 (br s, 2 H, CNCMe$_2$C*H*$_2$O), 0.44 (br s, 1 H, AlCH$_2$C*H*Me$_2$), 0.17-0.16 (m, 6 H, AlCH$_2$CH*Me*$_2$), –0.48 (br s, 2 H, CNCMe$_2$C*H*$_2$O), -1.48 (s, 2 H, C$_6$H$_5$), –1.56 (br m, 18 H, CNC*Me*$_2$CH$_2$O, AlCH$_2$CH*Me*$_2$), –2.54 (br s, 1 H, AlCH$_2$C*H*Me$_2$), –3.05 (s, 2 H, AlC*H*$_2$CHMe$_2$). $^{13}$C{$^1$H} NMR (benzene-*d*$_6$, 150 MHz): δ 124.62 (p-C$_6$H$_5$), 123.78 (C$_6$H$_5$), 122.88 (C$_6$H$_5$), 68.02 (CN*C*Me$_2$CH$_2$O), 63.91 (CNCMe$_2$*C*H$_2$O), 31.08 (AlCH$_2$*C*HMe$_2$), 27.91 (AlCH$_2$CH*Me*$_2$), 26.27 (CNC*Me*$_2$CH$_2$O), 25.65 (CNC*Me*$_2$CH$_2$O), 25.24 (AlCH$_2$*C*HMe$_2$), 24.58 (AlCH$_2$CH*Me*$_2$), 23.05 (AlCH$_2$CH*Me*$_2$), 22.98 (Al*C*H$_2$CHMe$_2$), 22.52 (AlCH$_2$CH*Me*$_2$), 21.50 (Al*C*H$_2$CHMe$_2$). $^{11}$B NMR (benzene-*d*$_6$, 192 MHz): δ –40.12. IR (KBr, cm$^{-1}$): 3072 w, 3049 w, 2948 s, 2887 m, 2863 m, 1593 m (C=N), 1555 m, 1463 m, 1432 w, 1374 m, 1361 m, 1317 w, 1292 m, 1257 w, 1196 s, 1161 m, 1070 m, 1053 m, 1037 m, 968 m, 888 w, 842 w, 801 w, 773 w, 702 s, 668 s. Anal. Calcd for $C_{37}H_{67}BN_2O_2Al_3Nd$: C, 55.01; H, 8.30; N, 3.46. Found: C, 55.02; H, 8.83; N, 3.46. Mp: 110-115 °C, dec.

**General Procedure for Catalytic Aluminations.** ***Caution:*** *Trialkylaluminum and alkynyldialkylaluminum compounds are pyrophoric liquids and must be handled under inert atmospheres.* The terminal alkyne and trialkylaluminum reactants were added via syringe to a solution of the catalyst (3 mol %) in benzene-*d*$_6$ at room temperature, and the reaction mixture was placed in a Teflon-sealed J Young-style NMR tube. The NMR tube was heated at 60 °C. Conversion of the starting materials was monitored by $^1$H NMR spectroscopy. Following full conversion, the volatile materials were removed *in vacuo*. Anhydrous *n*-pentane (2 mL) was added to the crude mixture of product and catalyst, and the resulting suspension was stirred for 10 min. The suspension was filtered, pentane was removed at reduced pressure, and the product dried under vacuum for 12 h. The isolated alkynylaluminum products were characterized by $^1$H, $^{13}$C{$^1$H} and FT-IR spectroscopy. Elemental analysis was performed using inductively coupled plasma-optical electronic spectroscopy (ICP-OES) to determine Al weight %. CHNS analysis did not provide consistent % C and % H values, likely as a result of the air sensitivity of organoaluminum compounds.

*1-Hexyn-1-yl-dimethylaluminum*. This compound was previously synthesized by salt metathesis and used in situ.[67] Trimethylaluminum (200 µL, 2.10 mmol), 1-hexyne (240 µL, 2.10 mmol), and **1**$^{\mathbf{Y}}$ (0.0420 g, 63 µmol) were allowed to react for 6 h at 60 °C. The product was isolated per the aforementioned procedure (0.254 g, 1.83 mmol, 87%). $^1$H NMR (benzene-*d*$_6$): δ 1.79 (t, $^3J_{HH}$ = 6.8 Hz, 2 H, AlC≡CC*H*$_2$CH$_2$CH$_2$CH$_3$), 1.12 (m, 4 H, AlC≡CCH$_2$C*H*$_2$C*H*$_2$CH$_3$), 0.66 (t, $^3J_{HH}$ = 7.2 Hz, 3 H, AlC≡CCH$_2$CH$_2$CH$_2$C*H*$_3$), –0.11 (br s, 6 H, Al*Me*$_2$). $^{13}$C{$^1$H} NMR (benzene-*d*$_6$, 150 MHz): δ 139.97 (AlC≡*C*CH$_2$CH$_2$CH$_2$CH$_3$), 90.09 (Al*C*≡CCH$_2$CH$_2$CH$_2$CH$_3$), 29.77 (AlC≡CCH$_2$*C*H$_2$CH$_2$CH$_3$), 23.36 (AlC≡CCH$_2$*C*H$_2$*C*H$_2$CH$_3$), 21.06 (AlC≡C*C*H$_2$CH$_2$CH$_2$CH$_3$), AlC≡CCH$_2$CH$_2$CH$_2$*C*H$_3$), –6.40 (br, Al*Me*$_2$). IR (KBr, cm$^{-1}$): 3335 w, 3327 w, 3016 w, 2961 s, 2937 s, 2893 m, 2875 m, 2825 w, 2141 w, 2094 s (C≡C), 1593 w, 1465 m, 1427 w, 1381 w, 1322 w, 1303 w, 1250 w, 1190 s, 1106 w, 1057 w, 1011 w, 986 w, 939 w, 845 w, 796 w, 695 s, 634 m, 569 m, 462 w, 438 w. Anal. Calcd for $C_8H_{15}Al$: Al, 19.53. Found: Al, 19.66.

*Dimethyl(2-phenylethynyl)aluminum.* This compound was previously characterized by analysis of hydrolysis products.[25] Trimethylaluminum (200 µL, 2.10 mmol), phenylacetylene (230 µL, 2.10 mmol), and **1**$^{\mathbf{Y}}$ (0.0420 g, 63 µmol) were allowed to react for 6 h at 60 °C. The product was isolated per the aforementioned procedure (0.321 g, 2.03 mmol, 97%). $^1$H NMR (benzene-*d*$_6$): δ 7.32 (d, $^3J_{HH}$ = 7.5 Hz, 2 H, o-C$_6$H$_5$), 6.90 (vt, $^3J_{HH}$ = 7.5 Hz, 1 H, p-C$_6$H$_5$), 6.79 (vt, $^3J_{HH}$ = 7.7 Hz, 2 H, m-C$_6$H$_5$), 0.03 (br s, 6 H, Al*Me*$_2$). $^{13}$C{$^1$H} NMR (benzene-*d*$_6$, 150 MHz): δ 134.15 (o-C$_6$H$_5$), 131.92 (p-C$_6$H$_5$), 129.17 (m-C$_6$H$_5$), 120.26 (ipso-C$_6$H$_5$), 116.56 (PhC≡*C*AlMe$_2$), 97.12 (Ph*C*≡CAlMe$_2$), –6.45 (br, Al*Me*$_2$). IR (KBr, cm$^{-1}$): 3078 w, 3058 w, 3031 w, 3018 w, 2933 m, 2891 w, 2851 w, 2822 w, 2128 m, 2073 s (C≡C), 1595 w, 1572 w, 1486 m, 1443 m, 1204 m, 1069 w, 1026 m, 976 m, 917 w, 812 m, 800 m, 783 m, 758 s, 689 s, 577 w, 550 m, 536 m, 420 m, 397 w, 387 w. Anal. Calcd for $C_{10}H_{11}Al$: Al, 17.06. Found: Al, 17.27.

*Dimethyl(p-tolylethynyl)aluminum.* The compound was previously generated and used in situ.[68, 69] Trimethylaluminum (100 µL, 1.05 mmol), 4-ethynyltoluene (132.5 µL, 1.05 mmol), and **1**$^{\mathbf{Y}}$ (0.0210 g, 31.5 µmol) were allowed to react for 6 h at 60 °C. The product was isolated per the aforementioned procedure (0.165 g, 0.95 mmol, 91%). $^1$H NMR (benzene-*d*$_6$): δ 7.30 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, C$_6$H$_4$), 6.64 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, C$_6$H$_4$), 1.87 (s, 3 H, 4-*Me*C$_6$H$_4$), 0.05 (br s, 6 H, Al*Me*$_2$). $^{13}$C{$^1$H} NMR (benzene-*d*$_6$, 150 MHz): δ 142.84 (Me*C*$_{Ph}^{ipso}$), 136.11 (C≡C*C*$_{Ph}^{ipso}$), 134.36 (3’-*C*$_6$H$_4$), 130.04 (2’-*C*$_6$H$_4$), 117.33 (*C*≡CAlMe$_2$), 96.76 (C≡*C*AlMe$_2$), 21.82 (*Me*-C$_6$H$_4$), –6.43 (AlMe$_2$). IR (KBr, cm$^{-1}$): 3031 w, 2935 m, 2891 w, 2853 w, 2821 w, 2127 w, 2079 s (C≡C), 1913 w, 1651 w, 1603 m, 1505 m, 1459 w, 1179 s, 1105 w, 1039 w, 1019 w, 980 m, 951 w, 816 s, 732 s, 694 s, 569 m, 548 m, 535 w, 494 w. Anal. Calcd for $C_{11}H_{13}Al$: Al, 15.67. Found: Al, 15.86.

*Dimethyl(2-cyclohexylmethylethynyl)aluminum*. Trimethylaluminum (20 µL, 0.21 mmol), 3-cyclohexyl-1-propyne (30.2 µL, 0.21 mmol), and **1**$^{\mathbf{Y}}$ (0.0042 g, 6.3 µmol) were allowed to react for 6 h at 60 °C. The product was isolated per the aforementioned procedure (0.0360 g, 0.20 mmol, 95%). $^1$H NMR (benzene-*d*$_6$): δ 1.79 (d, $^3J_{HH}$ = 6.70 Hz, 2 H, CyC*H*$_2$C≡CAlMe$_2$), 1.54 (m, 4 H, (-C*H*$_2$CH$_2$CH$_2$CH$_2$C*H*$_2$CH-)CH$_2$C≡CAlMe$_2$), 1.22 (m, 1 H, (-CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$C*H*-)CH$_2$C≡CAlMe$_2$), 1.01 (m, 4 H, (-CH$_2$C*H*$_2$CH$_2$C*H*$_2$CH$_2$CH-)CH$_2$C≡CAlMe$_2$), 0.76 (m, 2 H, (CH$_2$CH$_2$C*H*$_2$CH$_2$CH$_2$CH-)CH$_2$C≡CAlMe$_2$), –0.03 (br s, 6 H, Al*Me*$_2$). $^{13}$C{$^1$H} NMR (benzene-*d*$_6$, 150 MHz): δ 139.79 (CyCH$_2$*C*≡CAlMe$_2$), 90.61 (CyCH$_2$C≡*C*AlMe$_2$), 30.88 (-CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$*C*H-), 36.87 (-CH$_2$*C*H$_2$CH$_2$CH$_2$CH$_2$CH-), 32.97 (-CH$_2$CH$_2$*C*H$_2$CH$_2$CH$_2$CH-), 29.13 (Cy*C*H$_2$C≡CAlMe$_2$), 26.47 (-*C*H$_2$CH$_2$CH$_2$CH$_2$*C*H$_2$CH-), –6.25 (Al*Me*$_2$). IR (KBr, cm$^{-1}$): 2926 s, 2853 s, 2141 w, 2093 m (C≡C), 1590 w, 1554 w, 1450 m, 1426 w, 1372 w, 1322 w, 1263 w, 1199 m, 1067 w, 1053 w, 1010 w, 986 m, 930 w, 891 w, 843 w, 777 w, 696 s, 576 w, 519 w, 457 w, 444 w, 419 w. Anal. Calcd for $C_{11}H_{19}Al$: Al, 15.14. Found: Al, 15.24.

*2-(1-Cyclohexen-1-yl)ethynyl)dimethylaluminum.* The compound was previously prepared and used in situ.[70] Trimethylaluminum (20 µL, 0.21 mmol), 1-ethylnyl-1-cyclohexane (24.5 µL, 0.21 mmol), and **1**$^{\mathbf{Y}}$ (0.0042 g, 6.3 µmol) were allowed to react for 6 h at 60 °C. The product was isolated per the aforementioned procedure (0.0272 g, 0.17 mmol, 80%). $^1$H NMR (benzene-*d*$_6$): δ 6.24 (m, 1 H, (-CH$_2$CH$_2$CH$_2$CH$_2$C*H*=C-)CH$_2$C≡CAlMe$_2$), 1.92 (m, 2 H, (-

$\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_2CH_2CH{=}C}$-)$\mathrm{CH_2C{\equiv}CAlMe_2}$), 1.58 (m, 2 H, (-$\mathrm{CH_2CH_2CH_2C}\mathit{H}_2\mathrm{CH{=}C}$-)$\mathrm{CH_2C{\equiv}CAlMe_2}$), 1.18-1.07 (m, 4 H, (-$\mathrm{CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2CH{=}C}$-)$\mathrm{CH_2C{\equiv}CAlMe_2}$), –0.01 (br s, 6 H, $\mathrm{Al}\mathit{Me}_2$). $^{13}$C{$^1$H} NMR (benzene-$d_6$, 150 MHz): δ 145.21 (-$\mathrm{CH_2CH_2CH_2CH_2}\mathit{C}\mathrm{H{=}C}$-), 138.12 ($\mathit{C}\mathrm{{\equiv}CAlMe_2}$), 119.92 (-$\mathrm{CH_2CH_2CH_2CH_2CH{=}}\mathit{C}$-), 94.03 ($\mathrm{C{\equiv}}\mathit{C}\mathrm{AlMe_2}$), 28.42 (-$\mathit{C}\mathrm{H_2CH_2CH_2CH_2CH{=}C}$-), 26.38 (-$\mathrm{CH_2CH_2CH_2}\mathit{C}\mathrm{H_2CH{=}C}$-), 22.16 (-$\mathrm{CH_2}\mathit{C}\mathrm{H_2CH_2CH_2CH{=}C}$-), 21.27 (-$\mathrm{CH_2CH_2}\mathit{C}\mathrm{H_2CH_2CH{=}C}$-), –6.10 ($\mathrm{Al}\mathit{Me}_2$). IR (KBr, cm$^{-1}$): 3748 w, 3675 w, 3027 w, 2934 s, 2889 m, 2860 m, 2059 s (C≡C), 1618 m (C=C), 1588 w, 1449 m, 1435 m, 1350 w, 1268 w, 1186 m, 1153 w, 1137 w, 1078 w, 1042 w, 967 w, 920 m, 859 m, 847 m, 798 w, 765 w, 693 s, 566 m, 530 m, 480 m, 451 m, 418 m. Anal. Calcd for $\mathrm{C_{10}H_{15}Al}$: Al, 16.63. Found: Al, 16.76.

*1-Hexyn-1-yl-diethylaluminum*. The compound was previously prepared and used in situ.[71] Triethylaluminum (30 µL,0.21 mmol), 1-hexyne (24 µL, 0.21 mmol), and **1**$^{\mathrm{Y}}$ (0.0042 g, 6.3 µmol) were allowed to react for 2 h at 60 °C. The product was isolated per the aforementioned procedure (0.0328 g, 0.20 mmol, 94%). $^1$H NMR (benzene-$d_6$): δ 1.85 (vt, $^3J_{\mathrm{H,H}}$ = 7.0 Hz, 2 H, $\mathrm{C{\equiv}CC}\mathit{H}_2\mathrm{CH_2CH_2CH_3}$), 1.46 (t, $^3J_{\mathrm{H,H}}$ = 8.1 Hz, 6 H, $\mathrm{AlCH_2C}\mathit{H}_3$), 1.15 (m, 4 H, $\mathrm{C{\equiv}CCH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 0.68 (vt, $^3J_{\mathrm{H,H}}$ = 7.1 Hz, 3 H, $\mathrm{C{\equiv}CCH_2CH_2CH_2C}\mathit{H}_3$), 0.51 (q, $^3J_{\mathrm{H,H}}$ = 8.1 Hz, 4 H, $\mathrm{AlC}\mathit{H}_2\mathrm{CH_3}$). $^{13}$C{$^1$H} NMR (benzene-$d_6$, 150 MHz): δ 140.91 ($\mathrm{C{\equiv}}\mathit{C}\mathrm{CH_2CH_2CH_2CH_3}$), 85.86 ($\mathit{C}\mathrm{{\equiv}CCH_2CH_2CH_2CH_3}$), 30.16 ($\mathrm{C{\equiv}CCH_2}\mathit{C}\mathrm{H_2CH_2CH_3}$), 22.35 ($\mathrm{C{\equiv}CCH_2CH_2}\mathit{C}\mathrm{H_2CH_3}$), 21.02 ($\mathrm{C{\equiv}C}\mathit{C}\mathrm{H_2CH_2CH_2CH_3}$), 13.74 ($\mathrm{C{\equiv}CCH_2CH_2CH_2}\mathit{C}\mathrm{H_3}$), 10.08 ($\mathrm{AlCH_2}\mathit{C}\mathrm{H_3}$), 3.42 ($\mathrm{Al}\mathit{C}\mathrm{H_2CH_3}$). IR (KBr, cm$^{-1}$): 3326 w, 2959 s, 2935 s, 2900 s, 2862 s, 2790 w, 2722 w, 2142 w, 2090 s (C≡C), 1591 w, 1553 w, 1463 m, 1408 w, 1375 w, 1321 w, 1294 w, 1228 w, 1197 m, 1104 w, 1054 m, 988 w, 949 m, 919 m, 898 w, 845 w, 785 w, 728 w, 654 s, 634 s, 540 w, 456 w, 447 w, 419 w. Anal. Calcd for $\mathrm{C_{10}H_{19}Al}$: Al, 16.23. Found: Al, 15.99.

*Diethyl(2-phenylethynyl)aluminum.* The compounds was previously generated and used in situ.[72] Triethylaluminum (30 µL,0.21 mmol), phenylacetylene (23 µL, 0.21 mmol), and **1**$^{\mathrm{Y}}$ (0.0042 g, 6.3 µmol) were allowed to react for 2 h at 60 °C. The product was isolated per the aforementioned procedure (0.0372 g, 0.20 mmol, 95%). $^1$H NMR (benzene-$d_6$): δ 7.40 (m, 2 H, m-$\mathrm{C_6H_5}$), 6.91 (vt, $^3J_{\mathrm{HH}}$ = 7.5, 1 H, p-$\mathrm{C_6H_5}$), 6.81 (vt, $^3J_{\mathrm{HH}}$ = 7.5, 2 H, o- $\mathrm{C_6H_5}$), 1.50 (t, $^3J_{\mathrm{HH}}$ = 8.1 Hz, 6 H, $\mathrm{AlCH_2C}\mathit{H}_3$), 0.64 (q, $^3J_{\mathrm{HH}}$ = 8.1 Hz, 4 H, $\mathrm{AlC}\mathit{H}_2\mathrm{CH_3}$). $^{13}$C{$^1$H} NMR (benzene-$d_6$, 150 MHz): δ 136.43 ($\mathrm{Ph}\mathit{C}\mathrm{{\equiv}CAlEt_2}$), 134.34 (m-$\mathit{C}_6\mathrm{H_5}$), 131.90 (p-$\mathit{C}_6\mathrm{H_5}$), 129.21 (o-$\mathit{C}_6\mathrm{H_5}$), 120.39 (ipso-$\mathit{C}_6\mathrm{H_5}$), 93.33 ($\mathrm{PhC{\equiv}}\mathit{C}\mathrm{AlEt_2}$), 10.17 ($\mathrm{AlCH_2}\mathit{C}\mathrm{H_3}$), 3.63 ($\mathrm{Al}\mathit{C}\mathrm{H_2CH_3}$). IR (KBr, cm$^{-1}$): 3080 w, 3061 w, 2936 s, 2899 s, 2861 s, 2789 w, 2724 w, 2130 m, 2073 s (C≡C), 1596 w, 1487 m, 1446 m, 1406 w, 1393 w, 1373 w, 1290 w, 1208 m, 1166 w, 1100 m, 1053 m, 1027 m, 988 m, 951 w, 918 m, 898 m, 868 w, 811 m, 798 m, 781 m, 758 s, 689 s, 654 s, 564 m, 537 m, 442 w, 420 w. Anal. Calcd for $\mathrm{C_{12}H_{15}Al}$: Al, 14.49. Found: Al, 14.63.

*(3,3-dimethylbut-1-yn-1-yl)diethylaluminum*. The compound was previously synthesized by salt metathesis.[73] Triethylaluminum (300 µL, 2.10 mmol), 3,3-dimethyl-1-butyne (260 µL, 2.10 mmol), and **1**$^{\mathrm{Y}}$ (0.0420 g, 63 µmol) were reacted for 2 h at 60 °C. The product was isolated per the aforementioned procedure (0.3072 g, 1.85 mmol, 88%). $^1$H NMR (benzene-$d_6$): δ 1.43 (t, $^3J_{\mathrm{HH}}$ = 8.0 Hz, 6 H, $\mathrm{AlCH_2C}\mathit{H}_3$), 1.01 (s, 9 H, $\mathrm{C}\mathit{Me}_3$), 0.46 (q, $^3J_{\mathrm{HH}}$ = 8.0 Hz, 4 H, $\mathrm{AlC}\mathit{H}_2\mathrm{CH_3}$). $^{13}$C{$^1$H} NMR (benzene-$d_6$, 150 MHz): δ 149.88 ($\mathrm{Me_3C}\mathit{C}\mathrm{{\equiv}CAl}$), 81.92 ($\mathrm{Me_3CC{\equiv}}\mathit{C}\mathrm{Al}$), 30.13 ($\mathit{Me}_3\mathrm{CC{\equiv}CAl}$), 30.02 ($\mathrm{Me_3}\mathit{C}\mathrm{C{\equiv}CAl}$), 10.04 ($\mathrm{AlCH_2}\mathit{C}\mathrm{H_3}$), 3.89 ($\mathrm{Al}\mathit{C}\mathrm{H_2CH_3}$). IR (KBr, cm$^{-1}$): 3327 w, 3317 w, 2974 s, 2936 s, 2900 s, 2863 s, 2790 w, 2723 w, 2128 w, 2077 s (C≡C), 1594 w, 1553 w, 1459 m, 1407 w, 1366 m, 1247 m, 1201 m, 1103 w, 1054 w, 990 m, 951 w, 920 w, 898 w, 789 w, 722 m, 654 s, 633 w, 539 m, 458 m, 436 m. Anal. Calcd for $\mathrm{C_{10}H_{19}Al}$: Al, 16.23. Found: Al, 16.48.

*1-Hexyn-1-yl-diisobutylaluminum.*[74] Triisobutylaluminum (53.4 µL, 0.21 mmol), 1-hexyne (24 µL, 0.21 mmol), and 2 (0.0042 g, 6.3 µmol) were reacted for 1 h at 60 °C. The product was isolated per the aforementioned procedure (0.0425 g, 0.19 mmol, 91%). $^1$H NMR (benzene-$d_6$): δ 2.25 (v sept, $^3J_{\mathrm{HH}}$ = 6.6 Hz, 2 H, $\mathrm{AlCH_2C}\mathit{H}\mathrm{Me_2}$), 1.90 (t, $^3J_{\mathrm{HH}}$ = 7.0 Hz, 2 H, $\mathrm{CH_3CH_2CH_2C}\mathit{H}_2\mathrm{C{\equiv}C}$), 1.27 (d, $^3J_{\mathrm{HH}}$ = 6.6 Hz, 12 H, $\mathrm{AlCH_2CH}\mathit{Me}_2$), 1.23-1.13 (m, 4 H, $\mathrm{CH_3C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2C{\equiv}C}$), 0.71 (t, $^3J_{\mathrm{HH}}$ = 7.3 Hz, 3 H, $\mathrm{C}\mathit{H}_3\mathrm{CH_2CH_2CH_2C{\equiv}C}$), 0.60 (d, $^3J_{\mathrm{HH}}$ = 6.9 Hz, 4 H, $\mathrm{AlC}\mathit{H}_2\mathrm{CHMe_2}$). $^{13}$C{$^1$H} NMR (benzene-$d_6$, 150 MHz): δ 142.59 ($\mathit{C}\mathrm{{\equiv}CAlCH_2CHMe_2}$), 87.22 ($\mathrm{C{\equiv}}\mathit{C}\mathrm{AlCH_2CHMe_2}$), 29.96 ($\mathrm{CH_3}\mathit{C}\mathrm{H_2CH_2CH_2C{\equiv}C}$), 28.69 ($\mathrm{AlCH_2CH}\mathit{Me}_2$), 27.30 ($\mathrm{AlCH_2}\mathit{C}\mathrm{HMe_2}$), 25.68 ($\mathrm{Al}\mathit{C}\mathrm{H_2CHMe_2}$), 22.38 ($\mathrm{CH_3CH_2}\mathit{C}\mathrm{H_2CH_2C{\equiv}C}$), 21.33 ($\mathrm{CH_3CH_2CH_2}\mathit{C}\mathrm{H_2C{\equiv}C}$), 13.76 ($\mathit{C}\mathrm{H_3CH_2CH_2CH_2C{\equiv}C}$). IR (KBr, cm$^{-1}$): 2956 s, 2872 m, 2143 w, 2091 w (C≡C), 1466 m, 1397 w, 1365 w, 1321 w, 1182 w, 1064 m, 1023 m, 946 w, 909 w, 851 w, 823 w, 668 m, 457 w, 419 w. Anal. Calcd for $\mathrm{C_{14}H_{27}Al}$: Al, 12.13. Found: Al, 12.29.

*1,8-bis(dimethylalumino)-1,7-octadiyne.* Trimethylaluminum (40.0 µL, 0.42 mmol), 1,7-octadiyne (27.7 µL, 0.21 mmol), and 2 (0.0042 g, 6.3 µmol) were reacted for 6 h at 60 °C. The product was isolated per the aforementioned procedure (0.0417 g, 0.19 mmol, 91%). $^1$H NMR (benzene-$d_6$): δ 1.64 (m, 4 H, $\mathrm{C{\equiv}CC}\mathit{H}_2\mathrm{CH_2CH_2C}\mathit{H}_2\mathrm{C{\equiv}C}$), 1.09 (m, 4 H, $\mathrm{C{\equiv}CCH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2C{\equiv}C}$), –0.11 ($\mathrm{Al}\mathit{Me}_2$). $^{13}$C{$^1$H} NMR (benzene-$d_6$, 150 MHz): δ 138.83 ($\mathrm{C{\equiv}}\mathit{C}\mathrm{CH_2CH_2CH_2CH_2}\mathit{C}\mathrm{{\equiv}C}$), 90.64 ($\mathit{C}\mathrm{{\equiv}CCH_2CH_2CH_2CH_2C{\equiv}}\mathit{C}$), 26.60 ($\mathrm{C{\equiv}CCH_2}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2CH_2C{\equiv}C}$), 20.65 ($\mathrm{C{\equiv}C}\mathit{C}\mathrm{H_2CH_2CH_2}\mathit{C}\mathrm{H_2C{\equiv}C}$), –6.28 ($\mathrm{Al}\mathit{Me}_2$). IR (KBr, cm$^{-1}$): 3331 w, 3016 w, 2937 s, 2891 m, 2867 m, 2822 w, 2095 s (C≡C), 1595 w, 1553 w, 1459 m, 1415 m, 1325 m, 1188 s, 1019 w, 978 w, 922 w, 693 s, 567 m, 458 w, 419 w. Anal. Calcd for $\mathrm{C_{12}H_{20}Al_2}$: Al, 24.72. Found: Al, 24.77.

### Description of kinetics experiments

**Stoichiometric reaction of 1$^{\mathrm{Y}}$ and *t*BuC≡CH.** A solution (0.5 mL total volume) of **1**$^{\mathrm{Y}}$ (0.157 M), *t*BuC≡CH (0.155 M), and hexamethylbenzene (0.068 M) standard in $\mathrm{C_6D_6}$ was prepared. The NMR probe was pre-heated to 60 °C, and the reaction mixture was placed in the probe. Single-pulse scans were acquired every 30 seconds. Consumption of starting materials was monitored by integration of corresponding signals in the $^1$H NMR spectra, and concentrations were determined by the proportionality to the standard. A linear plot of ln{[**1**$^{\mathrm{Y}}$]/[*t*BuC≡CH]} vs time provides the second-order rate constant.

**Catalytic rate law determination.** A solution (0.5 mL) containing *t*BuC≡CH (0.487 M), triethylaluminum (0.731 M), hexamethylbenzene standard (0.048 M), and 3 mol % **1**$^{\mathrm{Y}}$ (0.014 M) in $\mathrm{C_6D_6}$ was prepared and placed in a J-Young-style NMR tube. The NMR probe was preheated to 60 °C, and the NMR tube was placed in the probe. Single-repetition scans were acquired every 30 seconds. The signals of triethylaluminum and alkyne reagents were monitored over the reaction, and concentrations were determined by integration relative to the internal standard. Plots of [*t*BuC≡CH] vs time fit by nonlinear least squares regression analysis to obtain second-order rate constants $k_{\mathrm{obs}}$. Alternatively, plots of ln{[$\mathrm{AlEt_3}$]/[*t*BuC≡CH]} vs time are linear and provide equivalent values for $k_{\mathrm{obs}}$.

Experiments to determine the order in lanthanide pre-catalyst were conducted using 0.5 mL solutions of *t*BuC≡CH (0.487 M), triethylaluminum (0.731 M), hexamethylbenzene (0.048 M) as above, with a series of concentrations of **1**$^{\mathrm{Y}}$ (4-13 mM) in $\mathrm{C_6D_6}$ at 60 °C. Second-order plots were used to obtain $k_{\mathrm{obs}}$ values at the different [**1**$^{\mathrm{Y}}$] concentrations. A linear correlation confirms the first-order dependence on the pre-catalyst.

**Saturation and isotope effects.** *t*BuC≡CH and *n*BuLi (2.5 M in hexanes) were allowed to react at –30 °C in pentane for 1 h, followed by solvent removal *in vacuo* to generate *t*BuC≡CLi. *t*BuC≡CLi (0.360 g, 4.09 mmol) and $\mathrm{D_2O}$ (70 µL, 3.88 mmol) were allowed to react in $\mathrm{C_6D_6}$ (4 mL). The reaction mixture was filtered and dried over $\mathrm{P_2O_5}$ to yield a 0.430 M solution of *t*BuC≡CD in $\mathrm{C_6D_6}$, which was then used for isotope effect studies.

Saturation experiments were performed with solutions containing *t*BuC≡CH (0.096 M), **1**$^{\mathrm{Y}}$ (0.012 M), and hexamethylbenzene (0.127 M), while concentration of triethylaluminum (0.194-1.419 M) was varied. These mixtures were prepared with equivalent total volumes (0.5 mL) in $\mathrm{C_6D_6}$, placed in J-Young type NMR tubes, and inserted into the preheated NMR probe and allowed to react at 60 °C. Concentration of starting materials were followed by integration of $^1$H NMR signals, and these changes were used to calculate initial reaction rates (10-15% of conversion). A similar procedure was employed for saturation and kinetic isotope effect studies with the deuterated alkyne *t*BuC≡CD (0.079 M), **1**$^{Y}$ (0.010 M), hexamethylbenzene (0.084 M) and 0.206-1.208 M triethylaluminum in 0.5 mL $C_6D_6$). Saturation curves for protio and deuterated systems were obtained by plotting normalized initial rates (initial rates divided by {[**1**$^{Y}$][alkyne]}) against triethylaluminum concentrations. The true second-order rate constants $k_2^{(H)}$ and $k_2^{(D)}$ were obtained from nonlinear least-squares fits to the equation $d[Et_2Al{\equiv}CtBu]/dt = A[AlEt_3]/\{[AlEt_3] + B\}$, where $A = k_2[\mathbf{1}^{Y}][HC{\equiv}CtBu]$ and $B = (k_{-1} + k_2[HC{\equiv}CtBu])/k_1$.

**EXSY.** $^1$H EXSY experiments were conducted using a solution of **1**$^{Y}$ (0.114 M) and triethylaluminum (0.120 M) in $C_6D_6$ (0.5 mL). The total rate of exchange $k' = k_{on}+k_{off}$ was obtained by conducting experiments at different mixing times ($t_m$ = 200-400 ms) as described by Perrin.[53] Repeating this procedure at different temperatures (25-60 °C) provided a series of $k'$ values which enabled the calculation of activation parameters $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ from an Eyring plot.

## Computational Methods

The ground state geometry optimization and IR frequency calculations on **1**$^{\mathbf{Y\text{-}CALC}}$ were performed using Truhlar's Minnesota 06-2X[46] meta-GGA functional, as implemented in NWChem.[75] The Los Alamos National Laboratory double-ζ valence basis set (LANL2DZ)[45] was used along with effective core potentials (ECPs) for Al and Y. Grimme's dispersion corrections were empirically added through a long-range contribution (DFT-D3) for all calculations.[47] Ground state geometry optimizations and IR frequency calculations on the alkynylaluminum compounds **(CyCH₂C≡CAlMe₂)₂-calc**, **(*t*BuC≡CAlEt₂)₂-calc** and **(*n*BuC≡CAlMe₂)₂-calc** were performed using Minnesota 06-2X functional and the 6-31G$^{**}$ basis set.[49] IR frequencies were corrected by the scaling factors of 0.960 (**1**$^{\mathbf{Y\text{-}CALC}}$ ) and 0.961 (**(CyCH₂C≡CAlMe₂)₂-calc**, **(*t*BuC≡CAlEt₂)₂-calc**) and **(*n*BuC≡CAlMe₂)₂-calc**. The NMR chemical shift calculations of alkynylaluminums were performed using the GIAO method,[51] using the 6-31G$^{**}$ basis set for all atoms and dispersion corrected Becke's three-parameter hybrid density functional (B3LYP-D3).[52] The $^1$H and $^{13}$C chemical shifts were calculated by taking the difference of the isotropic shielding values of the compounds of interest with tetramethylsilane (TMS), also calculated at the same level of theory.

## Acknowledgements

The authors gratefully thank the National Science Foundation (CHE-1900393) for financial support, and K. Basemann and T. Windus for assistance with DFT calculations, and A. Venkatesh and A. Rossini for help implementing heteronuclear 2D NMR.

**Keywords:** rare earth • catalysis • CH bond activation • saturation kinetics • aluminate

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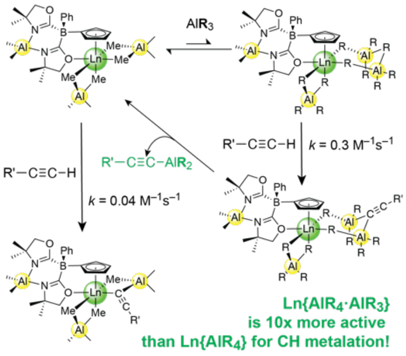

Alkynylaluminum compounds are synthesized directly from terminal alkynes and abundant, inexpensive trialkylaluminum reagents via catalytic C-H bond functionalization using rare earth aluminate compounds, in contrast to transition-metal complexes which catalyze carboaluminations. A saturated lanthanide aluminate adduct, implicated by kinetic studies, provides a rationale for C-H bond alumination occurring rather than addition.

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