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Zirconium-Catalyzed C−H Alumination of Polyolefins, Paraffins, and Methane

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ABSTRACT: C−H/Et-Al exchange in zirconium-catalyzed reactions of saturated hydrocarbons and $AlEt_3$ affords versatile organoaluminum compounds and ethane. The grafting of commercially available $Zr(OtBu)_4$ on silica/alumina gives monopodal $\equiv SiO−Zr(OtBu)_3$ surface pre-catalyst sites that are activated in situ by ligand exchange with $AlEt_3$. The catalytic C−H alumination of dodecane at 150 °C followed by quenching in air affords *n*-dodecanol as the major product, revealing selectivity for methyl group activation. Shorter hydrocarbon or alcohol products were not detected under these conditions. Catalytic reactions of cyclooctane and $AlEt_3$, however, afford ring-opened products, indicating that C−C bond cleavage occurs readily in methyl group-free reactants. This selectivity for methyl group alumination enables the C−H alumination of polyethylenes, polypropylene, polystyrene, and poly-α-olefin oils without significant chain deconstruction. In addition, the smallest hydrocarbon, methane, undergoes selective mono-alumination under solvent-free catalytic conditions, providing a direct route to Al−Me species.

C−H alumination of small and large hydrocarbons
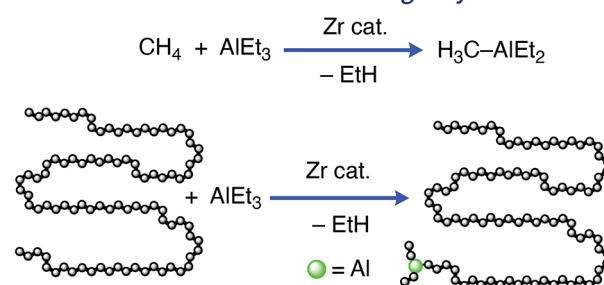
INTRODUCTION

New catalytic conversions of C−H bonds are needed to provide direct and efficient routes from aliphatic hydrocarbon feedstocks to commodity chemicals or materials. Such transformations, however, must be scalable to match or exceed conventional manufacturing practices. Hydrocarbon oxidations,[1] carbenoid or nitrenoid insertions,[2] or C−H bond elementations such as borylation might be considered for such processes (Figure 1).[3] Exothermic oxidations, however, are controlled by bond strengths that often constrain selectivity, resulting in, for example, over-oxidation. Other methods consume expensive, high-energy reagents and/or require precious metal catalysts. Moreover, many existing catalytic methods for C−H bond functionalization are designed to simplify multistep syntheses of high-value targets rather than match the scale of commodity chemicals. An alternative strategy based on thermoneutral or nearly thermoneutral exchange reactions could avoid the costs of high-energy reagents and the driving force for over-functionalization by leveraging σ-bond metathesis type steps. Such processes would interchange a sacrificial hydrocarbyl ligand for one from a hydrocarbon reactant.

C−H/C′−Al exchange reactions utilizing trialkylaluminum reagents may be advantageous for this purpose. Simple trialkylaluminum reagents, such as $AlEt_3$, are readily available,
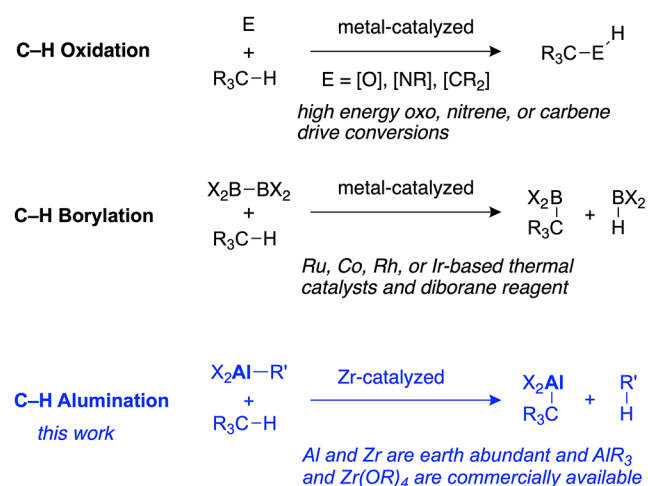

Figure 1. Approaches for introducing heteroatoms into C−H bonds of aliphatic hydrocarbons.

atom-economically and directly synthesized from H_2, alkenes, and terrestrially abundant Al, and find wide-ranging applications.[4] For example, hydroalumination and carboalumination of alkenes afford alkylaluminum intermediates that are readily transformed into alcohols, acids, or organohalides.

Although alkylaluminums are important in industrial chemical manufacturing of, for example, surfactants, transformations of saturated hydrocarbons utilizing aluminum reagents are surprisingly limited. The only examples of catalytic C−H bond alumination involve palladium-catalyzed reactions of diketiminate-supported aluminum(I) or dihydride reagents to give arylaluminum products.[5,6] Catalytic C−H bond aluminations of aliphatic hydrocarbons have not previously been demonstrated using commercial alkylaluminum reactants. These reactions could also provide one-step routes to compounds that are otherwise inaccessible by addition chemistry, such as in conversions of methane or in the post-use repurposing of polyolefins.

Such functionalized polyolefins have improved barrier or adhesive properties, can function as ionomers, or can covalently link polyolefin chains to other materials.[7−11] Post-synthetic derivatization of polyolefins has mainly relied upon existing catalytic or radical chemistries, with mild conditions needed to avoid chain cleavage or cross-linking from steps that often accompany C−H bond activations.[12−14] For instance, rhodium-catalyzed borylation of paraffins with bis(pinacolato)diboron (B_2pin_2) has been adapted to give polymers that are sparsely decorated with hydroxy-terminated side groups.[15−17] The related borylation of methane yields MeBpin,[18−20] showing the dramatic range of sizes of molecules amenable to this chemistry. Radical functionalization and catalytic oxidations, which also afford hydroxy polyolefins,[21−24] are typically governed by reactant bond dissociation energies to favor C−H bond cleavage at tertiary positions and by relative rates of rebound and chain scission.[25−27]

We recently reported that polyolefins are catalytically deconstructed by surface-supported organozirconium species into a distribution of moderate chain length (ca. C_{35}) alkylaluminums, involving C−C bond cleavage and alkyl group transfer to aluminum.[28] The combination of $ZrNp_n$@SiO_2/Al_2O_3 ($Np = CH_2CMe_3$) as precatalyst and AlR_3 (R = iBu, H, Et) in the deconstruction and alumination of polyolefins predominately resulted in cleavage; however, infrared (IR) spectroscopy revealed that the residual polymeric solid had also reacted prior to complete deconstruction. That observation motivated the present study to introduce C−H bond alumination as a new approach for hydrocarbon functionalization.

RESULTS AND DISCUSSION

Catalytic Alumination of Liquid Hydrocarbons. Exploratory experiments identified the combination of $AlEt_3$ as the reagent and $Zr(OtBu)_3$@SiO_2/Al_2O_3 as a precatalyst for selective C−H bond alumination of low-density polyethylene (LDPE) without extensive degradation of the chains (Table S1). $Zr(OtBu)_3$@SiO_2/Al_2O_3 (Figure 2) was synthesized by the grafting reaction of $Zr(OtBu)_4$ and SiO_2/Al_2O_3 (partially dehydroxylated by pretreatment under vacuum at 700 °C). A ν_{SiOH} band at 3740 cm^{-1}, assigned to isolated silanols in partially dehydroxylated SiO_2/Al_2O_3, was not detected in the IR spectrum of $Zr(OtBu)_3$@SiO_2/Al_2O_3. The Zr loading, determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) measurements, matched the silanol
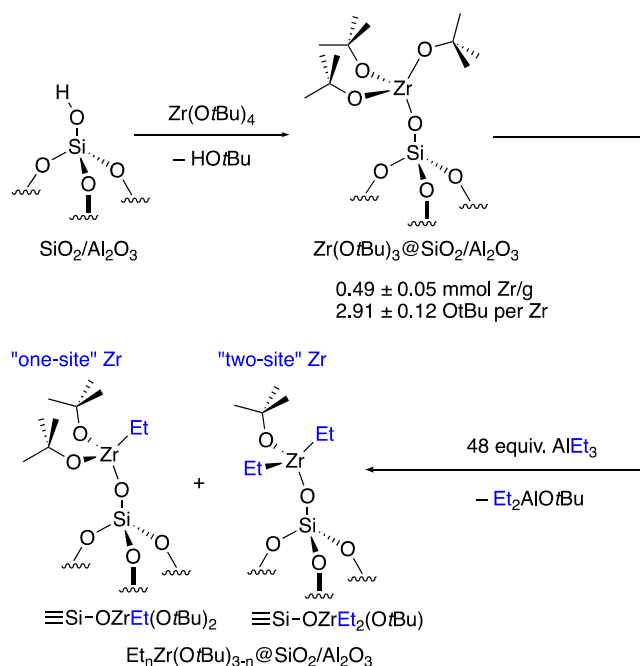

Figure 2. Grafting of tetrakis(*tert*-butoxy)zirconium and ethylation by reaction with $AlEt_3$ to produce surface ethylzirconium species with one or more reactive Zr−C bonds.

loading in the initial SiO_2/Al_2O_3 material. These data indicated near-quantitative grafting. In addition, micromolar-scale grafting experiments, analyzed by ^1H NMR spectroscopy, indicated that 1 equiv of HOtBu was formed for each equivalent of $Zr(OtBu)_4$ adsorbed from solution. Titration of $Zr(OtBu)_3$@SiO_2/Al_2O_3 using formic acid, in combination with the Zr loading, revealed 2.91 ± 0.12 OtBu groups per zirconium center. A dynamic nuclear polarization (DNP)-enhanced ^{13}C cross-polarization magic angle spinning (CPMAS) nuclear magnetic resonance (NMR) spectrum contained signals at 80 and 33 ppm, assigned to the quaternary carbon and methyl groups, respectively, of the OtBu. The two signals correlated exclusively with the ^1H NMR methyl signal at 1.3 ppm in a $^{13}C\{^1H\}$ heteronuclear correlation (HETCOR) experiment. These data, along with surface−ligand distance measurements,[29] are consistent with ≡SiO−Zr-(OtBu)$_3$ groups as the predominant surface zirconium species.

Ethylation of $Zr(OtBu)_3$@SiO_2/Al_2O_3 using $AlEt_3$ yielded $Et_nZr(OtBu)_{3−n}$@SiO_2/Al_2O_3, which is likely a mixture of mono ≡SiO−ZrEt(OtBu)$_2$ and dialkyl ≡SiO−ZrEt$_2$(OtBu) species (Figure 2). These sites were inferred based upon the ca. 1.5 *tert*-butoxyaluminum groups per Zr center present in the solution mixture of $Et_2Al(OtBu)$ and $EtAl(OtBu)_2$. During this reaction, the catalytic material became brown. Solid-state ^{27}Al and ^{29}Si NMR spectroscopy and the formation of ethylsilane species indicated that new aluminum sites were inserted into the support, displacing some silicon atoms.[30] This assertion is corroborated by a DNP-enhanced 13C{27Al} dipolar recoupling experiment that evidences equivalent average proximities between Et and tBu groups.

The combination of $AlEt_3$ and $Zr(OtBu)_3$@SiO_2/Al_2O_3 was then investigated in conversions of small hydrocarbons. *n*-Dodecane and $AlEt_3$ reacted in the presence of $Zr(OtBu)_3$@SiO_2/Al_2O_3, followed by quenching with compressed air, to afford alcohols in 55% yield with respect to $AlEt_3$ as the limiting reagent (Figure 3A). A phase-sensitive 2D ^1H−^{13}C heteronuclear single quantum coherence (HSQC) experiment and
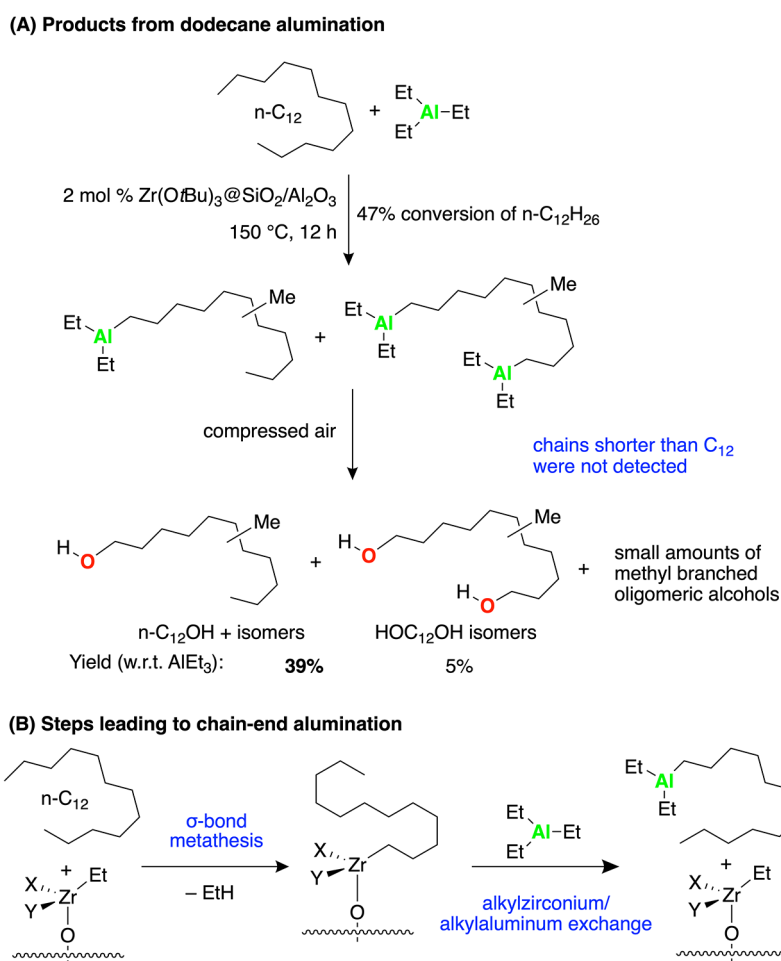
Figure 3. (A) Zr-catalyzed C−H alumination of dodecane. (B) Proposed C−H bond activation and AlEt$_3$ exchange.

integration of the ^{1}H NMR spectrum revealed that >95% of the hydroxy groups were primary, of the type CH$_2$OH. These signals appeared at 3.57 ppm (multiplet) and 3.31 ppm (broad) in the ^{1}H NMR spectrum. Trace amounts of tertiary alcohols were detected as an out-of-phase cross-peak at 4.28 ppm in the ^{1}H−^{13}C HSQC. Methine groups detected in the phase-sensitive ^{1}H-^{13}C HSQC indicated that branching had been introduced into both alkanes and alcohol products. Their methine peaks were coupled to methyl and methylene signals in a COSY experiment. Internal or terminal alkenes, if present, were below the detection limit of the ^{1}H NMR spectrum (a minor peak at 4.75 is possibly a vinylidene). Gas chromatography−mass spectrometry (GC-MS) analysis of the product mixture revealed that the major species present was 1-dodecanol (39%), which was confirmed by comparison with an authentic sample. Four additional clusters of small GC signals, each group corresponding to ca. 3−5% yield, were assigned to dodecane diols, as well as saturated or functionalized oligomers derived from dimerized or trimerized dodecane. Chains shorter than C$_{12}$, as well as species between C$_{12}$ and C$_{24}$, were notably absent from the GC-MS traces. The formation of 1-dodecanol as the primary product is consistent with C−H bond activation at a methyl group in *n*-dodecane followed by alkyl group exchange with AlEt$_3$, via well-established σ-bond metathesis and ZrR/AlR′ exchange (Figure 3B).[31−33] A larger excess of AlEt$_3$ leads to extensive ethylsilane formation accompanying support and catalyst degradation, as

revealed by GC and ^{1}H NMR of reaction mixtures and solid-state ^{27}Al and ^{29}Si NMR spectroscopy.

Subjecting a 1:1 mixture of dodecane and dodecane-d_{26} to these catalytic alumination conditions gave conversion of C$_{12}$H$_{26}$ only, with linear 1-C$_{12}$H$_{25}$OH as the primary product. Neither dodecanol-d_{25} nor isotopologues of dodecane or dodecanol (i.e., C$_{12}$H$_x$D$_{26-x}$ and C$_{12}$H$_x$D$_{25-x}$OH) was detected in ^{2}H NMR or GC-MS analyses, ruling out any H/D exchange and suggesting that C−D bonds are not cleaved under these catalytic conditions. Notably, the region between 3−4 ppm in the ^{2}H NMR spectrum was free of signals characteristic of HO-CD$_2$-R. These observations indicate that the C−H bond activation is governed by a large isotope effect, which is consistent with metalation via σ-bond metathesis. Typically, linear transfer of H in the β-position of the four-center transition state for σ-bond metathesis from hydrocarbon to alkyl ligand is associated with large kinetic isotope effects (KIEs).[34,35] In addition, the hydrocarbon activation process may involve adsorption onto the surface and at the zirconium site, leading to an equilibrium isotope effect (EIE) favoring coordination of C−H bonds of dodecane and AlEt$_3$. This idea is more speculative because there has been little experimental evidence for d^0 metal alkane adducts as intermediates in σ-bond metathesis steps. Nonetheless, zirconium aluminates are known to inhibit insertion during carboalumination,[36] and the combination of large EIE and KIE could further disfavor the conversion of dodecane-d_{26}.
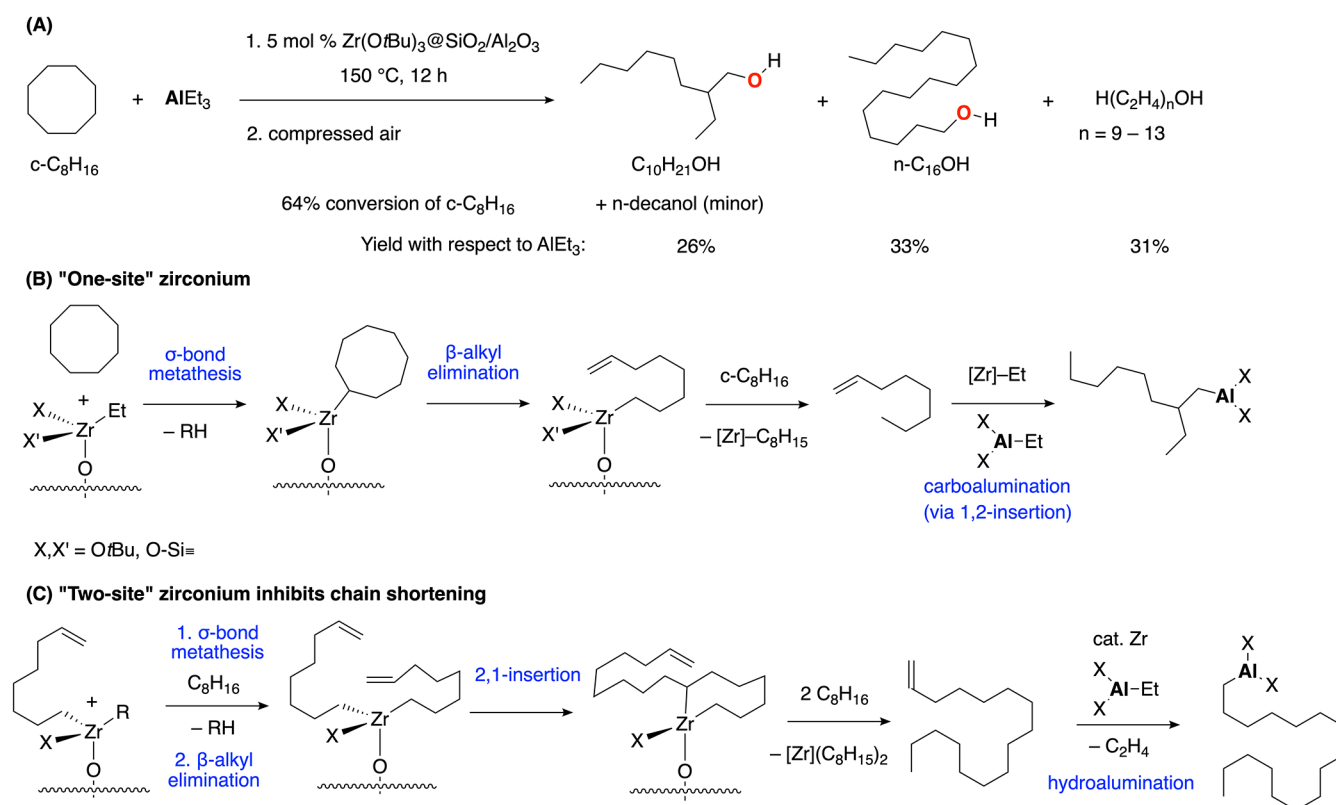
Figure 4. (A) Zr-catalyzed ring-opening and alumination of cyclooctane followed by quenching afforded primary alcohols in 88% yield with respect to AlEt$_3$. (B) Proposed mechanism of "one-site" zirconium species gives branched dodecanol. (C) Proposed mechanism of "two-site" zirconium species favoring 2,1-insertion.

Table 1. C−H Alumination/Oxygenation of Polyolefins Catalyzed by Zr(OtBu)$_3$@SiO$_2$/Al$_2$O$_3$[a] Occurs with Small Changes in Molecular Weight and Distribution

hydrocarbon polymer	initial MW (Da)	initial dispersity	product MW (Da)	product dispersity	OH/chain[b]
polyethylene (PE)	7000	3.8	8000	3.2	0.89
narrow dispersity ND(PE)[c]	2100	1.2	2100	1.2	0.86
NDPE	17 000	1.1	17 500	1.1	0.73
low-density (LD)PE	8100	4.7	7800	6.9	0.81
linear low density (LLD)PE	15 500	4.7	18 500	3.5	1.83
isotactic polypropylene (iPP)	57 400	6.8	49 600	5.1	3.08
poly-α-olefin-10 (PAO10)[d,e]	640	1	740	1.04	0.68
polystyrene (PS)-1000[e,f]	820	1.1	840	1.1	1.12
PS[g]	40 600	2.0	46 100	2.1	n.d.[h]

[a]General reaction conditions: polymer (0.05−0.6 g), Zr(OtBu)$_3$@SiO$_2$/Al$_2$O$_3$ (30−40 mg), AlEt$_3$ (50 μL), 150 °C, 12 h. [b]OH groups per chain = mol CH$_2$OH/mol polymer$_{post}$. [c]MW properties also determined by MALDI-TOF-MS; PE: M_n = 1920; Đ = 1.15; PE-OH: M_n = 1500, Đ = 1.15. [d]Reaction conditions: 0.1 mmol PAO10, 2 mmol AlEt$_3$, 0.02 mmol Zr. [e]MW properties also determined by MALDI-TOF-MS; PS 1000: M_n = 980; Đ = 1.09; PS-OH: M_n = 760, Đ = 1.09. [f]Reaction conditions: 0.1 mmol PS 1000 (based on M_n), 1.25 mmol AlEt$_3$, 0.03 mmol Zr. [g]Reaction conditions: 0.025 mmol PS, toluene as solvent (5 mL). [h]Not determined.

The apparent lack of shortened hydrocarbons contrasts the extensive chain cleavage in reactions of polyolefins and AlEt$_3$ under ZrNp$_n$@SiO$_2$/Al$_2$O$_3$-catalyzed conditions.[28] Moreover, new methyl branches indicated that skeletal rearrangements were occurring. Cyclooctane, as an end-group-free, strained hydrocarbon, was employed to investigate C−C cleavage phenomena to understand these seemingly incompatible observations. The reaction of cyclooctane and AlEt$_3$ catalyzed by Zr(OtBu)$_3$@SiO$_2$/Al$_2$O$_3$, followed by quenching with compressed air, afforded acyclic alcohols in 88% yield with respect to AlEt$_3$. The major products were 2-ethyl-octan-1-ol (C$_{10}$H$_{23}$OH) and linear n-hexadecane-1-ol (C$_{16}$H$_{33}$OH), along

with smaller quantities of linear C$_{10}$H$_{23}$OH, as well as longer linear and branched even carbon numbered C$_{18}$H$_{37}$OH− C$_{26}$H$_{53}$OH species (Figure 4A). n-Decanol, n-hexadecane-1-ol, and n-octadecanol were detected by GC-MS and conclusively identified by comparison with authentic samples. The parent ion of 2-ethyl-octan-1-ol was detected by GC-MS. 1D and 2D NMR experiments indicated that ethyl-branched products are extensively formed. Cyclooctanol, 1-octanol, 1,8-octanediol, and oct-7-en-1-ol were not detected by GC-MS in the reaction mixture.

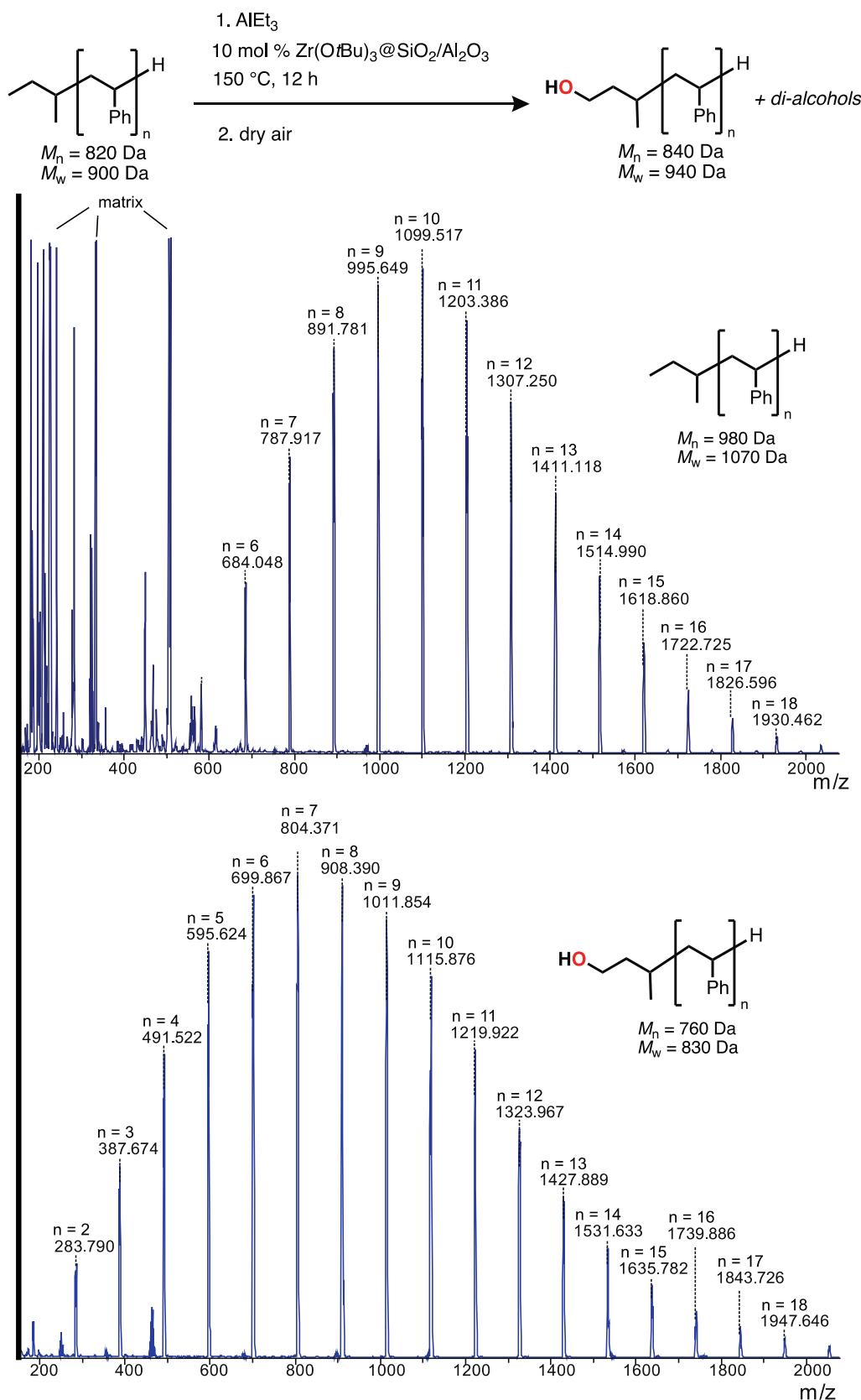2-Ethyl-octan-1-ol is likely produced via C−H bond activation by a zirconium alkyl, followed by β-alkyl elimination

Figure 5. MALDI-TOF-MS spectra of PS 1000 (top) starting material and its functionalized PS-OH product (bottom) from $Zr(OtBu)_3@SiO_2/Al_2O_3$-catalyzed alumination and air quenching.

to open the cyclooctyl ring bonded to zirconium. A σ-bond metathesis reaction of the oct-7-enylzirconium and cyclooctane generates free 1-octene, which reacts by catalytic carboalumi-

nation to give the ethyl-branched alkylaluminum intermediate that is oxidized upon workup (Figure 4B). Cyclooctylzirconium ring-opening is faster than exchange with $AlEt_3$, which would

Table 2. Catalytic C−H Alumination of Methane[a]

no.	catalyst	yield[b] (%)	TON[c]
1	$Zr(OtBu)_3$@SiO_2/Al_2O_3	23	21
2	$Zr(OtBu)_3$@SiO_2	4	3
3	$Zr(OtBu)_2$@γ-Al_2O_3	18	14
4	$Zr(OEt)_3$@SiO_2/Al_2O_3	14	11
5	$Zr(OnPr)_3$@SiO_2/Al_2O_3	3	3

[a]Conditions: CH_4 (700 psi, 2.04 mmol), $AlEt_3$ (0.60 mmol), Zr (0.008 mmol), 150 °C, 12 h. [b]NMR yield obtained by integration of MeAl signals against an internal standard (hexamethylbenzene), with respect to $AlEt_3$. [c]TON = mol MeAl/mol Zr.

have led to cyclooctanol (not detected). Likewise, oct-7-enylzirconium exchanges more rapidly with cyclooctane than with $AlEt_3$; the latter reaction would have led to decanediol (which was not detected). The observation of n-hexadecanol as a major product was also unexpected because typical 1,2-alkene insertion of an olefin into an alkylzirconium gives methyl-branched rather than linear species. The formation of linear products may be rationalized by intramolecular 2,1-insertion at the zirconium center with two active sites (Figure 4C), favored by the geometry of the cyclization reaction. An alternative mechanism is suggested by the formation of linear dodecane from di-hexylzirconium diethoxide, which was proposed to involve migration of an α-H from one alkyl to zirconium concerted with transfer of the other alkylzirconium to the insipient carbenoid.[37]

The isomerization of n-dodecane without chain shortening, noted above, may be related to reactions at zirconium centers with two active sites, in which a metallacycle undergoes β-alkyl elimination, rotation, and re-insertion. A related molecular species, dibutyldiethoxyzirconium formed from $Zr(OEt)_4$ and n-BuLi, metalates benzylic C−H bonds at room temperature, with the two reactive sites on zirconium persisting in refluxing THF.[38] Two active sites at a single zirconium center have been also invoked to rationalize isotactic-selective polymerizations of propene,[39] the formation of branched and linear butanes and pentanes from propane,[40] oxidative dimerization of hydro-carbons,[38,41] as well as β- and γ-abstractions, to give metallo-cycles.[42,43]

These studies provided insight into C−H bond alumination chemistry of aliphatic chains. First, C−H bond activations by ethyl, oct-7-enyl, and likely branched hydrocarbyl zirconium surface species are rapid and selective, favoring reactions at methyl groups over methylene groups for steric reasons. β-alkyl elimination from the terminal dodecylzirconium is slower than chain transfer or C−H activation. Carbon−carbon bond cleavage reactions are faster for the moderately strained cyclooctane than for linear chains, and the small amount of isomerization of linear chains likely involves two-site zirconium centers, which apparently do not lead to chain shortening processes. The free mono-substituted alkenes generated from one-site zirconium centers undergo rapid ethylalumination or hydroalumination.

There are parallels in this chemistry to that of $(\equiv SiO)_3ZrH$ and $(\equiv SiO)_2ZrH_2$ responsible for polymer chain shortening via hydrogenolysis.[44] The latter species activates methane more rapidly than the Zr monohydride does[45] and is also proposed to be responsible for C−C bond cleavage and chain growth of propane in the absence of an additional chain transfer reagent.[40]

Zr-Catalyzed C−H Alumination of Polyolefins. The lack of chain shortening above suggested that this catalysis might be

suitable for polyolefin functionalization, without molecular weight (MW) degradation. Low or high MW, narrow dispersity polyethylene (NDPE; ca. 1.7 branches per 100 carbons)[46] were reacted with $AlEt_3$ in the presence of $Zr(OtBu)_3$@SiO_2/Al_2O_3 and then oxidatively quenched, giving hydroxy-NDPE with similar MW and similar branching as the starting resin (eq 1 and Table 1, 1.5 branches per 100 carbons).

An average of 1 mid-chain cleavage event per 1,000 carbon−carbon bonds would have reduced the M_n of the longer chain NDPE sample from 17 000 Da to ca. 8500 Da. Thus, the high wt % yield and similar MW properties indicated that very few mid-chain C−C cleavage events have occurred. There were 0.86 and 0.73 OH groups per chain in the short- and long-chain hydroxy-NDPE products, respectively. Alkene impurities were not detected by ^{1}H NMR spectroscopy in the starting NDPE, ruling out product formation by hydroalumination or carboalumina-tion reactions.

$$\text{(1)}$$
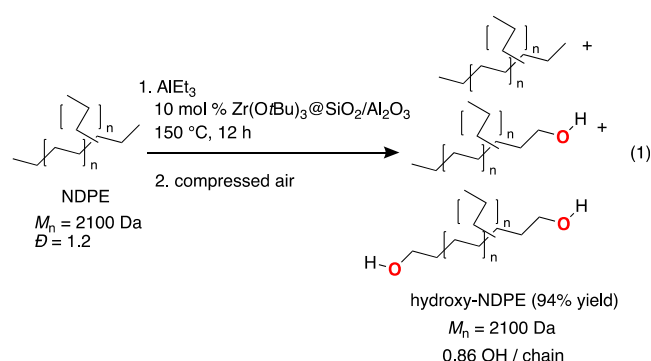
The chemical structure of the hydroxy-NDPE product was further established by a combination of 1D and 2D NMR spectroscopy, matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS), and through comparisons with the small-molecule chemistry. A signal at 3.6 ppm in the ^{1}H NMR spectrum (acquired at 120 °C) of the O_2-quenched product correlated with a ^{13}C NMR signal at 68 ppm in a [1]H−^{13}C multiplicity-edited HSQC experiment; the phase of this cross-peak matched that of the CH_2 backbone, allowing its assignment as a $−CH_2OH$ end group. Integration of the CH_2OH signal vs $Si(SiMe_3)_4$ as an internal standard of known concentration provided the yield of alcohol functionality in moles. The ∼0.9:1 ratio of CH_2OH and CH_3 is also in good agreement with the estimation based on molar yield.

MALDI-TOF-MS analysis of hydroxy-NDPE provided addi-tional insight through comparison with the MS of NDPE. For both materials, the MS contained peaks separated by 28 Da corresponding to their C_2H_4 repeat unit; however, the signals were offset by 16 Da in the MS of NDPE and hydroxy-NDPE, corresponding to a single additional oxygen atom as part of the latter (see Figures S52−S56). The NDPE and hydroxy-NDPE signals correspond to saturated and mono-alcohol species of the composition $C_nH_{2n+2}Ag^+$ and $C_nH_{2n+2}OAg^+$. The M_n deter-mined by MALDI-TOF-MS and GPC is in better agreement for NDPE (1920 and 2100 Da, respectively) than for the hydroxy-NDPE product (1500 and 2100 Da). The latter M_n from MALDI, however, represents only the $C_nH_{2n+2}OAg^+$ distribu-tion, while $C_nH_{2n+2}Ag^+$ and possible $C_nH_{2n+2}O_2Ag_2^{2+}$ species are not detected due to their relative sensitivity and the selection rules of the reflectron-configured MS experiment. Presumably, a statistical mixture of mono-alcohols and di-alcohols was formed in these reactions, as was observed in the dodecane experiments.
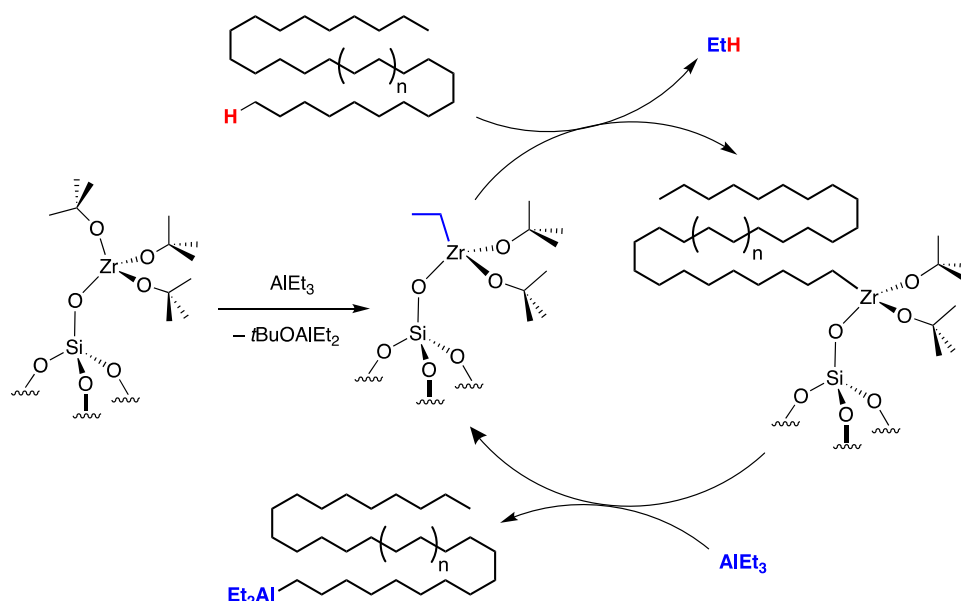
Figure 6. Proposed catalytic cycle for terminal C−H alumination of aliphatic hydrocarbons.

Similar results were observed for other hydrocarbon polymers (Table 1). LDPE and linear low-density (LLD)PE provided LDPE-OH and LLDPE-OH, with the latter containing ca. two hydroxy group per chain. High-molecular-weight *i*PP-OH was also produced by the zirconium-catalyzed alumination, which resulted in an average of three OH groups per chain. These experiments suggest that chain functionalization increases with more methyl groups per chain.

The reaction of branched synthetic lubricant poly-α-olefin-10 (PAO10) with AlEt$_3$, catalyzed by Zr(O*t*Bu)$_3$@SiO$_2$/Al$_2$O$_3$, yielded an oil with 68% of chains containing alcohol functionality after workup. NMR and IR spectroscopy and MALDI-TOF-MS data showed similar features as the functionalized polymers above. The ^{1}H NMR signals between 3.1 and 3.6 ppm correlated with ^{13}C signals between 58 and 70 ppm in a phase-sensitive ^{1}H−^{13}C HSQC experiment, consistent with −CH$_2$−OH groups. The MALDI-TOF-MS spectrum revealed a mixture of alkanes and mono-alcohols, each characterized by an equivalent MW and MW distribution (M_n = 740 Da, Đ = 1.04).

Competition between activation of aliphatic and aromatic C−H bonds was investigated through catalytic alumination of polystyrene (PS) samples. The reaction of low MW PS 1000 with AlEt$_3$ catalyzed by Zr(O*t*Bu)$_3$@SiO$_2$/Al$_2$O$_3$ followed by oxidation with air provided PS-OH (Figure 5 and Table 1). A broad ^{1}H NMR signal at 3.7−4.2 ppm was assigned to CH$_2$OH end groups based on the phase of a correlation with a ^{13}C NMR signal at 60 ppm in a phase-sensitive ^{1}H−^{13}C HSQC experiment. Weak signals in the ^{1}H NMR at 5 ppm correlated with ^{13}C signals at 66 ppm with the opposite phase as the broader CH$_2$−OH signals. These signals were assigned to CH−OH groups and accounted for 5% of the total alcohol signals by integration.

GPC analysis indicated equivalent molecular weight properties of PS 1000 and PS-OH products. The MALDI-TOF-MS of the hydroxylated polystyrene was consistent with the formation of monohydroxylated PS (Figure 5); unreacted PS chains were not detected in the PS-OH sample. In contrast to MW properties analyzed by GPC, simulation of the MALDI spectra indicated that the M_n of the PS-OH decreased from the starting material by ca. 2 monomers.

The reaction of high-molecular-weight PS and AlEt$_3$ in the presence of Zr(O*t*Bu)$_3$@SiO$_2$/Al$_2$O$_3$ in toluene gave a material with equivalent M_n and Đ to the starting PS, now terminated in hydroxy groups. A small amount of benzyl alcohol (0.08 mmol) was detected in the reaction mixture, presumably from the activation of toluene, while cresol was not detected. Thus, the reactivity of C−H bonds for Zr-catalyzed alumination in PS shows a high propensity for methyl end-group activation rather than activation of aromatic C−H bonds.

Zr-Catalyzed C−H Alumination of Methane. Given the apparently facile metalation of the least hindered C−H bonds in liquid hydrocarbons, poly-α-olefin oils, and even melted polyolefins, the smallest hydrocarbon methane was investigated as a reactant for C−H alumination. While AlEt$_3$ is readily synthesized from Al, C$_2$H$_4$, and H$_2$,[4] AlMe$_3$ preparation requires a multistep process involving alkali metal reduction of Me$_2$AlCl.[47] Thus, direct synthesis of AlMe species from methane activation and triethylaluminum could be considerably more efficient. Supported alkoxyzirconium catalysts, AlEt$_3$, and CH$_4$ were heated at 150 °C for 12 h (eq 2) and then analyzed by ^{1}H NMR spectroscopy (Table 2). The broad ^{1}H NMR singlet at −0.07 ppm in the spectrum of the reaction mixture was readily assigned to an AlMe group using a ^{1}H−^{13}C multiplicity-edited HSQC experiment. Zr(O*t*Bu)$_3$@SiO$_2$/Al$_2$O$_3$ was the most effective (23% yield, 21 TON) of the zirconium catalysts surveyed and gave similar TON as that of late metal-catalyzed methane C−H borylation using B$_2$pin$_2$.[18−20] The lower reactivity of Zr(O*n*Pr)$_3$@SiO$_2$/Al$_2$O$_3$ and Zr(ONp)$_2$@SiO$_2$/Al$_2$O$_3$, which was also observed in polyethylene alumination, may be related to the initial pre-catalyst alkylation via ZrOR/AlEt exchange.

$$CH_4 + AlEt_3 \xrightarrow[150\,°C,\ 12\ h]{\text{supported Zr catalyst}} AlMe_xEt_{3-x} + EtH \qquad (2)$$
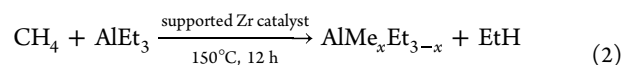
■ CONCLUSIONS

We have shown that Zr(O*t*Bu)$_3$@SiO$_2$/Al$_2$O$_3$-catalyzed C−H bond alumination is effective for derivatizing sp^3-hybridized C−H bonds in hydrocarbon chains, ranging in size all the way from large macromolecules to methane. The formation of alkylalu-

minum species as the primary products allows for versatile subsequent transformations, such as the oxygenation with O_2 employed here, as well as carboxylation with CO_2 or halogenation with I_2, catalytic chain growth in the presence of olefins, or organometal-catalyzed cross-coupling.[48] The earth-abundant, inexpensive, and readily available alkoxyzirconium molecular precatalyst and triethylaluminum reagent further add to the benefits of this new transformation.

A two-step catalytic sequence is proposed for the dominant pathway (Figure 6), involving hydrocarbon zirconation followed by heterobimetallic alkyl exchange of surface zirconium hydrocarbyl species and ethylaluminum. Production of terminal alcohols from linear and branched polyolefins with only minor changes in molecular weight indicates that this catalytic method is remarkably selective toward activation of the C−H bonds in methyl groups.

This zirconium-catalyzed C−H alumination is also complementary to our recently reported catalytic C−C alumination reaction,[28] in which facile zirconation of methylene groups within a chain and β-alkyl elimination leads to substantial chain shortening. Both processes offer routes to biodegradable fatty alcohols and fatty acids as an environmentally friendly end of life for used polyolefins. The C−H alumination reported here additionally and complementarily enables the functionalization of large and small hydrocarbons.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c11056.

> Experimental section for catalyst synthesis and characterization, catalytic alumination reaction conditions, and product characterization, accompanied by spectra (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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