

Half-Sandwich Rare-Earth-Catalyzed Olefin Polymerization, Carbometalation, and Hydroarylation

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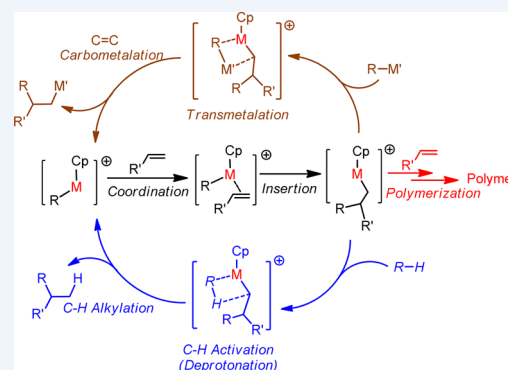
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CONSPECTUS: The search for new catalysts for more efficient, selective chemical transformations and for the synthesis of new functional materials has been a long-standing research subject in both academia and industry. To develop new generations of catalysts that are superior or complementary to the existing ones, exploring the potential of untapped elements is an important strategy. Rare-earth elements, including scandium, yttrium, and the lanthanides (La–Lu), constitute one important frontier in the periodic table. Rare-earth elements possess unique chemical and physical properties that are different from those of main-group and late-transition metals. The development of rare-earth-based catalysts by taking the advantage of these unique properties is of great interest and importance.

The most stable oxidation state of rare-earth metals is 3+, which is difficult to change under many reaction conditions. The oxidative addition and reductive elimination processes often observed in catalytic cycles involving late transition metals are generally difficult in the case of rare-earth complexes. The 18-electron rule that is applicable to late-transition-metal complexes does not fit rare-earth complexes, whose structures are mainly governed by the sterics (rather than the electron numbers) of the ligands. In the lanthanide series (La–Lu), the ionic radius gradually decreases with increasing atomic number because of the influence of the 4f electrons, which show poor shielding of nuclear charge. Rare-earth metal ions generally show strong Lewis acidity and oxophilicity. Rare-earth metal alkyl and hydride species are highly reactive, showing both nucleophilicity and basicity. The combination of these features, such as the strong nucleophilicity and moderate basicity of the alkyl and hydride species and the high stability, strong Lewis acidity, and unsaturated C–C bond affinity of the 3+ metal ions, can make rare-earth metals unique candidates for the formation of excellent single-site catalysts.

This Account is intended to give an overview of our recent studies on organo rare-earth catalysis, in particular the synthesis and application of half-sandwich rare-earth alkyl complexes bearing monocyclopentadienyl ligands for olefin polymerization, carbometalation, and hydroarylation. Treatment of half-sandwich rare-earth dialkyl complexes having the general formula CpMR₂ with an equimolar amount of an appropriate borate compound such as [Ph₃C][B(C₆F₅)₄] can generate the corresponding cationic monoalkyl species, which serve as excellent single-site catalysts for the polymerization and copolymerization of a wide range of olefin monomers such as ethylene, 1-hexene, styrene, conjugated and nonconjugated dienes, and cyclic olefins. The cationic half-sandwich rare-earth alkyl complexes can also catalyze the regio- and stereoselective alkylation of alkenes and alkynes through insertion of the unsaturated C–C bond into the metal–alkyl bond followed by transmetalation between the resulting new alkyl or alkenyl species and an alkylaluminum compound. Moreover, a combination of deprotonative C–H bond activation of appropriate organic compounds such as anisoles and pyridines by the rare-earth alkyl species and insertion of alkenes into the resulting new metal–carbon bond can lead to catalytic C–H bond alkylation of the organic substrates. Most of these transformations are unique to the rare-earth catalysts with selectivity and functional group tolerance different from those of late-transition-metal catalysts.



1. INTRODUCTION

The development of the organometallic chemistry of rare-earth elements has largely relied on the use of cyclopentadienyl (Cp) groups as supporting ligands. The Cp-ligated rare-earth complexes reported to date can be generally grouped into three types depending on the number of Cp ligands per metal (Figure 1a). Rare-earth complexes bearing three Cp ligands per metal (type A) were first reported in early 1950s.¹ Complexes of

this type do not show significant reactivity because all of the metal–ligand bonds are highly stable metal–Cp π bonds, except when the Cp ligands are very sterically crowded.² In early 1980s, monoalkyl and monohydride rare-earth complexes with two Cp ligands per metal (type B) were reported.³ These complexes

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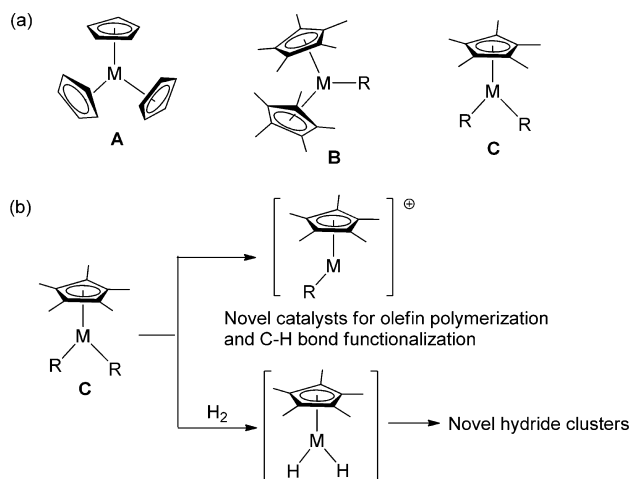


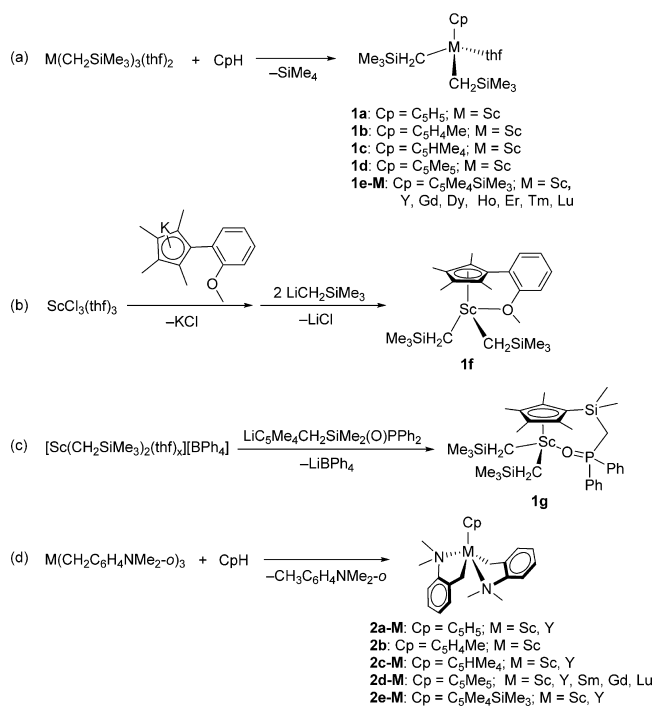
Figure 1. (a) Rare-earth complexes bearing different numbers of cyclopentadienyl and alkyl ligands per metal. (b) Transformation of half-sandwich rare-earth dialkyl complexes (C) to new active species.

possess highly reactive alkyl or hydride species and are effective for a number of chemical transformations,⁴ including the polymerization and copolymerization of ethylene and polar monomers such as alkyl acrylates and lactones through nucleophilic addition of the alkyl or hydride species to a metal-coordinated monomer.⁵ However, the polymerization activity of the neutral metallocene alkyl and hydride complexes for higher olefins such as 1-alkenes, styrene, dienes, and cyclic olefins is generally poor because the metal centers in these complexes are relatively saturated both electronically and sterically and it is therefore difficult for them to accept the coordination of less reactive higher olefins. Recently, dialkyl rare-earth complexes bearing one Cp ligand per metal (such as C) have received much attention.⁶ Removal of one of the two alkyl groups by an appropriate borate compound can generate the corresponding cationic monoalkyl species (Figure 1b), which possess a more electropositive, less sterically crowded metal center and can show much higher and unique catalytic activity for the polymerization and copolymerization of a wide range of olefins and other related transformations. Moreover, hydrogenolysis of the dialkyl complexes with H₂ has led to the formation of a new family of molecular hydride clusters showing novel features in both structure and reactivity (Figure 1b).^{6a,c,7} This Account focuses on the synthesis and catalytic applications of the half-sandwich and analogous rare-earth dialkyl complexes of type C.

2. SYNTHESIS OF HALF-SANDWICH RARE-EARTH DIALKYL COMPLEXES

The isolation of a highly reactive half-sandwich rare-earth metal dialkyl complex is usually more difficult than that of a monoalkyl complex bearing two Cp ligands because of ligand disproportionation problems. The use of an appropriate metal/ligand combination is rather critical. With an appropriate metal/ligand combination, a series of half-sandwich rare-earth dialkyl complexes have been synthesized either by acid–base reactions between trialkyl rare-earth complexes (MR₃) and neutral cyclopentadiene ligands (CpH) or by metathesis reactions between the alkali-metal salts of the Cp ligands and appropriate rare-earth precursors (Scheme 1). In the case of the smallest rare-earth metal, Sc, half-sandwich bis(trimethylsilylmethyl) complexes bearing Cp ligands with and without substituents on the Cp ring (e.g., 1a–d, 1e-Sc, 1f and, 1g) have been isolated and

Scheme 1. Typical Reactions for the Synthesis of Half-Sandwich Rare-Earth Dialkyl Complexes



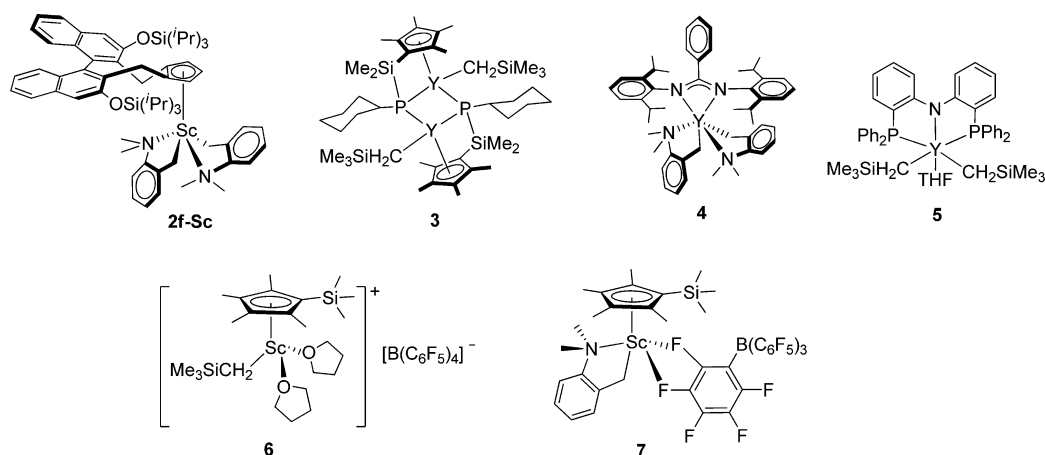
structurally characterized.⁸ In contrast, the isolation of the analogous half-sandwich complexes of larger metals such as Y, Gd, Dy, Ho, Er, Tm, and Lu (1e-M) required the use of the sterically demanding ligand C₅Me₄SiMe₃ to prevent ligand redistribution.^{7c,8a,9} When the dimethylaminobenzyl group, *o*-CH₂C₆H₄NMe₂, is used as an alkyl ligand in place of the trimethylsilylmethyl group, CH₂SiMe₃, relatively smaller cyclopentadienyl ligands such as C₅H₅ and C₅Me₅ can also afford the isolable half-sandwich dialkyl complexes of a wide range of rare-earth metals (2-M) because of intramolecular coordination of the amino group to the metal center (Scheme 1d).^{10–12} Enantiopure half-sandwich rare-earth bis(aminobenzyl) complexes such as 2f-Sc can also be prepared similarly by using chiral Cp ligands (Chart 1).¹³ Bimetallic rare-earth dialkyl complexes such as 3 supported by silylene-linked Cp–phosphido ligands¹⁴ and mononuclear dialkyl complexes such as 4¹⁵ and 5¹⁶ bearing non-Cp ligands were prepared analogously.

The reaction of the half-sandwich bis(trimethylsilylmethyl)-scandium complex 1e-Sc with an equimolar amount of [Ph₃C][B(C₆F₅)₄] followed by recrystallization in tetrahydrofuran (THF) gave the structurally characterizable separated-ion-pair complex 6.^{8b} The similar reaction of the bis(aminobenzyl) complex 2e-Sc with [PhNMe₂H][B(C₆F₅)₄] in chlorobenzene afforded the contact-ion-pair complex 7, in which there are weak interactions between the metal center and two F atoms in the borate anion unit [B(C₆F₅)₄], as shown by X-ray diffraction analysis.¹¹

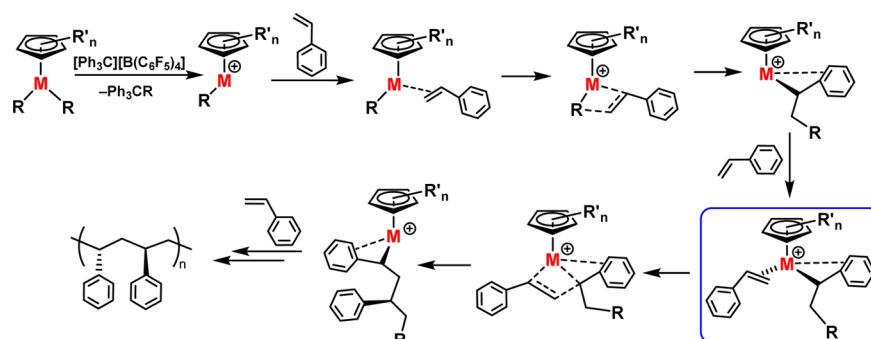
3. OLEFIN POLYMERIZATION AND COPOLYMERIZATION

The cationic rare-earth monoalkyl species generated by the reaction of the dialkyl precursors with an appropriate borate compound such as [Ph₃C][B(C₆F₅)₄] or [PhNMe₂H][B(C₆F₅)₄] showed excellent catalytic activity for the polymerization and copolymerization of a wide range of olefins.

Chart 1. Selected Examples of Rare-Earth Dialkyl Complexes and their Cationic Monoalkyl Derivatives



Scheme 2. General Process for Syndiospecific Polymerization of Styrene by a Half-Sandwich Rare-Earth Catalyst



Significant influences of the ancillary ligands and the metal ion on the catalyst activity and selectivity were observed in many cases.

The half-sandwich Sc complexes with relatively small Cp ligands such as C_5H_5 (**1a** and **2a-Sc**) and C_5H_4Me (**1b** and **2b**) are active for the polymerization of styrene but gave atactic polymers without showing stereoselectivity.^{8c} In contrast, the Sc complexes with larger Cp ligands such as C_5HMe_4 (**1c** and **2c-Sc**), C_5Me_5 (**1d** and **2d-Sc**), and $C_5Me_4SiMe_3$ (**1e-Sc** and **2e-Sc**) showed excellent syndiotactic selectivity and livingness for the polymerization of styrene (Scheme 2).^{8a,c,17} In a series of rare-earth alkyl complexes bearing the $C_5Me_4SiMe_3$ ligand, the smallest one, **1e-Sc**, showed the highest activity, while complexes of larger metals (such as **1e-Y**, **1e-Gd**, and **1e-Lu**) showed much lower activities (albeit with similarly high syndiotacticity) under the same conditions, probably because the interaction between a larger metal center and the phenyl group of a benzylic species is stronger, which could retard the subsequent styrene insertion (see Scheme 2).^{8a,18} In agreement, a Lu half-sandwich complex with a coordinative pyridyl substituent on the Cp ligand was found to show higher activity than the pyridyl-free analogue.¹⁹

In the presence of both styrene and ethylene, the $C_5Me_4SiMe_3$ -ligated Sc complex **1e-Sc** showed excellent activity and selectivity for the copolymerization of the two monomers, affording for the first time multiblock styrene–ethylene copolymers with unique syndiotactic polystyrene (sPS) blocks connected by polyethylene units (Scheme 3a).^{8a,18} The resulting copolymers showed much-improved mechanical properties together with excellent heat and chemical resistance²⁰ compared with homo-sPS, which is brittle and difficult to process. Similarly, the copolymerization of styrene with 1,3-conjugated dienes such as isoprene and butadiene by **1e-Sc**/[Ph₃C][B(C₆F₅)₄]^{21,22} or a

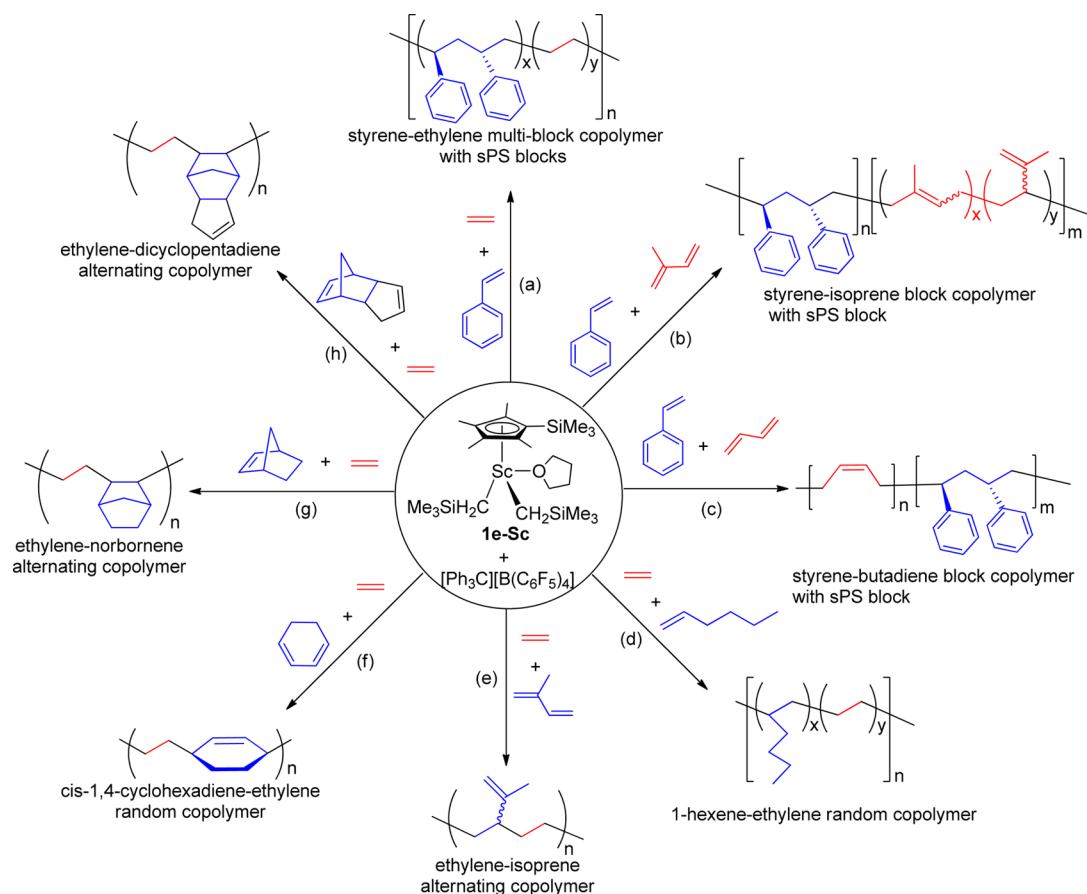
modified Lu analogue¹⁹ gave the corresponding block copolymers containing stereoregular syndiotactic polystyrene blocks (Scheme 3b,c).

Copolymerizations of ethylene with a wide range of olefin monomers such as 1-hexene, isoprene, 1,3-cyclohexadiene (CHD), norbornene, dicyclopentadiene, and 1,6-heptadiene have also been achieved by using **1e-Sc**/[Ph₃C][B(C₆F₅)₄]. The copolymerization of ethylene with 1-hexene afforded copolymers containing isolated butyl branches in the chain backbone (Scheme 3d).²³ The catalyst activity reached as high as 2.3×10^3 kg (mol of Sc)⁻¹ atm⁻¹ h⁻¹ at room temperature, which is comparable to those reported for the most active group-4 metal catalysts. The copolymerization of ethylene with isoprene by **1e-Sc**/[Ph₃C][B(C₆F₅)₄] yielded for the first time alternating isoprene–ethylene copolymers (Scheme 3e),^{8b} and the copolymerization of CHD with ethylene afforded the first random CHD–ethylene copolymers with high *cis*-1,4 selectivity (Scheme 3f).²⁴ Copolymerizations of ethylene with cyclic olefins such as norbornene and dicyclopentadiene took place in an alternating fashion with extremely high activity (Scheme 3g,h).^{25,26}

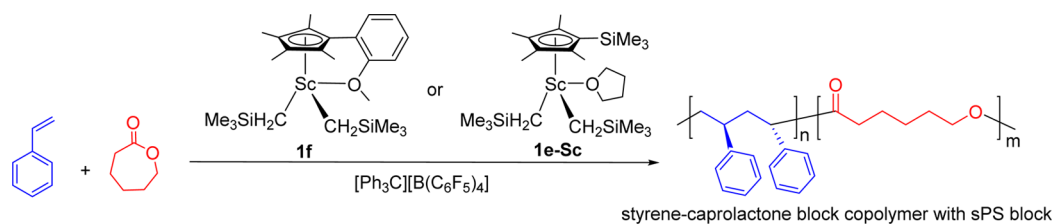
The sequential copolymerization of styrene and ϵ -caprolactone in the presence of **1e-Sc** or **1f-Sc** with [Ph₃C][B(C₆F₅)₄] afforded diblock copolymers with well-controlled molecular weight and molecular weight distribution (Scheme 4).²⁷ The resulting copolymers possess a hydrophobic hard syndiotactic polystyrene block and a hydrophilic soft polycaprolactone block, thus exhibiting unique physical and mechanical properties.

The bis(trimethylsilylmethyl)scandium complex bearing a Cp ligand with a phosphine oxide side arm (**1g**) is especially efficient for the copolymerization reactions of 1,6-heptadiene. In the presence of 1,6-heptadiene and styrene, **1g**/[Ph₃C][B(C₆F₅)₄]

Scheme 3. Selected Examples of Half-Sandwich Scandium-Catalyzed Copolymerization Reactions



Scheme 4. Block Copolymerization of Styrene with Caprolactone



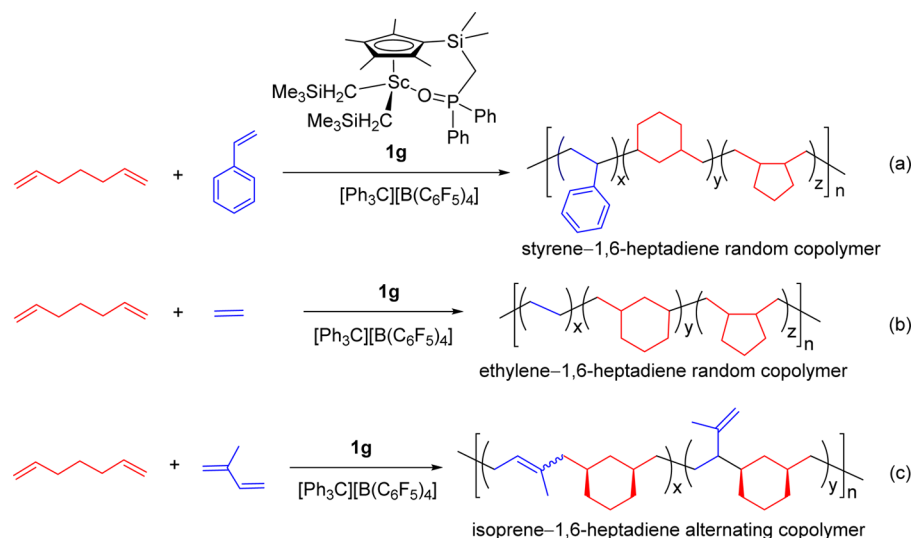
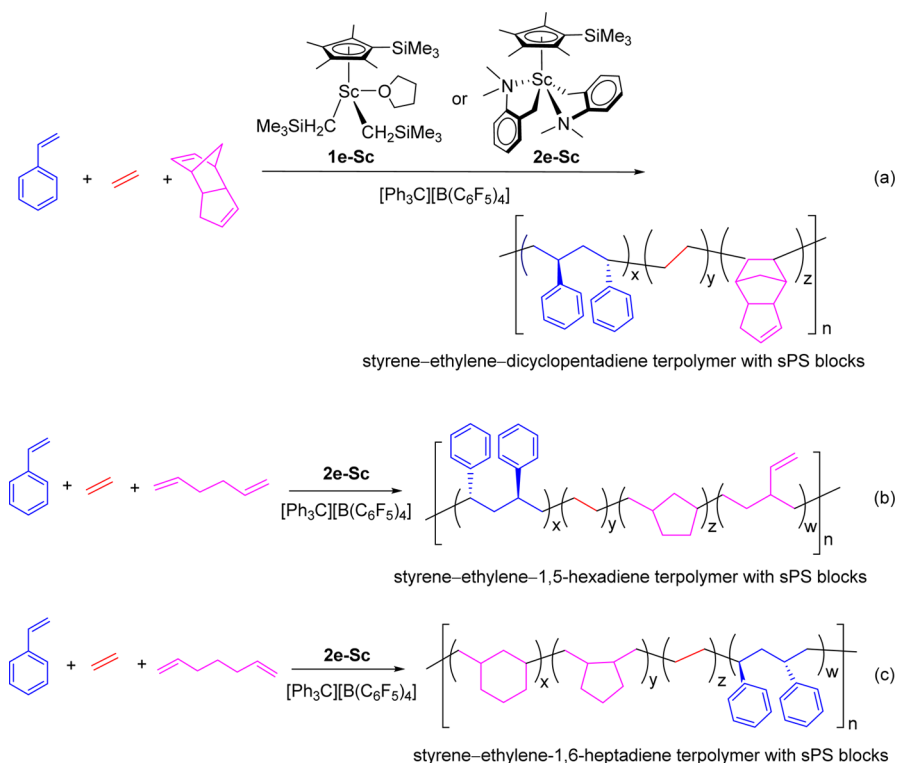
selectively afforded the random cyclocopolymers having both five- and six-membered-ring cyclic units together with atactic polystyrene units (Scheme 5a), while side-arm-free scandium complexes such as **1e-Sc** and **2e-Sc** gave a mixture of homopolymers under the same conditions.²⁸ The copolymerization of 1,6-heptadiene with ethylene by **1g** selectively gave soluble 1,6-heptadiene–ethylene random copolymers (Scheme 5b), whereas the THF-coordinated complex **1e-Sc** yielded a significant amount of insoluble materials, possibly resulting from cross-linking reactions.²⁹ The cyclocopolymerization of 1,6-heptadiene with isoprene by **1g** yielded alternating copolymers in which 1,6-heptadiene was selectively cyclized to a methylene-1,3-cyclohexane unit with high *cis* selectivity (99%) (Scheme 5c).^{8d}

Complex **1e-Sc** or **2e-Sc** in combination with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ also served as an excellent catalyst for the terpolymerization of styrene, ethylene, and a cyclic olefin such as dicyclopentadiene (DCPD) (Scheme 6a) to afford the corresponding terpolymers, which show unique optical and mechanical properties due to the presence of syndiotactic styrene–styrene sequences.^{26,30} The cycloterpolymerization of

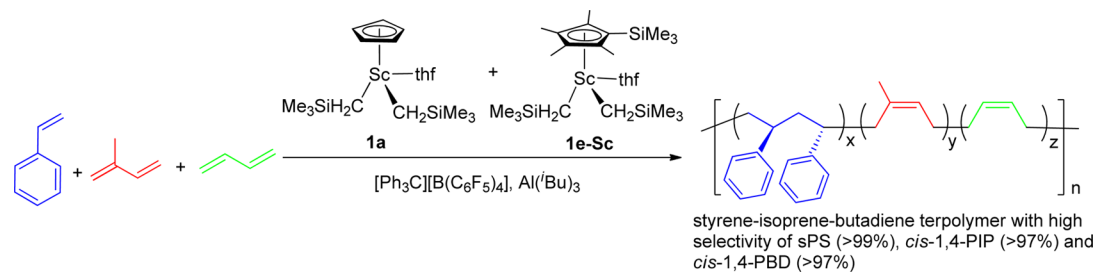
nonconjugated α,ω -dienes such as 1,5-hexadiene^{8c} and 1,6-heptadiene³¹ with styrene and ethylene was achieved using the THF-free scandium complex **2e-Sc** (Scheme 6b,c), while the THF-coordinated complex **1e-Sc** yielded cross-linked insoluble polymers under the same conditions.

Significant influences of the ancillary ligands on the regio- and stereoselectivity of isoprene polymerization were observed. For example, the sterically demanding $\text{C}_5\text{Me}_4\text{SiMe}_3$ -ligated complex **1e-Sc** did not show significant regio- or stereoselectivity (3,4/1,4 \approx 65/35 at room temperature), while the smaller C_3H_5 -ligated complex **1a** showed high *cis*-1,4 selectivity (95%) under the same conditions.^{8b,32} The binuclear dialkylttrium complex **3** in combination with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ showed high 3,4-selectivity and high isospecificity for the polymerization of isoprene, affording for the time almost perfect isotactic 3,4-polyisoprene (3,4-selectivity = 100%, *mmmm* > 99%).¹⁴ The resulting isotactic 3,4-polyisoprene is a crystalline polymer with a melting point of 162 °C. The amidinate-ligated bis(aminobenzyl)ttrium complex **4** also showed high isotactic 3,4-selectivity for isoprene polymerization (3,4-selectivity up to 99.5%, *mmmm* up to

Scheme 5. Copolymerization of 1,6-Heptadiene with Styrene, Ethylene, and Isoprene

Scheme 6. Terpolymerization of Styrene, Ethylene, and Dicyclopentadiene or α,ω -Dienes

Scheme 7. Regio- and Stereospecific Chain-Shuttling Terpolymerization of Styrene, Isoprene, and Butadiene



99%).^{15b} In contrast, the bis(phosphinophenyl)amido (PNP)-ligated dialkylttrium complex combined with $[\text{PhMe}_2\text{NH}][\text{B}$

$(\text{C}_6\text{F}_5)_4$] showed high *cis*-1,4 selectivity and excellent livingness for the polymerization of isoprene, yielding for the first time

polyisoprene with both high *cis*-1,4 content (>99%) and a narrow molecular weight distribution ($M_w/M_n < 1.10$).¹⁶

In the presence of a chain-shuttling agent such as triisobutylaluminum, the combination of the $C_5Me_4SiMe_3$ -ligated catalyst **1e-Sc**, which is highly active for the syndiospecific polymerization of styrene but less active for the polymerization of isoprene, with the C_5H_5 -ligated catalyst **1a**, which is highly active for the *cis*-1,4-polymerization of isoprene but less active for styrene, enabled the first regio- and stereospecific copolymerization of styrene and isoprene, yielding copolymers containing perfect syndiotactic polystyrene and *cis*-1,4-polyisoprene blocks.³³ In a similar fashion, the regio- and stereospecific three-component copolymerization of styrene, isoprene, and butadiene has also been accomplished (Scheme 7).³³ The analogous chain-shuttling copolymerization of styrene and isoprene by combination of a half-sandwich lanthanum catalyst and a neodymium metallocene catalyst afforded amorphous copolymers containing *trans*-1,4-isoprene blocks and atactic styrene sequences.³⁴

4. METHYLALUMINATION OF ALKENES AND ALKYNES HAVING AN ETHER TETHER GROUP

The methylalumination of alkenes and alkynes is of much interest and importance, as it can simultaneously incorporate a

Table 1. Regioselective Methylalumination of Terminal and Internal Alkenes Having an Ether Tether Group

run	alkene	[Sc]	product (yield)
1		2e-Sc	 93%
2		2e-Sc	 94%
3		2e-Sc	 83%
4		2e-Sc	 86%
5		2d-Sc	 80%

methyl group and a reactive aluminum species into carbon skeletons.³⁵ Group-4 metallocenes were previously known to serve as catalysts for this transformation. Analogously, the half-sandwich dialkylscandium complexes **2d-Sc** and **2e-Sc** in combination with $[Ph_3C][B(C_6F_5)_4]$ could also serve as excellent catalysts for the regioselective methylalumination of alkenes having an alkoxy or siloxy tether group (Table 1).³⁶ In contrast to group-4 metal catalysts, with the scandium catalysts

Table 2. Regio- and Stereoselective Methylalumination of Aryl- and Alkyl-Substituted Alkynes Having an Ether Tether Group

run	alkyne	E^+	product (yield)
1		H_3O^+	 98%
2		H_3O^+	 87%
3		HCHO	 84%
4		Br-CH=CH2	 90%
5		PhI	 77%

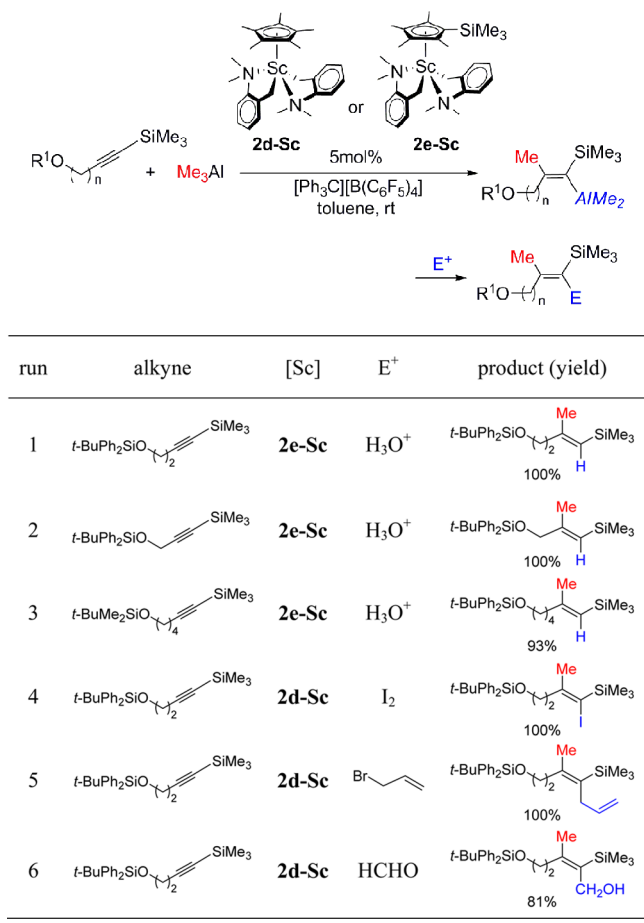
the aluminations took place at the carbon atom proximal to the ether group and the methylation distal to the ether group, possibly because of the initial strong interaction between the electropositive scandium ion and the ether group.³⁶ The corresponding secondary alcohols were obtained in high yields upon oxidation of the resulting alkenylaluminum species with O_2 (Table 1).

The regio- and stereoselective methylalumination of alkynes could also be achieved in a similar fashion (Tables 2 and 3).³⁶ Trapping the resulting alkenylaluminum intermediates with electrophiles led to the formation of a variety of multisubstituted alkenes with high selectivity in high yields.

5. C–H ADDITION OF ANISOLES TO OLEFINS

The C–H bond addition of anisoles to alkenes is the most straightforward and atom-economical route for the synthesis of alkylated anisole derivatives, which are important structure motifs in many useful materials such as pharmaceuticals, natural products, and fluorescent dyes. Conventional Lewis acid and late-transition-metal catalysts usually show poor selectivity and give a mixture of ortho- and para-alkylation products. Neutral metallocene and half-sandwich rare-earth monoalkyl or hydride complexes can induce ortho-metalation³⁷ and -silylation³⁸ of anisoles in a regioselective fashion, but these neutral rare-earth complexes show no activity for the catalytic C–H addition of anisoles to alkenes because of their low reactivity with alkenes. In contrast, the cationic half-sandwich rare-earth alkyl complexes can serve as excellent catalysts for the ortho-selective C–H alkylation of anisoles with various alkenes because the cationic

Table 3. Regio- and Stereoselective Methylalumination of Trimethylsilyl-Substituted Alkynes Having an Ether Tether Group



rare-earth anisyl species formed by ortho-metalation of anisoles can show high activity for alkene insertion.

As shown in Table 4, the scandium catalyst **2d-Sc**/[Ph₃C][B(C₆F₅)₄] showed high activity and selectivity for the ortho C–H alkylation of anisole with 1-octene, norbornene, allyltrimethylsilane, and vinyltrimethylsilane.³⁹ In the case of 1-octene and allyltrimethylsilane, the branched alkylation products were formed in high yields, while in the case of vinyltrimethylsilane, the linear alkylation product was obtained exclusively.

In the reaction of anisole with styrene, **2d-Sc** gave a mixture of 1:1 and 1:2 addition products together with some oligomers formed by successive styrene insertion because of its extremely high activity for styrene polymerization.^{8a} In contrast, the analogous yttrium complex **2d-Y**, which is less effective for the polymerization (or successive insertion) of styrene,^{8a} exclusively afforded the 1:1 C–H addition product under the same conditions. In all cases, the linear alkylation products were formed exclusively (Table 5).³⁹ Halogen and allyl substituents are compatible with the catalyst.

In the case of 2-methyl-substituted anisoles, the alkylation occurred exclusively at the benzylic sp³ C–H bond rather than at the aromatic sp² C–H bond because of steric influence, selectively affording the benzylic C–H alkylation products (Table 6).³⁹ In the reaction of 2,4,6-trimethylanisole with 1-octene, the alkylation took place predominantly at one of the two *o*-methyl groups, whereas no alkylation at the *p*-methyl group was observed (Table 6, run 4), suggesting that the interaction

Table 4. C–H Addition of Anisole to Olefins

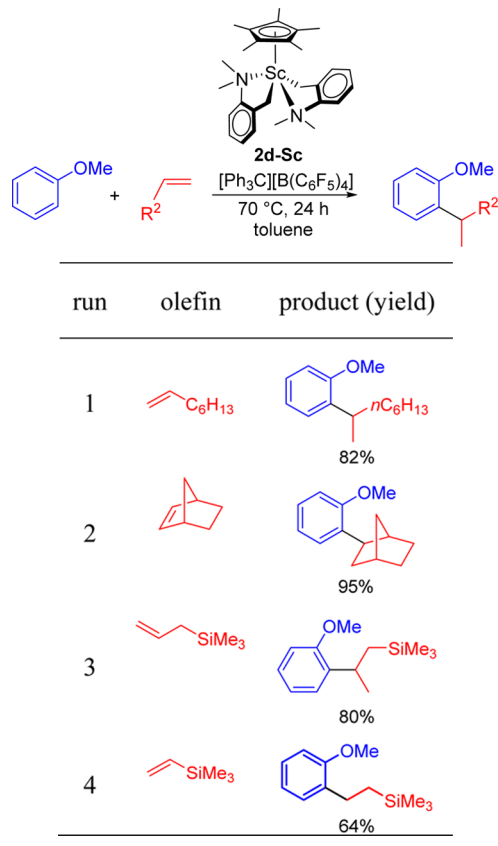


Table 5. C–H Addition of Anisoles to Styrenes

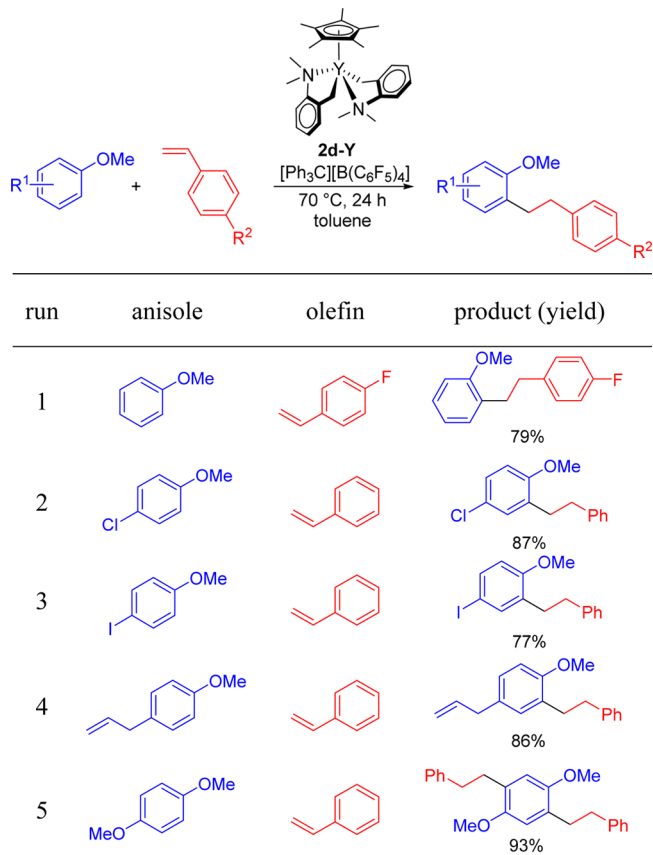
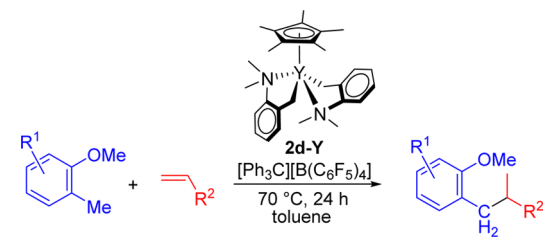
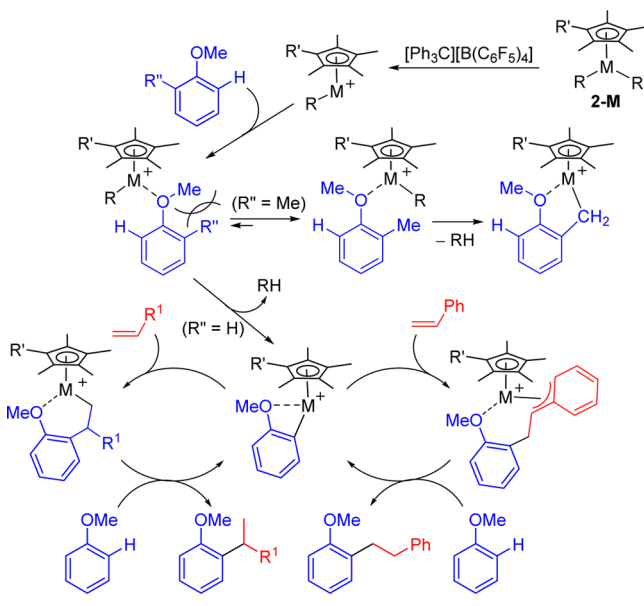


Table 6. C–H Addition of *o*-Methylanisoles to Olefins


run	methylanisole	olefin	product (yield)
1			 69%
2			 57%
3			 83%
4			 77%

Scheme 8. Possible Mechanism for the Catalytic C–H Alkylation of Anisoles with Olefins



between the methoxy group and the catalyst metal center is crucial in the present C–H alkylation reaction.

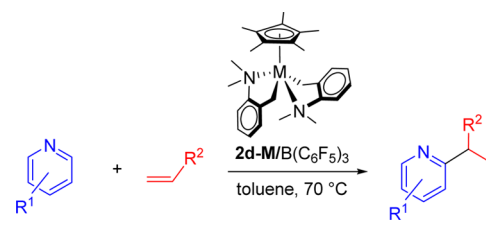
Mechanistically, the present ortho-selective C–H alkylation of anisoles with olefins could be initiated by coordination of the oxygen atom of an anisole compound to the electropositive metal center of the catalyst, followed by deprotonative activation of an ortho C–H bond with the rare-earth alkyl species. The

subsequent C=C double bond insertion into the newly formed metal–anisyl bond followed by deprotonation of another molecule of anisole completes the catalytic cycle (Scheme 8).³⁹ The polymerization or successive insertion of an olefin may be suppressed by the competitive anisole coordination and the subsequent C–H activation. Kinetic isotope effect studies suggested that C–H bond activation may not be involved in the rate-determining step, while the coordination of anisole to the catalyst metal center might play an important role.

6. C–H ADDITION OF PYRIDINES TO OLEFINS

Cationic zirconium metallocenes were known to serve as a catalyst for the C–H addition of α -picoline to propylene in the

Table 7. C–H Addition of 2-Substituted Pyridines to Various Olefins



run	pyridines	M	olefin	product (yield)
1		Sc		 98%
2		Y		 97%
3		Sc		 97%
4		Sc		 86%
5		Sc		 95%
6		Sc		 98%
7		Y		 74%

presence of H₂.⁴⁰ This transformation was accompanied by the hydrogenation of propylene with H₂ as a side reaction. Neutral yttrium metallocene complexes could catalyze the ethylation of pyridine with ethylene at high pressure (40 bar) and high temperature (110 °C) but showed no activity for higher olefins.⁴¹ In contrast, the cationic half-sandwich rare-earth alkyl complexes served as excellent catalysts for the C–H alkylation of pyridines

Table 8. C–H Addition of 2-Ethylpyridine to Styrenes

run	pyridines	olefin	product (yield)
1			94%
2			98%
3			94%
4			96%

with various olefins, similar to the C–H alkylation of anisoles described above.

As shown in Table 7, the combination of **2d-Sc** or **2d-Y** with $B(C_6F_5)_3$ showed excellent activity and selectivity for the ortho C–H addition of 2-substituted pyridines to various olefins such as ethylene, 1-hexene, 1,3-cyclohexadiene, and norbornene, affording the corresponding alkylated or allylated pyridine derivatives in high yields.⁴² In the case of styrenes (Table 8), the yttrium catalyst **2d-Y** showed better performance than the scandium analogue **2d-Sc**, selectively yielding linear alkylation products as in the case of anisoles. It is also worth noting that the selectivity of the rare-earth catalysts stands in contrast to that of late-transition-metal catalysts. The latter resulted in alkylation at the para position of pyridine and predominantly gave the linear product in the case of a 1-alkene and the branched product in the case of styrene.⁴³

Analogously to the reaction of anisoles, the C–H alkylation of pyridines may take place through initial coordination of the pyridine nitrogen atom to the catalyst metal center and subsequent ortho C–H bond activation by the rare-earth alkyl species, followed by the insertion of an olefin $C=C$ double bond into the resulting metal–pyridyl bond.^{42,44} Substituent-free pyridine did not undergo the catalytic C–H alkylation in any case, probably because the coordination of unsubstituted pyridine to the catalyst metal center is too strong. Kinetic isotope effect studies suggested that C–H bond activation could be involved in the rate-determining step in the present C–H alkylation reactions of pyridines.⁴² The analogous C–H bond addition of 2-substituted pyridines to allenes was also achieved by using **2d-Sc**/ $[Ph_3C][B(C_6F_5)_4]$ as a catalyst, affording the corresponding alkenylated pyridine derivatives in high yields with excellent regio- and stereoselectivity.⁴⁵

When 2,6-dialkyl-substituted pyridines such as 2,6-lutidine were reacted with an olefin in the presence of **2a-Y**/ $[Ph_3C][B-$

Table 9. C–H Addition of 2,6-Lutidine to Various Olefins

run	olefin	[Y]	product (yield)
1		2d-Y	70%
2		2a-Y	79%
3		2d-Y	67%
4		2d-Y	74%
5		2d-Y	69%
6		2d-Y	68%
7		2a-Y	97%
8		2a-Y	97%

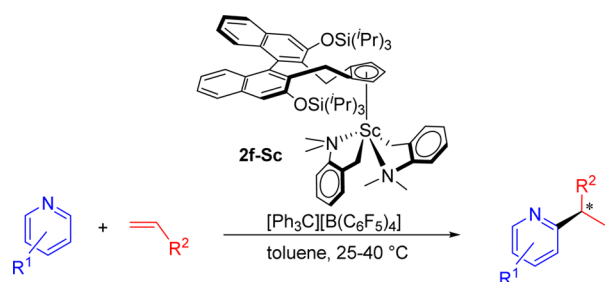
$(C_6F_5)_4]$ or **2d-Y**/ $[Ph_3C][B(C_6F_5)_4]$, the reaction took place selectively at the ortho benzylic sp^3 C–H bonds (Table 9).¹⁰ A significant influence of the Cp ligand was observed. For example, the sterically demanding C_5Me_5 -ligated complex **2d-Y** afforded the monoalkylation product as the major product in the reaction of 2,6-lutidine with 4 equiv of styrene (Table 9, run 1), while the smaller C_3H_5 -ligated complex **2a-Y** led to selective formation of the dialkylation product under the same conditions (Table 9, run 2). The reaction of 2,6-lutidine with ethylene (1 atm) catalyzed by **2a-Y**/ $[Ph_3C][B(C_6F_5)_4]$ gave the tetraethylation product exclusively (Table 9, run 7).



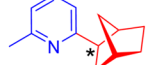


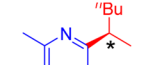


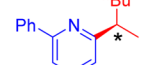


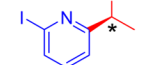


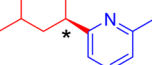


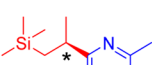
Very recently, the enantioselective C–H addition of 2-substituted pyridines to 1-alkenes was also achieved by using a chiral half-sandwich rare-earth alkyl catalyst such as **2f-Sc**/ $[Ph_3C][B(C_6F_5)_4]$, affording corresponding branched alkylation products with high enantioselectivity in high yields (Table 10).¹³

7. CONCLUSIONS AND PROSPECTS

We have demonstrated that the rare-earth metal dialkyl complexes bearing one monoanionic ancillary ligand (such as

Table 10. Enantioselective C–H Addition of Pyridines to Alkenes



run	pyridines	olefin	product (yield, er)
1			 92%, 89:11
2			 93%, 98:2
3			 94%, 92:8
4			 87%, 94:6
5			 95%, 90:10
6			 80%, 86:14

Cp) per metal can serve as excellent platforms for the formation of unique single-site catalysts for the polymerization and copolymerization of a wide range of olefins as well as for other chemical transformations such as methylalumination of alkenes and alkynes and C–H alkylation of anisoles and pyridines with alkenes. All of these catalytic transformations are initiated by similar cationic monoalkyl rare-earth species formed by removal of one alkyl group from the dialkyl precursors with an activator such as $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$. The catalyst activity and selectivity can be fine-tuned simply by changing the supporting ligands and/or central metal ion in a series of complexes having similar structures. Obviously, the unique performance of these catalysts should originate from the synergy of the characteristic features of the rare-earth elements, such as the Lewis acidity, heteroatom and C=C double bond affinity, and stability of the 3+ oxidation state of the metal ions and the strong nucleophilicity and basicity of the metal carbyl species.

It is also worth noting that hydrogenolysis of rare-earth metal dialkyl complexes such as **1**, **2**, **4**, and **5** has led to the formation of a new family of well-defined rare-earth metal hydride clusters that show novel features in both structure and reactivity.^{6,7} A similar approach to the analogous group-4 metal hydrides has recently led to the synthesis of a novel titanium hydride cluster that can cleave and hydrogenate dinitrogen (N_2)⁴⁶ and benzene⁴⁷ at room temperature. Moreover, half-sandwich rare-earth dialkyl complexes can also be used as building blocks for the synthesis of heteromultimetallic rare-earth/d-transition metal complexes.⁴⁸

With the features of rare-earth catalysis uncovered during the last several years and ever increasing results in hand, we are quite optimistic about further applications of half-sandwich and related rare-earth metal catalysts for the synthesis of polymer materials possessing new structures, new components, and possibly unique physical, mechanical, and optical properties as well as for other chemical transformations, including asymmetric C–H bond functionalization. Further progress in this area can be confidently expected in the following years.

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Notes

The authors declare no competing financial interest.

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Fang Guo received her Ph.D. from Dalian University of Technology (DUT) in 2011. She did her Ph.D. studies in the laboratory of Professor Zhaomin Hou at RIKEN as an International Program Associate (IPA) of RIKEN (2008–2011). Then she joined the “Thousand Talent Program” group of Prof. Zhaomin Hou at DUT and is now a Lecturer at DUT. Her research focuses on olefin polymerization catalyzed by organo rare-earth complexes.

Zhaomin Hou received his Ph.D. from Kyushu University in 1989. After postdoctoral studies at RIKEN (1989–1991) and the University of Windsor (1991–1993), he joined RIKEN as a tenured Research Scientist in 1993. He is now the Director of the Organometallic Chemistry Laboratory at RIKEN and holds a joint appointment as a Group Director and Deputy Center Director of the RIKEN Center for Sustainable Resource Science and Guest Professor at Dalian University of Technology supported by the “Thousand Talent Program” of China. Recent awards include the JSPS Prize (2007), the Chemical Society of Japan Award for Creative Work (2007), the Mitsui Chemicals Catalysis Science Award (2007), the Commendation for Science and Technology by the Minister of MEXT of Japan: the Prizes for Science and Technology (2008), the Rare-Earth Society of Japan Award (2009), the Award of the Society of Polymer Science, Japan (2012), the Chinese Chemical Society Yaozeng Huang Award in Organometallic Chemistry (2014), and the Nagoya Silver Medal (2015).

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