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Addition of C−H Bonds of Pyridine Derivatives to Alkenes Catalyzed by Zirconium Complexes Bearing Amine-Bridged Bis(phenolato) Ligands

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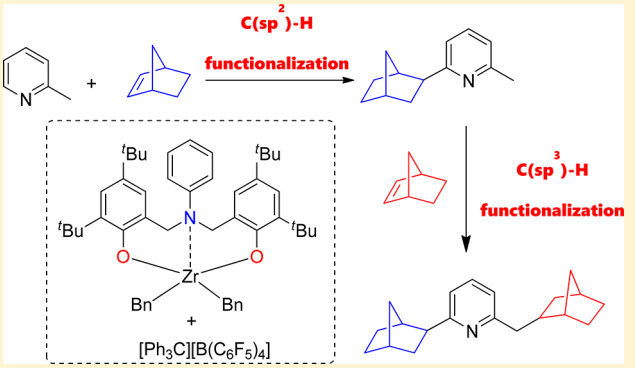
Supporting Information

ABSTRACT: Cationic zirconium complexes *in situ* generated from zirconium dibenzyl complexes bearing amine-bridged bis(phenolato) ligands have been developed to catalyze addition of C(sp^2)−H and C(sp^3)−H bonds of pyridine derivatives to alkenes. A series of zirconium complexes bearing different ligands have been synthesized, and their activities in catalyzing addition of C(sp^3)−H bonds of pyridine derivatives to alkenes have been studied and compared. Both reaction activity and regioselectivity are influenced by electronic and steric properties of ligand backbones. In addition, a cationic zirconium complex has been isolated and structurally characterized to shed some light on reaction mechanism.



INTRODUCTION

Pyridine skeletons find wide application in natural products, medicinal agents, ligands, and functional materials.[1] Recent development of transition-metal-catalyzed C−H bond functionalization allows the most atom- and step-economical way to introduce functional groups onto pyridine skeletons.[2] Direct addition of C−H bonds of pyridines to C−C unsaturated bonds has been intensively studied for alkylated pyridine derivative synthesis. In the literature, late transition metal complexes, typically Rh,[3] Ni,[4] Co,[5] Cr,[6] and Ru[7] complexes, are developed as versatile catalysts. For early transition metal catalysts, pioneering work on cationic zirconocene alkyl complexes-catalyzed addition of C−H bonds of pyridine derivatives was reported by Jordan and co-workers in 1989.[8a] Co-catalyst H_2 was essential to generate Zr−H compounds as active species.[8c] Teuben and co-workers reported a group 3 metal complex Cp*$_2$Y(η^2-pyridyl) which catalyzed ethylation of pyridine.[9a] Hou and co-workers reported cationic half-metallocene complexes of yttrium and scandium, which catalyzed the addition of *ortho*-C−H bonds of pyridine derivatives to various alkenes.[9b−e] Overall, examples of early transition metal catalysts are rare, and development of group 4 metal catalysts that are active in the absence of H_2 is highly desirable.

Comparing to C(sp^2)−H bond functionalization, reactions of more inert C(sp^3)−H bonds are generally more challenging. Reports on reactions of simple alkenes with benzylic C−H bonds of alkyl pyridines remain scarce. Teuben, Rieger, Wang, and Jordan reported the stoichiometric activation of C(sp^3)−H bonds by group 3 and 4 metal complexes.[10,11] Hou and co-workers reported the first example of catalytic reactions of benzylic C(sp^3)−H bonds of α-alkyl pyridines with simple alkenes in the presence of cationic half-sandwich yttrium alkyl complexes.[12] We have recently communicated cationic zirconium complexes-catalyzed addition of C(sp^3)−H bonds of alkylpyridines to alkenes.[13] A preliminary study revealed the influence of ligand backbones on reaction regioselectivity. As a continuation of this study, we investigated the structure−activity relationship of a range of zirconium complexes stabilized by different amine-bridged bis(phenolato) ligands. Herein, we report highly efficient, *ortho*-selective addition of C(sp^2)−H and benzylic C(sp^3)−H bonds of pyridine derivatives to alkenes catalyzed by cationic zirconium alkyl complexes.

RESULTS AND DISCUSSION

Synthesis of Complexes. Amine-bridged bis(phenol)s L^1H_2−L^9H_2 with different phenyl and *N*-substituents were synthesized (Figure 1)[14] to introduce different coordinating environments for metal center.

Metathesis reactions of $ZrBn_4$ and bis(phenol)s at room temperature provide an easy access to zirconium dialkyl complexes.[13,15,16] Complexes **1**−**9** were isolated in 90−95%

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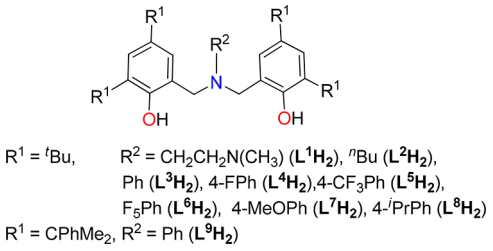

Figure 1. Ligand precursors.

yields (Scheme 1). All complexes were characterized by ^{1}H and ^{13}C NMR spectroscopy, elemental analysis, and single-crystal X-ray diffraction analysis (in the case of complex **3** as communicated earlier).[13]

Catalytic Studies. In a preliminary study, a mixture of $[Ph_3C][B(C_6F_5)_4]$ and complex **1** stabilized by an [ONNO]-type tetradentate ligand, which *in situ* generated cationic species, showed no activity in catalyzing the reaction of *α*-picoline with styrene (Table 1, entry 1). In comparison, complexes **2** and **3** bearing [ONO]-type tridentate ligand and $[Ph_3C][B(C_6F_5)_4]$ proved active in catalyzing addition of the *ortho*-C(sp^2)−H bond, which gave rise to linear product **12a** almost exclusively in 53% and 65% yields, respectively (Table 1, entries 2 and 3). Reducing coordination sites in bis(phenolato) ligands led to complexes of enhanced catalytic activity, which is consistent with previous findings on Zr-catalyzed hydroamination reactions.[16] It is noteworthy that this reaction worked in the absence of H_2, which is of more practical use compared to zirconium catalysts reported by Jordan et al.[8]

Detailed optimization of reaction conditions includes changing substrate ratios, temperatures, solvents, cationic reagents, and catalysts loadings (Table 1, entries 3−9). Screening of different substrate ratios revealed that a higher yield of 94% was obtained in the presence of excess alkene (Table 1, entries 3−4). Raising the reaction temperature from 80 to 110 °C led to the increase of yield from 37% to 94% (Table 1, entries 4−7). Reactions in different solvents (i.e., PhCl, toluene, THF) were conducted, and the best yield was obtained in PhCl, possibly due to good solubility of cationic complexes in PhCl (Table 1, entries 4, 8, 9). Overall, reaction with 2 equiv of **11a** at 100 °C in PhCl gave the best yield of 94% (Table 1, entry 4). Reducing the catalyst loading to 5 mol % gave equally good yield (Table 1, entries 10 and 11). Controlled experiments with TB or neutral complexes only were inactive (Table 1, entries 12 and 13). Apparently, a cationic zirconium complex is essential to achieve good transformations, due to accessible coordination site and a more Lewis acidic metal center comparing to neutral counterparts. Under each condition, almost exclusive formation of linear products was observed (*vide infra*), which is consistent with literature reports of Ni-, Ru-, Zr-, and Y-catalyzed reactions,[4a,7,8,9] but different from those of Co- and Cr-catalyzed reactions.[5,6]

Reactions of *α*-picoline with various alkenes were studied under optimized conditions, and results are summarized in Table 2.

Aromatic alkenes bearing either electron-donating (Me, ^{t}Bu, OMe) or electron-withdrawing (F, Cl) substituents reacted smoothly under established conditions, and afforded linear *ortho*-C(sp^2)−H addition products **12a−f** in 81−99% yields. Electron-deficient substrates (**11e** and **11f**) required longer reaction time and/or higher catalyst loading. Notably, with the introduction of a coordinating O atom in 4-methoxystyrene (**11d**), the catalytic activity remained, and the desired product **12d** formed in a good yield of 88%.

The cationic zirconium catalyst showed higher activity for reactions of aliphatic alkenes. The addition of the *o*-C(sp^2)−H bond of *α*-picoline with norbornene (**11g**), 1-octene (**11h**), 1-hexene (**11i**), and dicyclopentadiene (**11j**) gave desired products **12g−j** quantitatively within 6 h. It is noteworthy that branched products (**12h−i**) formed exclusively, which is different from results of styrene derivatives (*vide supra*). The cationic zirconium catalyst is also applicable for addition of the C−H bond of *α*-picoline to conjugated dienes, e.g., 1,3-

Scheme 1. Synthesis of Zirconium Complexes

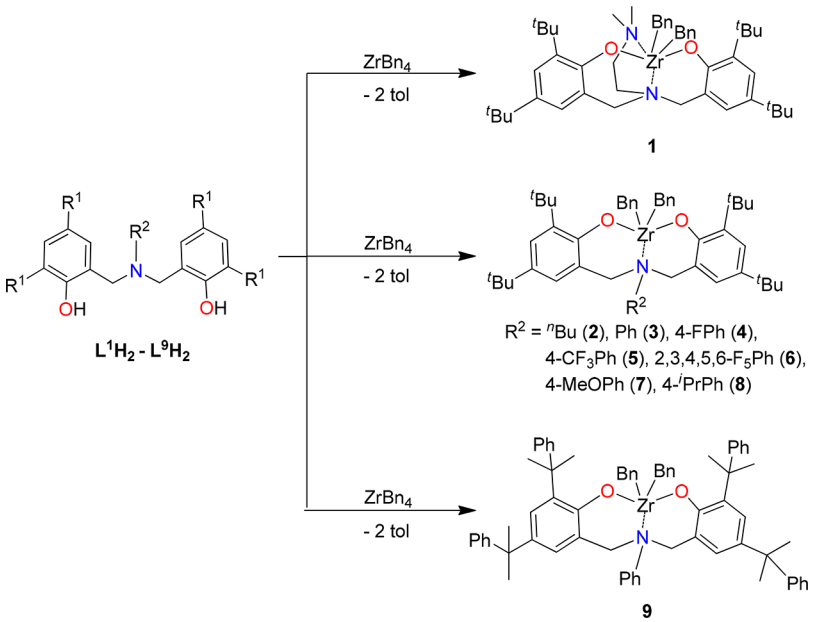

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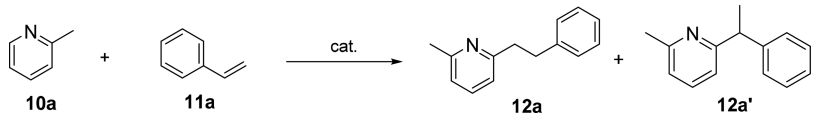
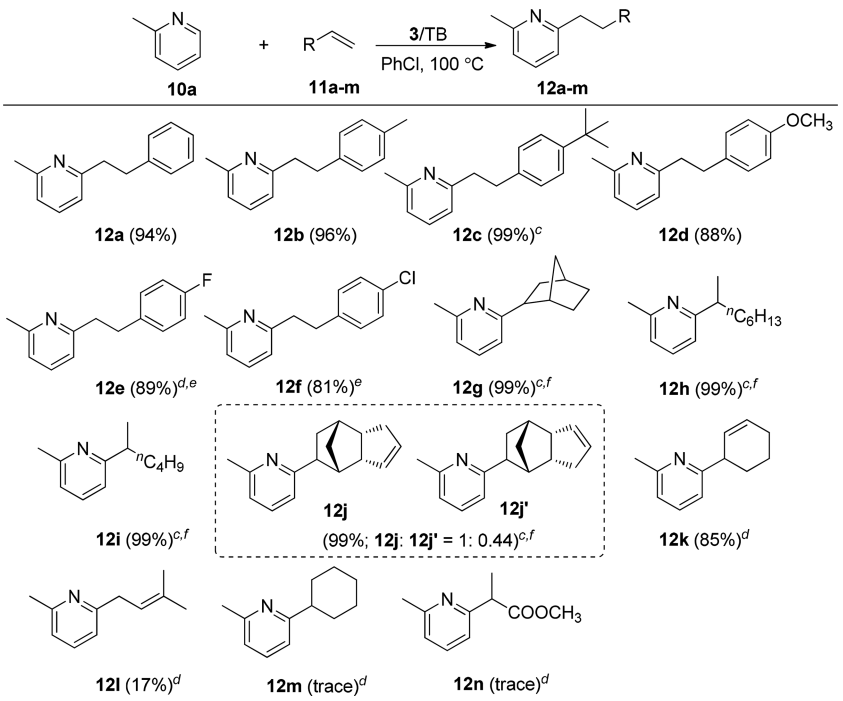
Table 1. Catalytic Addition of *ortho*-C(sp^2)−H Bond of α-Picoline 10a to Styrene 11a[a]



entry	cat.	10a:11a	T (°C)	cat. (mol %)	solvent	time (h)	yield (%)[b]	12a:12a'[c]
1	1/TB	1:1	100	10	PhCl	12	trace	
2	2/TB	1:1	100	10	PhCl	12	53	95:5
3	3/TB	1:1	100	10	PhCl	12	65	98:2
4	3/TB	1:2	100	10	PhCl	12	94	
5	3/TB	1:2	80	10	PhCl	12	37	
6	3/TB	1:2	90	10	PhCl	12	82	
7	3/TB	1:2	110	10	PhCl	12	94	
8	3/TB	1:2	100	10	Tol	24	83	
9	3/TB	1:2	100	10	THF	24	trace	
10	3/TB	1:2	100	5	PhCl	12	94	98:2
11	3/TB	1:2	100	2.5	PhCl	24	61	
12	3	1:1	100	10	PhCl	12	trace	
13	TB	1:2	100	10	PhCl	24	trace	

[a]Conditions: **10a** (0.099 mL, 1 mmol), **11a** (amount stated in each entry), complex (amount stated in each entry), $[Ph_3C][B(C_6F_5)_4]$ (TB) (46 mg, 0.05 mmol) if necessary, solvent (2 mL). [b]Isolated yield based on **10a**. [c]The product ratio was determined by ^1H NMR spectroscopy.

Table 2. Catalytic Addition of *ortho*-C(sp^2)−H Bond of α-Picoline to Various Alkenes[a,b]



[a]Conditions: **10a** (0.099 mL, 1 mmol), **11** (2 mmol), **3** (0.040 g, 0.05 mmol), $[Ph_3C][B(C_6F_5)_4]$ (TB) (46 mg, 0.05 mmol) in PhCl (2 mL) for 12 h at 100 °C. [b]Isolated yield. [c]4 mol % catalyst loading. [d]24 h reaction time. [e]10 mol % catalyst loading. [f]6 h reaction time.

cyclohexadiene (**11k**) and isoprene (**11l**), which generated 1,4-addition products in yields of 85% and 17%, respectively. This catalytic system showed limited activities when catalyzing the reaction of cyclohexene (**11m**) and methyl acrylate (**11n**).

Different pyridine derivatives were also studied in reactions with 1-hexene to further investigate the scope of the cationic zirconium complex-catalyzed addition of *ortho*-C(sp^2)−H bonds, and results are summarized in Table 3.

Substrates bearing an ethyl (**10b**), isopropyl (**10c**), or phenyl (**10d**) substituent reacted smoothly with 1-hexene under the afore-optimized conditions, and yielded selectively branched addition products **13b−d** in 97−99% yields. It is noteworthy that 2-phenylpyridine (**10d**) was alkylated selectively in the pyridine ring in 97% yield, instead of the phenyl group, which is different from late transition-metal-catalyzed reactions.[17] Bicyclo-compounds **10e−g** reacted selectively at the *ortho*-position of pyridine rings, and generated addition products **13e−g** in 91−95% yields. In contrast with cationic scandium-catalyzed reactions reported by Hou et al.,[9b] reactions of electron-deficient pyridine derivatives proceeded sluggishly, and gave neglectable yields (**13h−j**). Poor coordination of these pyridine derivatives to the zirconium center may account for their low reactivity.

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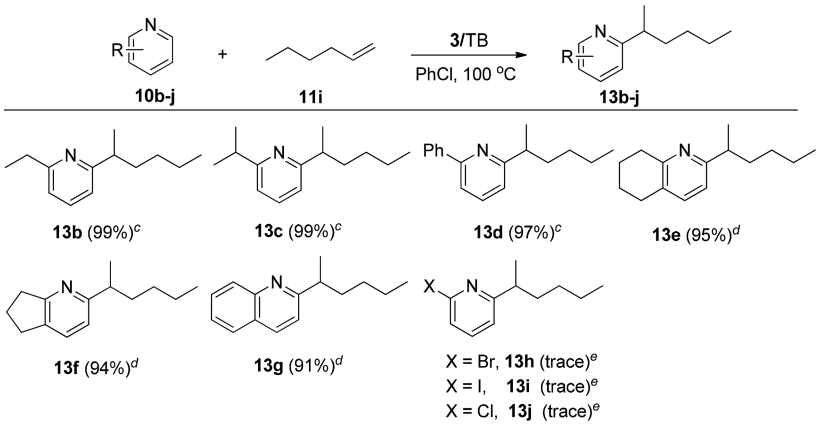
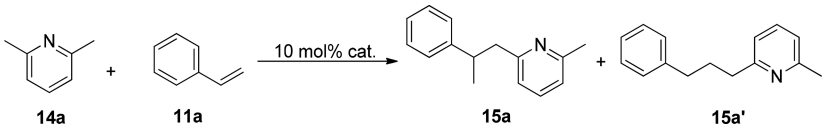
Table 3. Catalytic Addition of *ortho*-C(sp^2)−H Bonds of Pyridine Derivatives to 1-Hexene[a,b]



[a]Conditions: **10** (1 mmol), **11i** (0.248 mL, 2 mmol), **3** (0.040 g, 0.05 mmol), $[Ph_3C][B(C_6F_5)_4]$ (TB) (46 mg, 0.05 mmol) in PhCl (2 mL) at 100 °C. [b]Isolated yield. [c]6 h reaction time. [d]24 h reaction time. [e]48 h reaction time.

Table 4. Addition of Benzylic C(sp^3)−H Bonds to Styrene Catalyzed by Zirconium Complexes Bearing Different [ONO]-Type Ligands[a]



entry	cat.	T (°C)	solvent	time (h)	yield (%)[b]	**15a:15a′**[c]
1	**1**+TB	100	PhCl	24	trace	
2	**2**+TB	100	PhCl	24	75	1:5
3	**3**+TB	100	PhCl	24	81	10:1
4	**4**+TB	100	PhCl	24	80	10:1
5	**5**+TB	100	PhCl	36	62	10:1
6	**6**+TB	100	PhCl	48	trace	
7	**7**+TB	100	PhCl	24	77	5:1
8	**8**+TB	100	PhCl	24	82	3:1
9	**9**+TB	100	PhCl	24	81	1:1

[a]Conditions: **11a** (0.45 mL, 4 mmol), **14a** (0.116 mL, 1 mmol), complex (0.1 mmol), $[Ph_3C][B(C_6F_5)_4]$ (TB) (92 mg, 0.1 mmol), PhCl (2 mL). [b]Isolated yield. [c]The product ratio was determined by ^{1}H NMR spectroscopy.

Successful addition of C(sp^2)−H bonds of pyridines to alkenes encouraged us to explore the application of cationic zirconium complexes in catalyzing more challenging addition of C(sp^3)−H bonds. For α-picoline bearing both C(sp^2)−H and C(sp^3)−H bonds, reactions occurred selectively at the *ortho*-C(sp^2)−H bond (*vide supra*), while the addition of excess alkene or elevation of reaction temperature did not result in C(sp^3)−H activation. This finding is different from that of KHMDS-catalyzed reactions, which preferred C(sp^3)−H over the C(sp^2)−H bond.[18]

To achieve the addition of benzylic C(sp^3)−H bonds, reactions of 2,6-lutidine (**14a**) with 4 equiv of styrene were studied in the presence of complex **3** and TB, which generated the benzylic C(sp^3)−H addition product **15a** in 81% yield (Table 4, entry 3). Branched and linear products formed in the ratio of 10:1, which is different from results catalyzed by half-metallocene yttrium and scandium complexes reported by Hou et al.[12] Further screening of cationic zirconium complexes bearing different [ONO]-type ligands revealed significant differences. A lower yield (75%) was obtained in the presence of *n*-butylamine bridged bis(phenolato) zirconium bis(benzyl) complex **2** and $[Ph_3C][B(C_6F_5)_4]$. More importantly, reversed regioselectivity of 1:5 in preference of the linear product was observed (Table 4, entry 2). Similar to addition of the C(sp^2)−H bond of α-picoline, complex **1** carrying a tetradentate ligand did not show any activity (Table 4, entry 1) (*vide supra*). This is the first example of group 4 metal-based catalysts capable of catalyzing addition of benzylic C(sp^3)−H bonds of alkylpyridines to alkenes.[13]

Study to further tune the reaction regioselectivity was performed by changing the bridges and substituents of tridentate phenolato ligands. Different substituents, including F (**4** and **6**), CF_3 (**5**), OMe (**7**), and ^{i}Pr (**8**) groups, were introduced to *N*-phenyl groups. *para*-Fluoroaniline-bridged complex **4** showed similar activity and regioselectivity with that of complex **3** (Table 4, entry 4). Introduction of a CF_3 group in complex **5** resulted in a low yield of 62% while the regioselectivity maintained (Table 4, entry 5). Pentafluoroaniline-bridged complex **6** and TB showed no activity (Table 4, entry 6). It is thus conclusive that the presence of electron-withdrawing groups led to reduced activity and maintained regioselectivity. On the other hand, the presence of electron-donating groups in complexes **7** and **8** did not influence catalytic activity, but resulted in poor regioselectivity (Table 4, entries 7 and 8). Overall, mildly electron-deficient bridges result in good activity as well as regioselectivity, while changing

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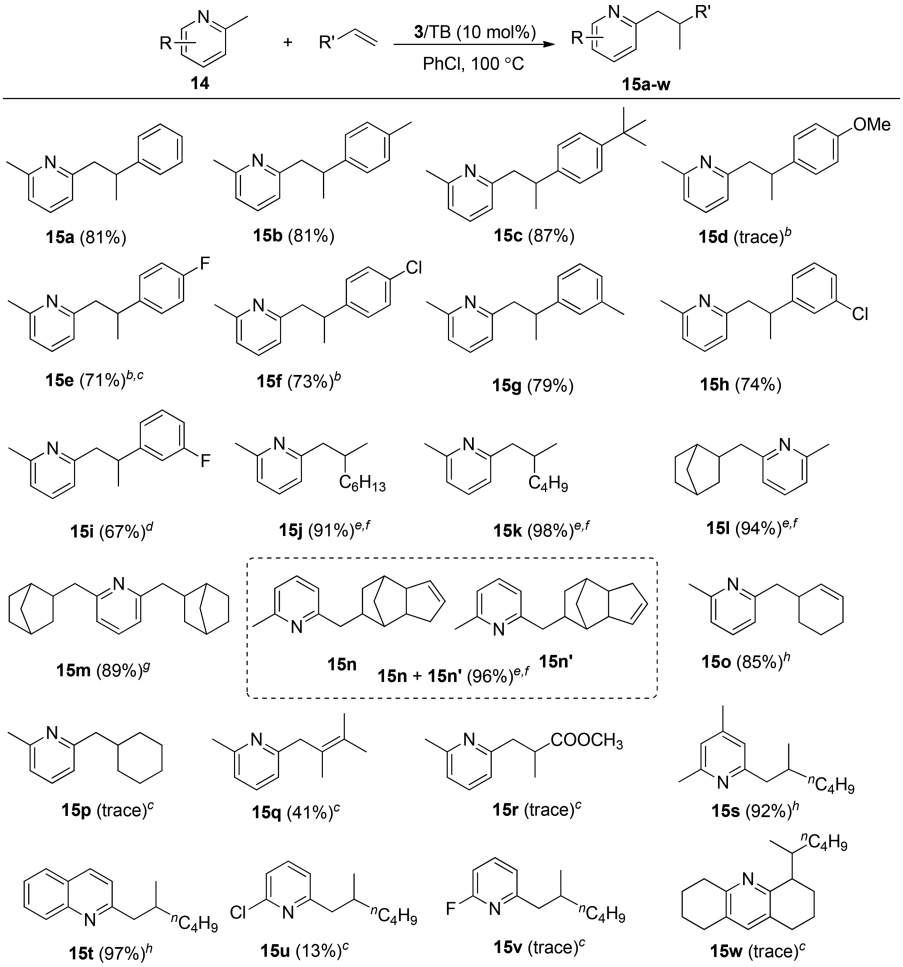
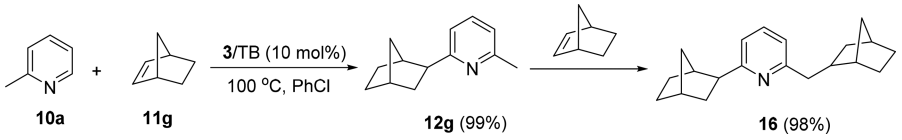
Table 5. Addition of Benzylic C(sp^3)−H Bonds of Pyridine Derivatives to Various Alkenes[a]



[a]Conditions: **14** (0.116 mL, 1 mmol), alkene (4 mmol), **3** (0.080 g, 0.1 mmol), $[Ph_3C][B(C_6F_5)_4]$ (TB) (92 mg, 0.1 mmol) in PhCl (2 mL) for 24 h at 100 °C. Isolated yield. [b]36 h reaction time. [c]12 mol % catalyst loading. [d]48 h reaction time. [e]8 mol % catalyst loading. [f]16 h reaction time. [g]6 equiv norbornene. [h]12 h at 100 °C.

Scheme 2. One-Pot, Two-Step Synthesis of 16



to an electron-donating alkyl bridge (in the case of **2**) gives rise to inversed regioselectivity, which is consistent with the computational finding that electronic effects play crucial roles in product distribution (*vide infra*).[13] Aniline-bridged complex **9** with bulkier substituents at phenolate groups led to poor regioselectivity of 1:1 with activity maintained, demonstrating the steric influence of ligands (Table 4, entry 9).

Aniline-bridged complex **3** showed overall the best activity and regioselectivity, and the substrate scope has been communicated.[13] A variety of substituted aromatic and aliphatic alkenes reacted with 2,6-lutidine, and generated branched C(sp^3)-H addition products in 41−98% yields, while pyridine derivatives were restricted to electron-rich α-methyl pyridines (Table 5).

Using the methodology developed for C−H bond functionalization, a successive addition of C(sp^2) and C(sp^3)−H bonds was performed by reacting 2-methylpyridine with excess norbornene, which generated double-addition product **16** in near quantitative yield (Scheme 2).

Characterization of Cationic Species. Attempts to isolate and characterize cationic compounds from reaction of **3** and $[Ph_3C][B(C_6F_5)_4]$ failed, due to coordination unsaturation of possible cationic species. Instead, reaction of complex **3** and $[PhMe_2NH][B(C_6F_5)_4]$ was conducted, which generated *N*,*N*-dimethyl aniline as one coordinating ligand to stabilize the zirconium center. The ^{1}H NMR spectrum shows clearly the disappearance of one benzyl group, and the presence of *N*,*N*-dimethyl aniline (Figure 2), proving the formation of cationic complex **3a** (Scheme 3). The ^{19}F NMR spectrum shows identical signals as those of $[PhMe_2NH][B(C_6F_5)_4]$, suggesting that there is no interaction between the cation and anion (Supporting Information).

The structure of ion-pair complex **3a** was also characterized by single-crystal X-ray diffraction analysis (Figure 3).

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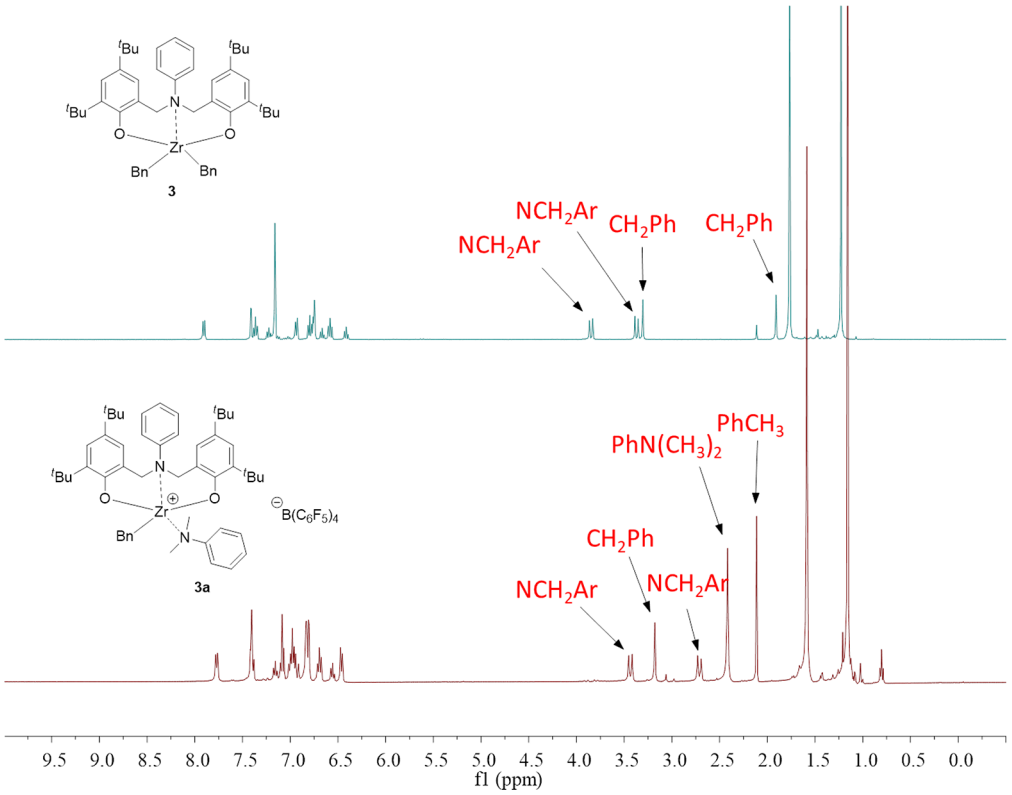
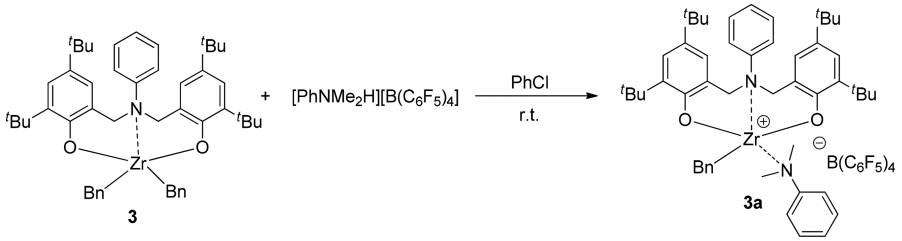


Figure 2. ^{1}H NMR spectra of complexes **3** and **3a**.

Scheme 3. Synthesis of Complex 3a



Comparing with neutral complex **3**, shorter Zr−O1 (1.971(2) vs 1.998(2) Å), Zr−O2 (1.978(6) vs 1.997(2) Å), and Zr−N1 (2.361(7) vs 2.512(3) Å) bonds are observed, while the Zr−C37 bond is found to be longer (2.284(7) vs 2.250(4) Å), due to the coordinating bulky *N*,*N*-dimethyl aniline.[13] This colorless crystalloid of **3a** also catalyzed the addition of 2,6-lutidine to styrene, which gave 77% yield in a 10:1 ratio of branched to linear products under conditions stated in Table 4. This result is comparable with that of complex **3** and TB (81% yield in 10:1 ratio, Table 4, entry 3), further corroborating that cationic species formed during the catalytic process.

Mechanistic Proposal. A mechanism is proposed for Zr-catalyzed addition of C(sp^2)−H bonds to alkenes (Scheme 4). Cationic zirconium alkyl species **A** was generated through reactions of neutral complexes with $[Ph_3C][B(C_6F_5)_4]$.[19] Coordination of pyridine to the zirconium center in **A** assisted C(sp^2)−H activation to give three-membered zirconacycles **B**.[8,20] Regioselectivity of this reaction is determined by substrate structures: migratory insertion of styrene into the Zr−C bond of **B** occurred in 1,2-mode, while insertion of aliphatic alkenes occurred in 2,1-mode.[9b] Hydrolysis of insertion products **C** or **D** with pyridine substrates gave linear (in the former) or branched (in the latter) products, as well as zirconacycles **B** for the next cycle.

The mechanism of Zr-catalyzed addition of a C(sp^3)−H bond follows a similar pathway (Scheme 5).[13] It is noteworthy that regioselectivity of addition of C(sp^3)−H bonds is both substrate- and ligand-controlled: reactions of aliphatic alkenes gave branched products regardless of catalyst structures; reactions of aromatic alkenes formed branched products when catalyzed by complexes of aryl-bridged ligands, while they formed linear products when catalyzed by complexes of alkyl-bridged ligands. As suggested by computational study (Scheme 6),[13] the ligand backbone influences the insertion of styrene into the Zr−C bond; i.e., 1,2-insertion is preferred in the case of the aniline bridged ligand, while 2,1-insertion is preferred in the case of the *n*-butyl amine bridged ligand.

The difference between C(sp^2)-H and C(sp^3)-H reactions may lie in the fact that the former has a lower barrier which does not differentiate the subtle differences between two types of ligands.

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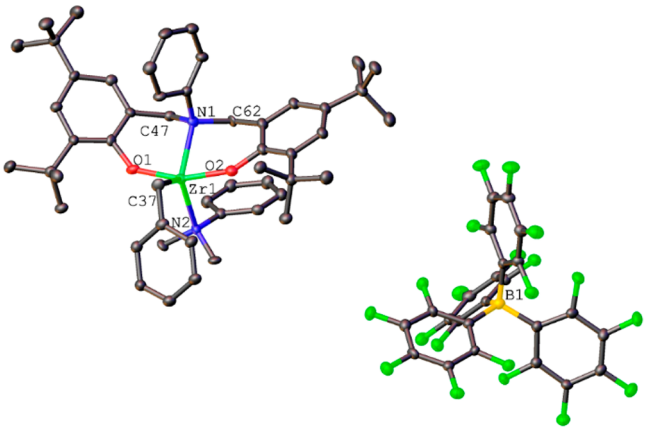


Figure 3. Molecular structure of **3a**·2C_6H_5Cl showing 30% probability ellipsoids; hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Zr1−O1 1.971(6), Zr1−O2 1.978(6), Zr1−N1 2.361(7), Zr1−N2 2.362(6), Zr1−C37 2.284(7); O1−Zr1−O2 159.9(2), O1−Zr1−C37 95.2(3), O2−Zr1−C37 94.2(3), O1−Zr1−N1 80.5(2), O2−Zr1−N1 79.5(2), C37−Zr1−N1 123.1(2), O1−Zr1−N2 95.9(2), O2−Zr1−N2 93.8(2), C37−Zr1−N2 122.7(3), N1−Zr1−N2 114.2(2).

CONCLUSION

In summary, we demonstrate that cationic zirconium complexes derived from zirconium dibenzyl complexes bearing a tridentate [ONO]-type amine-bridged bis(phenolato) ligand and $[Ph_3C][B(C_6F_5)_4]$ are active catalysts for *ortho*-selective addition of C(sp^2)−H bonds of pyridines to a variety of alkenes, which gave rise to alkylated pyridine derivatives in 100% atom-economy. This is the first example of group 4 metal-based catalysts capable of catalyzing *ortho*-selective C−H addition of pyridines in the absence of H_2. Meanwhile, these cationic zirconium complexes also catalyzed the *ortho*-selective addition of benzylic C−H bonds of various dialkylpyridines to alkenes. Regioselectivity of the addition of benzylic C(sp^3)−H bonds was significantly influenced by ligand backbones. For reactions of styrene derivatives, branched products formed as the majority in the presence of *N*-aryl amine-bridged bis(phenolato) Zr complexes, while linear addition products were preferred in the presence of *N*-alkyl amine-bridged bis(phenolato) Zr complexes. Development of group 4 metal-catalyzed C(sp^2/sp^3)−H functionalization reactions is ongoing in our laboratory.

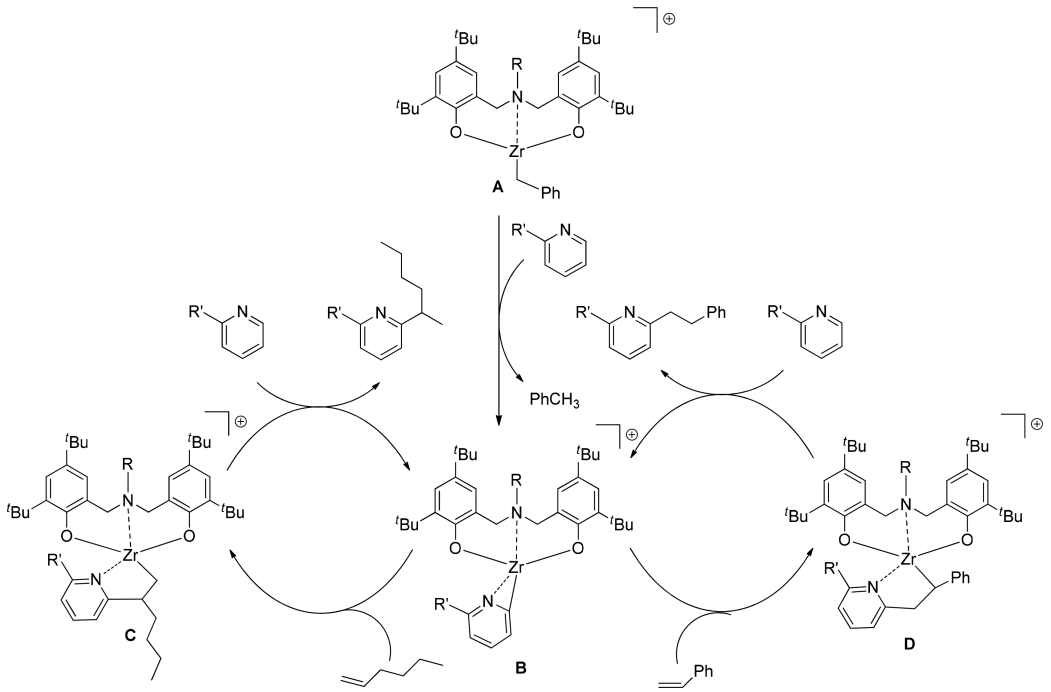
EXPERIMENTAL SECTION

General Considerations. All manipulations of air- and/or moisture-sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk or glovebox techniques. ^1H and ^{13}C NMR spectra were recorded on a Varian XL 400 MHz spectrometer. In a glovebox, a properly dried sample for elemental analysis was ground in a mortar, weighed into tin foil cups, and sealed in Schlenk tubes. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion with a Carlo-Erba EA-1110 instrument. X-ray crystallographic data were collected using a Bruker AXS D8 X-ray diffractometer. Toluene and hexane were freshly distilled by refluxing over sodium/benzophenone ketyl and distilled prior to use. C_6H_5Cl, C_6D_6, and C_6D_5Cl were degassed and distilled over CaH_2. $[Ph_3C][B(C_6F_5)_4]$ purchased from Strem Chemicals, Inc., was used without purification. $ZrBn_4$, ligand precursors $\mathbf{L^3H_2}$−$\mathbf{L^9H_2}$, and complexes **1**−**3** were prepared according to reported procedures.[13,15] Pyridines and olefins were distilled over CaH_2, flushed with argon, and stored over molecular sieves (4 Å).

General Procedure for Zirconium Complexes Synthesis. To a solution of $ZrBn_4$ (3 mmol) in toluene (10 mL) was added dropwise $\mathbf{L^nH_2}$ (3 mmol) in toluene (5 mL) at room temperature over 15 min. After stirring for 12 h at room temperature, toluene was removed under reduced pressure and the residue was washed with hexane (2 × 5 mL). Complexes **4**−**10** were obtained as colorless solids after recrystallization from toluene solution.

*$ZrBn_2L^4$ (**4**).* Complex **4** was isolated in 2.22 g (91% yield). ^1H NMR (400 MHz, C_6D_6): δ 7.87 (m, 2H, Ar), 7.42 (s, 2H, Ar), 7.36 (m, 2H, Ar), 7.22 (m, 1H, Ar), 6.91 (m, 2H, Ar), 6.79 (m, 2H, Ar), 6.72 (s, 2H, Ar), 6.66 (m, 1H, Ar), 6.60 (m, 2H, Ar), 6.20 (m, 2H,

Scheme 4. Possible Reaction Mechanism of Addition of C(sp^2)−H Bond to Alkenes



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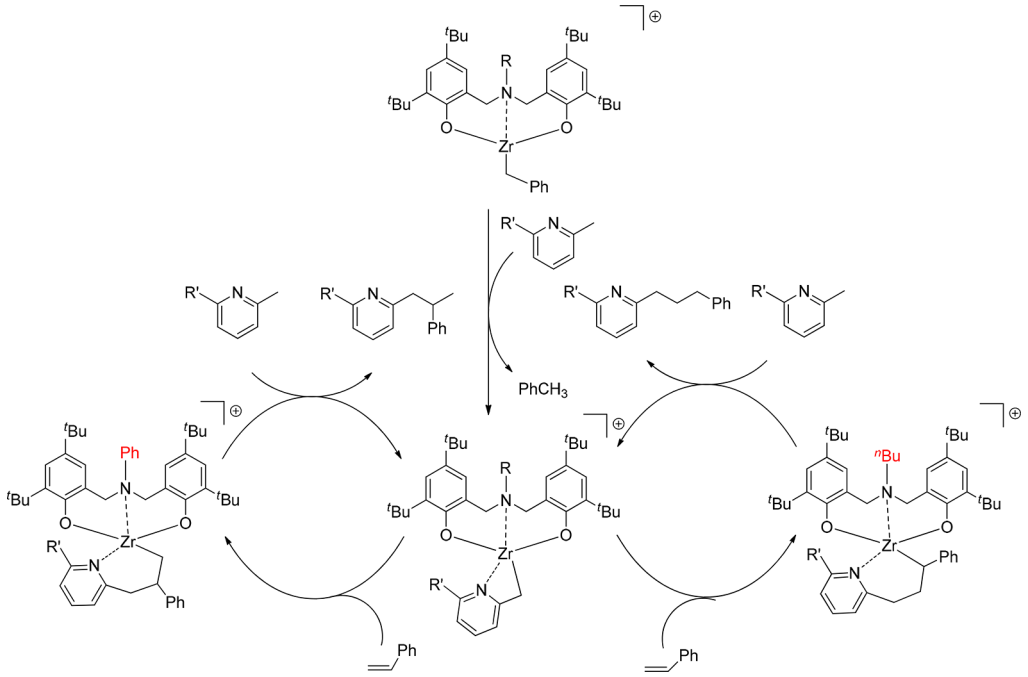
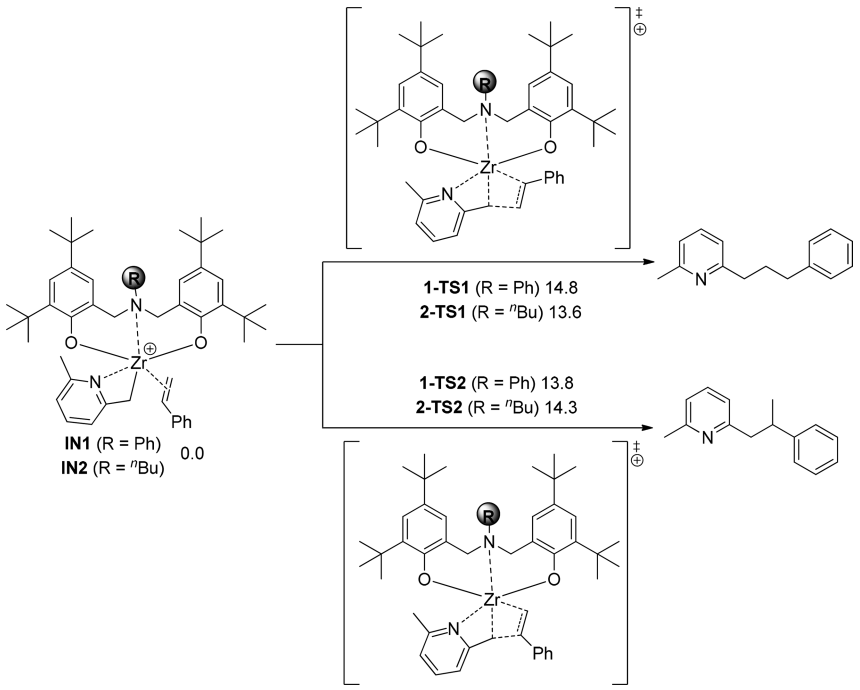
Scheme 5. Possible Reaction Mechanism of Addition of C(sp^3)−H Bonds to Styrene



Scheme 6. Computational Study on Regioselectivity[a]



[a]Relative free energies are in kcal/mol.

Ar), 3.81 (br d, J = 13.52 Hz, 2H, ArCH_2), 3.26 (br d, J = 13.68 Hz, 2H, ArCH_2), 3.23 (s, 2H, PhCH_2), 1.86 (s, 2H, PhCH_2), 1.76 (s, 18H, C(CH_3)$_3$), 1.22 (s, 18H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): 157.0, 149.3, 140.5, 135.1, 134.3, 130.7, 130.3, 127.9, 125.4, 124.4, 124.1, 123.9, 123.8, 123.4, 121.0, 115.1, 114.0 (Ar-C), 64.1 (ArCH_2N), 59.6 (PhCH_2), 34.5 (C(CH$_3$)$_3$), 33.4 (C(CH$_3$)$_3$), 30.9 (C(CH_3)$_3$), 29.5 (C(CH_3)$_3$). Anal. Calcd for $C_{50}H_{62}FNO_2Zr$: C, 80.95; H, 7.00; N, 1.22. Found: C, 81.01; H, 6.97; N, 1.23.

ZrBn$_2$L^5 ***(5)***. Complex **5** was isolated in 2.30 g (88% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 7.87−7.84 (m, 2H, Ar-*H*), 7.40−7.39 (m, 2H, Ar-*H*), 7.38−7.33 (m, 2H, Ar-*H*), 7.25−7.23 (m, 1H, Ar-*H*), 6.92−6.86 (m, 4H, Ar-*H*), 6.81−6.73 (m, 4H, Ar-*H*), 6.69−6.64 (m, 3H, Ar-*H*), 3.81 (br d, J = 18.04 Hz, 2H, ArCH_2), 3.26 (br d, J = 18.32 Hz, 2H, ArCH_2), 3.23 (s, 2H, PhCH_2), 1.85 (s, 2H, PhCH_2), 1.73 (s, 18H, C(CH_3)$_3$), 1.21 (s, 18H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): 157.5, 149.6, 146.9, 141.2, 135.8, 134.4, 131.2, 130.8, 128.5, 126.1, 125.6, 124.0, 124.3, 124.1, 123.5 (Ar-C), 64.4 (ArCH_2N), 60.1 (PhCH_2), 35.0 (C(CH$_3$)$_3$), 33.9 (C(CH$_3$)$_3$), 31.3 (C(CH$_3$)$_3$), 30.0 (C(CH_3)$_3$). Anal. Calcd for $C_{51}H_{62}F_3NO_2Zr$: C, 70.41; H, 7.10; N, 1.62. Found: C, 70.47; H, 7.19; N, 1.61.

ZrBn$_2$L^6 ***(6)***. Complex **6** was isolated in 2.41 g (90% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 7.83 (m, 2H, J = 7.44 Hz, Ar-*H*), 7.42 (s,

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2H, Ar-*H*), 7.32 (m, 2H, Ar-*H*), 7.22 (m, 1H, Ar-*H*), 7.16 (m, 1H, Ar-*H*), 6.84 (m, 6H, Ar-*H*), 6.65 (m, 1H, Ar-*H*), 4.07 (br d, *J* = 13.12 Hz, 2H, ArCH_2), 3.86 (br d, *J* = 13.28 Hz, 2H, ArCH_2), 3.48 (s, 2H, PhCH_2), 1.99 (s, 2H, PhCH_2), 1.76 (s, 18H, C(CH_3)$_3$), 1.14 (s, 18H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): 157.5, 150.4, 141.7, 138.7, 136.5, 130.6, 130.4, 128.4, 126.9, 125.5, 125.0, 124.3, 123.8, 121.2 (Ar-C), 65.5 (ArCH_2N), 64.9 (PhCH_2), 60.7 (PhCH_2), 35.1 (C(CH_3)$_3$), 33.8 (C(CH_3)$_3$), 31.2 (C(CH_3)$_3$), 29.8 (C(CH_3)$_3$). Anal. Calcd for $C_{50}H_{58}F_5NO_2Zr$: C, 67.36; H, 6.58; N, 1.55. Found: C, 67.38; H, 6.56; N, 1.57.

ZrBn$_2$L[7] ***(7)***. Complex **7** was isolated in 2.26 g (91% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 7.94 (m, 2H, Ar-*H*), 7.42 (s, 2H, Ar-*H*), 7.38 (m, 2H, Ar-*H*), 7.24 (m, 1H, Ar-*H*), 6.94 (m, 2H, Ar-*H*), 6.80 (m, 4H, Ar-*H*), 6.74 (m, 2H, Ar-*H*), 6.67 (m, 1H, Ar-*H*), 6.22 (m, 2H, Ar-*H*), 3.84 (br d, *J* = 13.60 Hz, 2H, ArCH_2), 3.37 (br d, *J* = 13.64 Hz, 2H, ArCH_2), 3.35 (s, 2H, PhCH_2), 2.65 (s, 3H, OCH_3), 1.92 (s, 2H, PhCH_2), 1.80 (s, 18H, C(CH_3)$_3$), 1.23 (s, 18H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): 158.0, 157.5, 149.8, 140.8, 135.4, 135.1, 131.2, 130.7, 129.0, 128.4, 128.2, 125.3, 125.0, 123.7, 123.4, 121.4, 113.9 (Ar-C), 64.7 (ArCH_2N), 60.0 (PhCH_2), 53.9 (OCH_3), 35.0 (C(CH_3)$_3$), 33.9 (C(CH_3)$_3$), 31.4 (C(CH_3)$_3$), 30.1 (C(CH_3)$_3$). Anal. Calcd for $C_{51}H_{65}NO_3Zr$: C, 63.66; H, 7.91; N, 1.66. Found: C, 63.69; H, 7.88; N, 1.68.

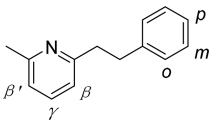
ZrBn$_2$L[8] ***(8)***. Complex **8** was isolated in 2.02 g (80% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 7.92 (m, 2H, Ar-*H*), 7.50 (m, 1H, Ar-*H*), 7.38 (m, 4H, Ar-*H*), 7.22 (m, 1H, Ar-*H*), 7.03 (m, 2H, Ar-*H*), 6.94 (m, 3H, Ar-*H*), 6.80 (m, 3H, Ar-*H*), 6.58 (m, 2H, Ar-*H*), 3.83 (br d, *J* = 18.00 Hz, 2H, ArCH_2), 3.38 (br d, *J* = 18.16 Hz, 2H, ArCH_2), 3.32 (s, 2H, PhCH_2), 3.18 (m, 1H, C*H*(CH_3)$_2$), 1.92 (s, 2H, PhCH_2), 1.76 (s, 18H, C(CH_3)$_3$), 1.24 (s, 18H, C(CH_3)$_3$), 0.65 (d, *J* = 9.24 Hz, 6H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): 157.6, 149.8, 147.6, 147.1, 140.8, 140.7, 135.4, 135.2, 131.1, 130.6, 129.0, 128.4, 128.2, 127.9, 126.6, 125.9, 125.7, 125.4, 125.3, 125.0, 124.9, 123.6, 122.4, 121.4 (Ar-C), 64.6 (ArCH_2N), 60.1 (PhCH_2), 37.8 (CH(CH_3)$_2$), 35.0 (C(CH_3)$_3$), 33.9 (C(CH_3)$_3$), 31.4 (C(CH_3)$_3$), 30.1 (C(CH_3)$_3$), 22.9 (CH(CH_3)$_2$). Anal. Calcd for $C_{53}H_{69}NO_2Zr$: C, 75.44; H, 8.27; N, 1.66. Found: C, 75.48; H, 8.25; N, 1.66.

ZrBn$_2$L[9] ***(9)***. Complex **9** was isolated in 3.11 g (91% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 7.37 (s, 2H, Ar), 7.17−7.10 (m, 18H, Ar), 7.05−6.97 (m, 12H, Ar), 6.92−6.86 (m, 3H, Ar), 6.83−6.79 (m, 2H, Ar), 6.70−6.68 (m, 2H, Ar), 6.64−6.60 (m, 1H, Ar), 6.49 (s, 2H, Ar), 6.23 (m, 2H, Ar), 3.66 (br d, *J* = 13.36 Hz, 2H, ArCH_2), 2.95 (br d, *J* = 13.60 Hz, 2H, ArCH_2), 2.11 (s, 3H, PhCH_3), 2.08 (s, 6H, C(CH_3)$_2$Ph), 1.57 (s, 6H, C(CH_3)$_2$Ph), 1.54 (s, 6H, C(CH_3)$_2$Ph), 1.51 (s, 6H, C(CH_3)$_2$Ph), 1.28 (s, 2H, PhCH_2), 0.84 (s, 2H, PhCH_2). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): 156.9, 150.9, 150.8, 149.8, 143.0, 139.6, 137.0, 134.8, 133.2, 131.1, 129.9, 128.5, 127.8, 127.7, 127.6, 127.4, 127.2, 127.0, 126.8, 126.3, 125.5, 125.4, 125.2, 124.9, 124.7, 124.5, 123.2, 120.4 (Ar-C), 64.0 (ArCH_2N) 62.4, 60.8, 57.5 (ArCH_2), 42.1 (PhCH_3), 41.9 (C(CH_3)$_2$Ph), 33.0 (C(CH_3)$_2$Ph), 31.1 (C(CH_3)$_2$Ph), 30.6 (C(CH_3)$_2$Ph), 30.1 (C(CH_3)$_2$Ph), 27.2, 20.6 (PhCH_2). Anal. Calcd for $C_{77}H_{77}NO_2Zr$: C, 80.90; H, 7.00; N, 1.22. Found: C, 81.01; H, 6.97; N, 1.23.

Synthesis of Cationic Zirconium Complex 3a. To a solution of complex **3** (0.160 g, 0.2 mmol) in PhCl (2 mL) was added dropwise [PhNMe$_2$H][B(C_6F_5)$_4$] (0.160 g, 0.2 mmol) in PhCl (2 mL) at room temperature over 15 min. After stirring for 15 min at room temperature, PhCl was removed under reduced pressure and the residue was washed with hexane (2 × 5 mL). Complexes **3a** were obtained as colorless solids after recrystallization from chlorobenzene and hexane solution.

Complex **3a** was isolated in 0.287 g (95% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 7.77 (m, 2H, Ar-*H*); 7.40 (m, 4H, Ar-*H*); 7.08 (m, 2H, Ar-*H*); 6.81 (m, 6H, Ar-*H*); 6.69 (m, 2H, Ar-*H*); 6.55 (m, 1H, Ar-*H*); 6.46 (m, 2H, Ar-*H*); 3.43 (d, *J* = 14.40 Hz, 2H, ArCH_2); 3.18 (s, 2H, PhCH_2); 2.71 (d, *J* = 14.32 Hz, 2H, ArCH_2); 2.62 (m, 2H, PhCH_2); 2.41 (s, 6H, N(CH_3)$_2$); 1.58 (s, 18H, C(CH_3)$_3$); 1.16 (s, 18H, C(CH_3)$_3$). ^{19}F{^{1}H} NMR (282 MHz, C_6D_6): δ −131.74 (d, *J* = 8.28 Hz), −162.5 (t, *J* = 17.72 Hz), −166.3 (t, *J* = 15.28 Hz). Anal. Calcd for $C_{75}H_{67}BF_{20}N_2O_2Zr$: C, 59.68; H, 4.39; N, 1.86. Found: C, 59.64; H, 4.47; N, 1.85.

General Procedure for Addition of *ortho*-C(sp^2)−H Bond of Pyridines to Various Olefins Catalyzed by 3 and [Ph$_3$C][B(C_6F_5)$_4$]. In a glovebox filled with nitrogen, a PhCl solution (1 mL) of [Ph_3C][B(C_6F_5)$_4$] (92 mg, 0.01 mmol) was added to a PhCl solution (2 mL) of **3** (80 mg, 0.01 mmol) under stirring. A color change from orange to colorless was observed immediately. After 5 min, alkene **10** (1 mmol) and pyridine derivative **11** (2 mmol) were added to the mixture successively. The resulting solution was stirred at 100 °C for the desired time. After the mixture was cooled to room temperature, the crude product obtained after removal of solvent was isolated by column chromatography (petroleum ether, silica gel, 0.5% NEt_3) as a viscous colorless oil and characterized by ^{1}H and ^{13}C NMR spectroscopy.



*6-Methyl-2-phenethyl-3,4-dihydropyridine (**12a**)*. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48−7.44 (m, 1H, γ-Py-*H*), 7.31−7.27 (m, 2H, *o*-Ar-*H*), 7.24−7.18 (m, 3H, *m*, *p*-Ar-*H*), 6.98 (d, 1H, *J* = 7.6 Hz, β-Py-*H*), 6.89 (d, 2H, *J* = 7. 64 Hz, β′-Py-*H*), 3.12−3.02 (m, 4H, CH_2), 2.58 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.7 (α-Py-C), 157.8 (α′-Py-C), 141.7 (CH_2Ar-C), 136.6 (γ-Py-C), 128.5 (*m*-Ar-C), 128.4 (*o*-Ar-C), 125.9 (*p*-Ar-C), 120.7 (β′-Py-C), 119.8 (β-Py-C), 40.3, 36.3 (CH_2), 24.6 (CH_3). HR MS (ESI+): Found 198.1288 [M + H]$^+$, calcd. for $C_{14}H_{16}N^+$: 198.1283.

*2-Methyl-6-(4-methylphenethyl)pyridine (**12b**)*. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45−7.42 (m, 1H, γ-Py-*H*), 7.11−7.06 (m, 4H, *o*,*m*-Ar-*H*), 6.95 (d, 1H, *J* = 7.6 Hz, β-Py-*H*), 6.88 (d, 2H, *J* = 7. 64 Hz, β′-Py-*H*), 3.06−3.95 (m, 4H, CH_2), 2.54 (s, 3H, CH_3), 2.30 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.8 (α-Py-C), 157.8 (α′-Py-C), 138.6 (CH_2Ar-C), 136.5 (γ-Py-C), 135.3 (*p*-Ar-C), 129.0 (*m*-Ar-C), 128.4 (*o*-Ar-C), 120.6 (β′-Py-C), 119.8 (β-Py-C), 40.4, 35.8 (CH_2), 24.6, 21.0 (CH_3). HR MS (ESI+): Found 212.1433 [M + H]$^+$, calcd. for $C_{15}H_{28}N^+$: 212.1439.

*2-(4-(tert-Butyl)phenethyl)-6-methylpyridine (**12c**)*. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47−7.43 (m, 1H, γ-Py-*H*), 7.32−7.30 (m, 2H, *o*-Ar-*H*), 7.19−7.17 (m, 2H, *m*-Ar-*H*), 6.96 (d, 1H, *J* = 7. 60 Hz, β-Py-*H*), 6.92 (d, 2H, *J* = 7. 64 Hz, β′-Py-*H*), 3.10−2.98 (m, 4H, CH_2), 2.56 (s, 3H, CH_3), 1.32 (s, 9H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.9 (α-Py-C), 157.8 (α′-Py-C), 149.7 (CH_2Ar-C), 138.7 (γ-Py-C), 136.6 (*p*-Ar-C), 128.2 (*m*-Ar-C), 125.2 (*o*-Ar-C), 120.6 (β′-Py-C), 119.8 (β-Py-C), 40.3, 35.8 (CH_2), 34.9 (CH_3). 31.5 (C(CH_3)$_3$), 24.6 (C(CH_3)$_3$). HR MS (ESI+): Found 254.1905 [M + H]$^+$, calcd. for $C_{18}H_{24}N^+$: 254.1909.

*2-(4-Methoxyphenethyl)-6-methylpyridine (**12d**)*. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44−7.41 (m, 1H, γ-Py-*H*), 7.10−7.08 (m, 2H, *o*-Ar-*H*), 6.95 (d, 1H, *J* = 7.6 Hz, β-Py-*H*), 6.85 (d, 2H, *J* = 7. 64 Hz, β′-Py-*H*), 6.80−6.78 (m, 2H, *m*-Ar-*H*), 3.76 (s, 3H, OCH_3), 3.03−2.90 (m, 4H, CH_2), 2.56 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.8 (α-Py-C), 157.8 (α′-Py-C, *p*-Ar-C), 136.5 (γ-Py-C), 133.8 (CH_2Ar-C), 129.4 (*o*-Ar-C), 120.6 (β′-Py-C), 119.8 (β-Py-C), 113.7 (*m*-Ar-C), 55.2 (OCH_3), 40.5, 35.4 (CH_2), 24.6 (CH_3). HR MS (ESI+): Found 228.1379 [M + H]$^+$, calcd. for $C_{15}H_{18}NO^+$: 228.1388.

*2-(4-Fluorophenethyl)-6-methylpyridine (**12e**)*. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44−7.40 (m, 1H, γ-Py-*H*), 7.13−7.09 (m, 2H, *o*-Ar-*H*), 6.96−6.90 (m, 3H, *m*-Ar-*H* and β-Py-*H*), 6.84 (d, 1H, *J* = 7.6 Hz, β′-Py-*H*), 3.04−2.96 (m, 4H, CH_2), 2.58 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.5 (*p*-Ar-C), 160.3 (α-Py-C), 160.1 (α-Py-C), 157.9 (α′-Py-C), 137.3 (CH_2Ar-C), 136.5 (γ-Py-C), 129.8 (*o*-Ar-C), 120.7 (β′-Py-C), 119.8 (β-Py-C), 115.1, 114.9 (*m*-Ar-C), 40.3, 36.5 (CH_2), 24.6 (CH_3). HR MS (ESI+): Found 216.1188 [M + H]$^+$, calcd. for $C_{14}H_{15}FN^+$: 216.1189.

*2-(4-Chlorophenethyl)-6-methylpyridine (**12f**)*. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45−7.41 (m, 1H, γ-Py-*H*), 7.21−7.19 (m, 2H, *o*-Ar-*H*), 6.10−6.08 (m, 2H, *m*-Ar-*H*), 6.96 (d, 1H, *J* = 7.6 Hz, β-Py-*H*), 6.83 (d, 1H, *J* = 7.6 Hz, β′-Py-*H*), 3.04−2.95 (m, 4H, CH_2), 2.53 (s,

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3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.2 (α-Py-*C*), 157.9 (α'-Py-*C*), 140.1(CH_2Ar-*C*), 136.6 (γ-Py-*C*), 131.6 (*p*-Ar-*C*), 129.9 (*o*-Ar-*C*), 128.4 (*m*-Ar-*C*), 120.8 (β'-Py-*C*), 119.8 (β-Py-*C*), 40.0, 35.5 (CH_2), 24.5 (CH_3). HR MS (ESI+): Found 232.0892 $[M + H]^+$, calcd. for $C_{14}H_{15}ClN^+$: 232.0893.

2-((1S,4R)-Bicyclo[2.2.1]heptan-2-yl)-6-methylpyridine (**12g**). ^1H NMR (400 MHz, $CDCl_3$): δ 7.44−7.40 (m, 1H, γ-Py-*H*), 6.95 (d, 1H, J = 7.6 Hz, β-Py-*H*), 6.88 (d, 1H, J = 7. Six Hz, β'-Py-*H*), 2.85−2.81 (m, 1H, C*H*), 2.49 (s, 3H, CH_3), 2.41 (s, 1H, C*H*), 2.33 (s, 1H, C*H*), 1.88−1.84 (m, 1H, C*H*), 1.74−1.69 (m, 1H, C*H*), 1.61−1.56 (m, 1H, C*H*), 1.41−1.38 (m, 1H, C*H*), 1.28−1.24 (m, 1H, C*H*), 1.15−1.12 (m, 1H, C*H*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 165.5 (α-Py-*C*), 157.4 (α'-Py-*C*), 136.2 (γ-Py-*C*), 120.0 (β-Py-*C*), 117.8 (β'-Py-*C*), 49.6, 42.8, 37.4, 36.9, 36.0, 30.4, 29.0 (alkyl-*C*), 24.7 (CH_3). HR MS (ESI+): Found 188.1439 $[M + H]^+$, calcd. for $C_{14}H_{18}N^+$: 188.1439.

2-Methyl-6-(octan-2-yl)pyridine (**12h**). ^1H NMR (400 MHz, $CDCl_3$): δ 7.43−7.39 (m, 1H, γ-Py-*H*), 6.88−6.86 (m, 2H, β,β'-Py-*H*), 2.84−2.75 (m, 1H, C*H*), 2.47 (s, 3H, CH_3), 1.71−1.62 (m, 1H, C*H*), 1.54−1.46 (m, 1H, C*H*), 1.27−1.10 (m, 11H, alkyl-*H*), 0.82−0.79 (m, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 166.4 (α-Py-*C*), 157.4 (α'-Py-*C*), 136.4 (γ-Py-*C*), 120.4 (β-Py-*C*), 117.6 (β'-Py-*C*), 42.2, 37.2, 31.8, 29.4, 27.6 (alkyl-*C*), 24.6 (CH_3), 22.6, 20.9, 14.0 (alkyl-*C*). HR MS (ESI+): Found 206.1910 $[M + H]^+$, calcd. for $C_{14}H_{24}N^+$: 206.1909.

2-(Hexan-2-yl)-6-methylpyridine (**12i**). ^1H NMR (400 MHz, $CDCl_3$): δ 7.41 (m, 1H, γ-Py-*H*), 6.86 (m, 2H, β,β'-Py-*H*), 2.83−2.74 (m, 1H, C*H*), 2.47 (s, 3H, CH_3), 1.71−1.62 (m, 1H, C*H*), 1.53−1.46 (m, 1H, C*H*), 1.27−1.19 (m, 6H, alkyl-*H*), 1.15−1.05 (m, 1H, C*H*), 0.82−0.78 (m, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 165.9 (α-Py-*C*), 156.9 (α'-Py-*C*), 135.9 (γ-Py-*C*), 119.9 (β-Py-*C*), 117.2 (β'-Py-*C*), 41.7, 36.4, 29.4 (alkyl-*C*), 24.1 (CH_3), 22.3, 20.4, 13.5 (alkyl-*C*). HR MS (ESI+): Found 178.1599 $[M + H]^+$, calcd. for $C_{12}H_{20}N^+$: 178.1596.

2-((3aR,4R,7R,7aR)-3a,4,5,6,7,7a-Hexahydro-1H-4,7-methanoinden-6-yl)-6-methylpyridine + 2-((3aS,4R,7R,7aS)-3a,4,5,6,7,7a-Hexahydro-1H-4,7-methanoinden-5-yl)-6-methylpyridine (**12j:12j′** *= 1:0.44*). ^1H NMR (400 MHz, $CDCl_3$): δ 7.41−7.37 (m, 1H, γ-Py-*H*), 6.92 (d, 1H, J = 7.6 Hz, β-Py-*H*), 6.85 (d, 2H, J = 7. 64 Hz, β'-Py-*H*), 5.73−5.67 (m, 1H, C*H*═C*H*), 5.66−5.58 (m, 1H, C*H*═C*H*), 3.17−3.04 (m, 1H, C*H*), 2.93−2.81 (m, 1H, C*H*), 2.55 (m, 3H, CH_3), 2.48 (s, 3H, CH_3), 2.41−2.36 (m, 1H, C*H*), 2.34−2.30 (m, 1H, C*H*), 2.26−2.21 (m, 2H, C*H*), 1.82−1.62 (m, 3H, C*H*), 1.40−1.36 (m, 1H, C*H*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 165.9 (α-Py-*C*), 165.7 (α-Py-*C*), 157.3 (α'-Py-*C*), 136.1 (γ-Py-*C*), 136.0 (γ-Py-*C*), 132.6 (CH═CH), 132.4 (CH═CH), 131.7 (CH═CH), 130.8 (CH═CH), 119.8 (β-Py-*C*), 119.8 (β-Py-*C*), 118.2 (β'-Py-*C*), 118.0 (β'-Py-*C*), 53.74, 52.55, 47.21, 45.56, 44.14, 42.79, 42.10, 41.35, 41.29, 40.21, 39.12, 38.83, 33.06, 32.56, 32.28, 29.04, 24.74. (alkyl-*C*). HR MS (ESI+): Found 226.1599 $[M + H]^+$, calcd. for $C_{16}H_{20}N^+$: 226.1596.

2-(Cyclohex-2-en-1-yl)-6-methylpyridine (**12k**). ^1H NMR (400 MHz, $CDCl_3$): δ 7.47 (m, 1H, γ-Py-*H*), 6.94 (m, 2H, β,β'-Py-*H*), 5.78−5.70 (m, 2H C*H*═C*H*), 2.97−2.89 (m, 1H, C*H*), 2.51 (s, 3H, CH_3), 2.35−2.07 (m, 4H, alkyl-*H*), 1.99−1.94 (m, 1H, C*H*), 1.82−1.72 (m, 1H, C*H*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 165.4 (α-Py-*C*), 157.4 (α'-Py-*C*), 136.6 (γ-Py-*C*), 126.9 (CH═CH), 126.5 (CH═CH), 120.6 (β-Py-*C*), 117.6 (β'-Py-*C*), 42.3 (CH_3), 31.7, 28.7 25.6, 24.6 (alkyl-*C*). HR MS (ESI+): Found 174.1280 $[M + H]^+$, calcd. for $C_{12}H_{16}N^+$: 174.1283.

2-Ethyl-6-(hexan-2-yl)pyridine (**13b**). ^1H NMR (400 MHz, $CDCl_3$): δ 7.48−7.44 (m, 1H, γ-Py-*H*), 6.92−6.89 (m, 2H, β,β'-Py-*H*), 2.86−2.73 (m, 3H, Alkyl-*H*), 1.74−1.65 (m, 1H, C*H*), 1.57−1.48 (m, 1H, C*H*), 1.27−1.22 (m, 9H, alkyl-*H*), 1.16−1.09 (m, 1H, C*H*), 0.88−0.80 (m, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 165.8 (α-Py-*C*), 162.2 (α'-Py-*C*), 135.9 (γ-Py-*C*), 118.4 (β-Py-*C*), 117.4 (β'-Py-*C*), 41.6, 36.4, 31.0 (alkyl-*C*), 29.3 (CH_2), 22.1 (CH_3), 20.4, 13.6, 13.5 (alkyl-*C*). HR MS (ESI+): Found 192.1750 $[M + H]^+$, calcd. for $C_{13}H_{22}N^+$: 192.1752.

2-(Hexan-2-yl)-6-isopropylpyridine (**13c**). ^1H NMR (400 MHz, $CDCl_3$): δ 7.49−7.45 (m, 1H, γ-Py-*H*), 6.94−6.88 (m, 2H, β,β'-Py-*H*), 3.05−2.96 (m, 1H, C*H*), 2.87−2.78 (m, 1H, C*H*), 1.78−1.67 (m, 1H, C*H*), 1.58−1.49 (m, 1H, C*H*), 1.31−1.23 (m, 12H, alkyl-*H*), 1.17−1.10 (m, 1H, C*H*), 0.85−0.82 (m, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 166.0 (α'-Py-*C*), 165.4 (α-Py-*C*), 135.8 (γ-Py-*C*), 117.6 (β'-Py-*C*), 116.6 (β-Py-*C*), 41.5, 36.4, 35.9 (alkyl-*C*), 29.3 (*C*H), 22.3 (CH_3), 22.2, 22.1, 20.4, 13.6 (alkyl-*C*). HR MS (ESI+): Found 206.1901 $[M + H]^+$, calcd. for $C_{14}H_{24}N^+$: 206.1909.

2-(Hexan-2-yl)-6-phenylpyridine (**13d**). ^1H NMR (400 MHz, $CDCl_3$): δ 8.07−8.05 (m, 2H, *o*-Ar-*H*), 7.66−7.62 (m, 1H, γ-Py-*H*), 7.54−7.53 (m, 1H, β-Py-*H*), 7.49−7.45 (m, 2H, *m*-Ar-*H*), 7.42−7.38 (m, 1H, *p*-Ar-*H*), 7.07−7.05 (m, 1H, β'-Py-*H*), 3.00−2.92 (m, 1H, C*H*), 1.89−1.80 (m, 1H, C*H*), 1.36−1.29 (m, 6H, alkyl-*H*), 1.26−1.18 (m, 1H, C*H*), 0.91−0.87 (m, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 166.1 (α'-Py-*C*), 155.9 (α-Py-*C*), 139.5 (γ-Py-*C*), 136.3 (Py-Ar-*C*), 128.2 (*m*,*p*-Ar-*C*), 126.5 (*o*-Ar-*C*), 119.3 (β'-Py-*C*), 117.1 (β-Py-*C*), 41.6, 36.4, 29.4 (alkyl-*C*), 22.4 (CH_3) 20.4, 13.6 (alkyl-*C*). HR MS (ESI+): Found 240.1755 $[M + H]^+$, calcd. for $C_{17}H_{22}N^+$: 240.1752.

2-(Hexan-2-yl)-5,6,7,8-tetrahydroquinoline (**13e**). ^1H NMR (400 MHz, $CDCl_3$): δ 7.26 (d, J = 7.8 Hz, 1H, γ-Py-*H*), 6.87 (d, J = 7.9 Hz, 1H, β-Py-*H*), 2.89 (m, 2H, CH_2), 2.86−2.76 (m, 1H, C*H*), 2.72 (m, 2H, CH_2), 1.93−1.84 (m, 2H, CH_2), 1.83−1.75 (m, 2H, CH_2), 1.69 (m, 1H, C*H*), 1.54 (m, 1H, C*H*), 1.35−1.22 (m, 6H, alkyl-*H*), 1.21−1.11 (m, 1H, C*H*), 0.90−0.80 (m, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 163.4 (α'-Py-*C*), 155.7 (α-Py-*C*), 136.6 (γ-Py-*C*), 128.6 (β-Py-*C*), 117.3 (β'-Py-*C*), 41.4, 36.5, 32.1, 29.4, 28.0, 22.8, 22.4, 20.5, 13.6 (alkyl-*C*). HR MS (ESI+): Found 218.1904 $[M + H]^+$, calcd. for $C_{15}H_{24}N^+$: 218.1909.

2-(Hexan-2-yl)-6,7-dihydro-5H-cyclopenta[b]pyridine (**13f**). ^1H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, J = 7.36 Hz, 1H, γ-Py-*H*), 6.83 (d, J = 7.8 Hz, 1H, β-Py-*H*), 3.07−2.91 (m, 2H, CH_2), 2.80 (m, 3H, alkyl-*H*), 2.16−1.95 (m, 2H, CH_2), 1.74−1.62 (m, 1H, C*H*), 1.58−1.43 (m, 1H, C*H*), 1.32−1.19 (m, 6H, alkyl-*H*), 1.19−1.01 (m, 1H, C*H*), 0.87−0.73 (m, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 164.4 (α'-Py-*C*), 164.3 (α-Py-*C*), 133.4 (γ-Py-*C*), 131.7 (β-Py-*C*), 117.7 (β'-Py-*C*), 41.4, 36.6, 33.9, 29.9, 29.45, 22.7, 22.3, 20.6, 13.6 (alkyl-*C*). HR MS (ESI+): Found 204.1757 $[M + H]^+$, calcd. for $C_{14}H_{22}N^+$: 204.1752.

2-(Hexan-2-yl)quinoline (**13g**). ^1H NMR (400 MHz, $CDCl_3$): δ 8.06−8.03 (m, 2H, 4,8-Ar-*H*), 7.75−7.73 (m, 1H, 5-Ar-*H*), 7.67−7.63 (m, 1H, 7-Ar-*H*), 7.46−7.43 (m, 1H, 6-Ar-*H*), 7.27 (d, J = 7.27 Hz, 1H, 3-Ar-*H*), 3.12−3.03 (m, 1H, C*H*), 1.84−1.76 (m, 1H, CH_2), 1.71−1.62 (m, 1H, C*H*), 1.58−1.43 (m, 1H, C*H*), 1.36−1.26 (m, 6H, alkyl-*H*), 1.20−1.12 (m, 1H, C*H*), 0.85−0.81 (m, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 166.8 (2-Ar-*C*), 147.3 (9-Ar-*C*), 135.8 (4-Ar-*C*), 128.7 (7-Ar-*C*), 128.6 (8-Ar-*C*), 127.0 (5-Ar-*C*), 126.5 (10-Ar-*C*), 125.1 (6-Ar-*C*), 119.1 (3-Ar-*C*), 42.5, 36.4, 29.5, 22.3, 20.4, 13.6 (alkyl-*C*). HR MS (ESI+): Found 214.1599 $[M + H]^+$, calcd. for $C_{15}H_{20}N^+$: 214.1596.

General Procedure for Benzylic C(sp^3)−H Addition of Pyridine Derivatives to Various Olefins Catalyzed by 3 and $[Ph_3C][B(C_6F_5)_4]$. In a glovebox filled with nitrogen, a PhCl solution (1 mL) of $[Ph_3C][B(C_6F_5)_4]$ (92 mg, 0.01 mmol) was added to a PhCl solution (2 mL) of **3** (80 mg, 0.01 mmol) under stirring. A color change from orange to colorless was observed immediately. After 5 min, **14** (1 mmol) and **11** (4 mmol) were added to the mixture successively. The resulting solution was stirred at 100 °C for the desired time. After the mixture was cooled to room temperature, the crude product obtained after removal of solvent was isolated by column chromatography (petroleum ether, silica gel, 0.5% NEt_3) as a viscous colorless oil and characterized by ^1H and ^{13}C NMR spectroscopy.

Successive C(sp^2)−H and C(sp^3)−H Addition of α-Picoline to Norbornene. In a glovebox filled with nitrogen, a PhCl solution (1 mL) of $[Ph_3C][B(C_6F_5)_4]$ (92 mg, 0.01 mmol) was added to a PhCl solution (2 mL) of **3** (80 mg, 0.01 mmol) under stirring. A color change from orange to colorless was observed immediately. After 5 min, α-picoline (**10a**) (1 mmol) and norbornene (**11g**) (2 mmol)

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were added to the mixture successively. The resulting solution was stirred at 100 °C for 12 h. After the mixture was cooled to room temperature, another portion of norbornene (4 mmol) was added. The resulting mixture was heated at 100 °C for another 12 h. The product **16** was isolated by column chromatography (petroleum ether, silica gel, 0.5% NEt_3) as a viscous colorless oil (276 mg, 0.98 mmol, 98%). Compound **16**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (t, 1H, J = 7.6 Hz, γ-Py-*H*), 6.95 (d, 1H, J = 7.6 Hz, β-Py-*H*), 6.86 (d, 1H, J = 7.6 Hz, β'-Py-*H*), 2.87−2.84 (m, 1H, C*H*), 2.74−2.68 (m, 1H, C*H*), 2.60−2.54 (m, 1H, C*H*), 2.42 (s, 1H, C*H*), 2.36 (s, 1H, C*H*), 2.22 (s, 1H, C*H*), 2.01−1.93 (m, 3H, C*H*), 1.74−1.66 (m, 2H, C*H*), 1.60−1.56 (m, 2H, C*H*), 1.48−1.36 (m, 5H, C*H*), 1.30−1.29 (m, 1H, C*H*), 1.20−1.09 (m, 5H, C*H*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 165.4 (α'-Py-*C*), 160.4 (α-Py-*C*), 135.7 (γ-Py-*C*), 119.8 (β'-Py-*C*), 118.2 (β'-Py-*C*), 49.6, 45.2, 43.0, 42.3, 40.8, 37.9, 37.3, 37.2, 36.9, 36.8, 36.0, 35.3, 30.4, 30.1, 29.1, 28.9 (alkyl-*C*).

X-ray Crystallographic Structure Determination. Suitable single crystals of complex **3a** were sealed in a thin-walled glass capillary for determination of the single-crystal structures. Intensity data were collected with a Rigaku Mercury CCD area detector in ω scan mode using Mo−Kα radiation (λ = 0.71070 Å). The diffracted intensities were corrected for Lorentz/polarization effects and empirical absorption corrections.

The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. The hydrogen atoms in these complexes were generated geometrically, assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All of the hydrogen atoms were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinement. The structures were solved and refined using SHELXL-97 programs.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b01959.

^{1}H and ^{13}C NMR spectra of complexes **3a**, **4**−**9** and addition products **12a**−**k**, **13b**−**g**, and **16** (PDF)

Accession Codes

CCDC 1855756 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Bull, J. A.; Mousseau, J. J.; Pelletier, G.; Charette, A. B. Synthesis of Pyridine and Dihydropyridine Derivatives by Regio- and Stereoselective Addition to N-Activated Pyridines. *Chem. Rev.* **2012**, *112*, 2642. (b) Hill, M. D. Recent Strategies for the Synthesis of Pyridine Derivatives. *Chem. - Eur. J.* **2010**, *16*, 12052. (c) Campeau, L.-C.; Fagnou, K. Applications of and Alternatives to π-Electron-Deficient Azine Organometallics in Metal Catalyzed Cross-Coupling Reactions. *Chem. Soc. Rev.* **2007**, *36*, 1058. (d) Schlosser, M.; Mongin, F. Pyridine Elaboration through Organometallic Intermediates: Regiochemical Control and Completeness. *Chem. Soc. Rev.* **2007**, *36*, 1161. (e) Bianchini, C.; Giambastiani, G.; Luconi, L.; Meli, A. Olefin Oligomerization, Homopolymerization and Copolymerization by Late Transition Metals Supported by (Imino)pyridine Ligands. *Coord. Chem. Rev.* **2010**, *254*, 431. (f) Michael, J. P. Quinoline, Quinazoline and Acridone Alkaloids. *Nat. Prod. Rep.* **2005**, *22*, 627. (h) Yamaguchi, J.; Muto, K.; Itami, K. Recent Progress in Nickel-Catalyzed Biaryl Coupling. *Eur. J. Org. Chem.* **2013**, *2013*, 19.

(2) (a) Waterman, R. σ-Bond Metathesis: A 30-Year Retrospective. *Organometallics* **2013**, *32*, 7249. (b) Tsurugi, H.; Yamamoto, K.; Nagae, H.; Kaneko, H.; Mashima, K. Direct Functionalization of Unactivated C−H bonds Catalyzed by Group 3−5 Metal Alkyl Complexes. *Dalton Trans.* **2014**, *43*, 2331. (c) Arnold, P. L.; McMullon, M. W.; Rieb, J.; Kuhn, F. E. C-H Bond Activation by f-Block Complexes. *Angew. Chem., Int. Ed.* **2015**, *54*, 82. (d) Nishiura, M.; Guo, F.; Hou, Z. Half-Sandwich Rare-Earth-Catalyzed Olefin Polymerization, Carbometalation, and Hydroarylation. *Acc. Chem. Res.* **2015**, *48*, 2209. (e) Engle, K. M.; Yu, J.-Q. Developing Ligands for Palladium(II)-Catalyzed C−H Functionalization: Intimate Dialogue between Ligand and Substrate. *J. Org. Chem.* **2013**, *78*, 8927. (f) Zhang, X.-S.; Chen, K.; Shi, Z.-J. Transition Metal-Catalyzed Direct Nucleophilic Addition of C−H Bonds to Carbon−Heteroatom Double Bonds. *Chem. Sci.* **2014**, *5*, 2146. (g) He, J.; Wasa, M.; Chan, K. S. L.; Shao, Q.; Yu, J.-Q. Palladium-Catalyzed Transformations of Alkyl C−H Bonds. *Chem. Rev.* **2017**, *117*, 8754.

(3) Rh-catalyzed catalyst: (a) Lewis, J. C.; Bergman, R. G.; Ellman, J. A. Rh(I)-Catalyzed Alkylation of Quinolines and Pyridines via C-H Bond Activation. *J. Am. Chem. Soc.* **2007**, *129*, 5332. (b) Yotphan, S.; Bergman, R. G.; Ellman, J. A. Synthesis of Multicyclic Pyridine and Quinoline Derivatives via Intramolecular C-H Bond Functionalization. *Org. Lett.* **2010**, *12*, 2978.

(4) Ni catalyst: (a) Nakao, Y.; Yamada, Y.; Kashihara, N.; Hiyama, T. Selective C-4 Alkylation of Pyridine by Nickel/Lewis Acid Catalysis. *J. Am. Chem. Soc.* **2010**, *132*, 13666. (b) Nakao, Y.; Kanyiva, K. S.; Hiyama, T. A Strategy for C-H Activation of Pyridines: Direct C-2 Selective Alkenylation of Pyridines by Nickel/Lewis Acid Catalysis. *J. Am. Chem. Soc.* **2008**, *130*, 2448. (c) Tsai, C.-C.; Shih, W.-C.; Fang, C.-H.; Li, C.-Y; Ong, T.-G.; Yap, G. P. A. Bimetallic Nickel Aluminun Mediated *Para*-Selective Alkenylation of Pyridine: Direct Observation of η^2, η^1-Pyridine Ni(0)-Al(III) Intermediates Prior to C-H Bond Activation. *J. Am. Chem. Soc.* **2010**, *132*, 11887.

(5) Co catalyst: (a) Yamamoto, S.; Saga, Y.; Andou, T.; Matsunaga, S.; Kanai, M. Cobalt-Catalyzed C-4 Selective Alkylation of Quinolines. *Adv. Synth. Catal.* **2014**, *356*, 401. (b) Andou, T.; Saga, Y.; Komai, H.; Matsunaga, S.; Kanai, M. Cobalt-Catalyzed C4-Selective Direct Alkylation of Pyridines. *Angew. Chem., Int. Ed.* **2013**, *52*, 3213.

(6) Cr catalyst: Li, Y.; Deng, G.; Zeng, X. Chromium-Catalyzed Regioselective Hydropyridination of Styrenes. *Organometallics* **2016**, *35*, 747.

(7) Ru catalyst: Grigg, R.; Savic, V. Transition Metal Catalysed Alkylation of Pyridines and Indoles. *Tetrahedron Lett.* **1997**, *38*, 5737.

(8) Zr catalysts: (a) Jordan, R. F.; Taylor, D. F. Zirconium-Catalyzed Coupling of Propene and α-Picoline. *J. Am. Chem. Soc.* **1989**, *111*, 778. (b) Rodewald, S.; Jordan, R. F. Stereoselective Olefin Insertion Reactions of Chiral (EBI)Zr(η^2-pyrid-2-yl)$^+$ and (EBTHI)Zr(η^2-pyrid-2-yl)$^+$ Complexes. *J. Am. Chem. Soc.* **1994**, *116*, 4491. (c) Bi, S.; Lin, Z.; Jordan, R. F. Theoretical Investigation of C-H/Olefin Coupling Catalyzed by Zirconium(IV) Complexes. *Organometallics* **2004**, *23*, 4882.

DOI: 10.1021/acs.inorgchem.8b01959
Inorg. Chem. XXXX, XXX, XXX−XXX

(9) RE catalyst: (a) Deelman, B.; Stevels, W. M.; Teuben, J. H.; Lakin, M. T.; Spek, A. L. Insertion Chemistry of Cp^*_2Y(2-pyridyl) and Molecular Structure of the Unexpected CO Insertion Product $(Cp^*_2Y)_2$ (μ-η^2: η^2 -$OC(NC_5H_4)_2$). *Organometallics* **1994**, *13*, 3881. (b) Guan, B.-T.; Hou, Z. Rare-Earth-Catalyzed C-H Bond Addition of Pyridines to Olefins. *J. Am. Chem. Soc.* **2011**, *133*, 18086. (c) Luo, G.; Luo, Y.; Qu, J.; Hou, Z. Mechanistic Investigation on Scandium-Catalyzed C−H Addition of Pyridines to Olefins. *Organometallics* **2012**, *31*, 3930. (d) Song, G.; O, W. W. N.; Hou, Z. Enantioselective C−H Bond Addition of Pyridines to Alkenes Catalyzed by Chiral Half-Sandwich Rare-Earth Complexes. *J. Am. Chem. Soc.* **2014**, *136*, 12209. (e) Song, G.; Wang, B.; Nishiura, M.; Hou, Z. Catalytic C-H Bond Addition of Pyridines to Allenes by a Rare-Earth Catalyst. *Chem. - Eur. J.* **2015**, *21*, 8394. (f) Mizumori, T.; Hata, T.; Urabe, H. Alkylation of Pyridines at Their 4-Positions with Styrenes plus Yttrium Reagent or Benzyl Grignard Reagents. *Chem. - Eur. J.* **2015**, *21*, 422. (g) Nagae, H.; Shibata, Y.; Tsurugi, H.; Mashima, K. Aminomethylation Reaction of *ortho*-Pyridyl C−H Bonds Catalyzed by Group 3 Metal Triamido Complexes. *J. Am. Chem. Soc.* **2015**, *137*, 640.

(10) (a) Duchateau, R.; van Wee, C. T.; Teuben, J. H. Insertion and C-H Bond Activation of Unsaturated Substrates by Bis(benzamidinato)yttrium Alkyl, $[PhC(NSiMe_3)_2]_2YR$ (R = CH_2Ph·THF, $CH(SiMe_3)_2$), and Hydrido, $\{[PhC(NSiMe_3)_2]_2Y(\mu\text{-}H)\}_2$, Compounds. *Organometallics* **1996**, *15*, 2291. (b) Duchateau, R.; Brussee, E. A. C.; Meetsma, A.; Teuben, J. H. Synthesis and Reactivity of Bis(alkoxysilylamido)yttrium η^2-Pyridyl and η^2-α-Picolyl Compounds. *Organometallics* **1997**, *16*, 5506. (c) Pahl, P.; Schwarzenböck, C.; Herz, F. A. D.; Soller, B. S.; Jandl, C.; Rieger, B. Core-First Synthesis of Three-Armed Star-Shaped Polymers by Rare Earth Metal-Mediated Group Transfer Polymerization. *Macromolecules* **2017**, *50*, 6569. (d) Zhu, X.; Li, Y.; Guo, D.; Wang, S.; Wei, Y.; Zhou, S. Versatile Reactivities of Rare-earth Metal Dialkyl Complexes Supported by a Neutral Pyrrolylfunctionalized β-Diketiminato Ligand. *Dalton Trans.* **2018**, *47*, 3947.

(11) (a) Guram, A. S.; Jordan, R. F.; Taylor, D. F. Insertion Chemistry of $Cp_2Zr(\eta^2$-C,N-CH_2{6-Me-pyrid-2-yl}$)^+$: Facile Zirconium-Mediated Functionalization of Methyl C-H Bonds of 2,6-Lutidine. *J. Am. Chem. Soc.* **1991**, *113*, 1833. (b) Jordan, R. F.; Guram, A. S. Scope and Regiochemistry of Ligand C-H Activation Reactions of $Cp_2Zr(CH_3)$ $(THF)^+$. *Organometallics* **1990**, *9*, 2116. (c) Guram, A. S.; Swenson, D. C.; Jordan, R. F. Synthesis and Characterization of $Cp_2Zr(CH\{Me\}\{6\text{-ethylpyrid-2-y1}\})(CO)^+$, a d^0 Metal Alkyl Carbonyl Complex. Coordination Chemistry of the Four-Membered Azazirconacycle $Cp_2Zr(\eta^2$-*C,N*-CH{Me}{6-ethylpyrid-2-y1}$)^+$. *J. Am. Chem. Soc.* **1992**, *114*, 8991.

(12) Guan, B.-T.; Wang, B.; Nishiura, M.; Hou, Z. Yttrium-Catalyzed Addition of Benzylic C-H Bonds of Alkyl Pyridines to Olefins. *Angew. Chem., Int. Ed.* **2013**, *52*, 4418.

(13) Sun, Q.; Xie, P.; Yuan, D.; Xia, Y.; Yao, Y. Regioselective Addition of C(sp^3)-H Bonds of Alkyl Pyridines to Olefins Catalysed by Cationic Zirconium Complexes. *Chem. Commun.* **2017**, *53*, 7401.

(14) Carpentier, J.-F. Rare-Earth Complexes Supported by Tripodal Tetradentate Bis(phenolate) Ligands: A Privileged Class of Catalysts for Ring-Opening Polymerization of Cyclic Esters. *Organometallics* **2015**, *34*, 4175.

(15) Tshuva, E. Y.; Goldberg, I.; Kol, M.; Goldschmidt, Z. Zirconium Complexes of Amine-Bis(phenolate) Ligands as Catalysts for 1-Hexene Polymerization: Peripheral Structural Parameters Strongly Affect Reactivity. *Organometallics* **2001**, *20*, 3017.

(16) (a) Sun, Q.; Wang, Y.; Yuan, D.; Yao, Y.; Shen, Q. Synthesis of Group 4 Metal Complexes Stabilized by an Amine-Bridged Bis(phenolato) Ligand and Their Catalytic Behavior in Intermolecular Hydroamination Reactions. *Organometallics* **2014**, *33*, 994. (b) Sun, Q.; Wang, Y.; Yuan, D.; Yao, Y.; Shen, Q. Zirconium Catalysed Intermolecular Hydroamination Reactions of Secondary Amines with Alkynes. *Chem. Commun.* **2015**, *51*, 7633. (c) Sun, Q.; Wang, Y.; Yuan, D.; Yao, Y.; Shen, Q. Zirconium Complexes Stabilized by Amine-bridged Bis(phenolato) Ligands as Precatalysts for Intermolecular Hydroamination Reactions. *Dalton Trans.* **2015**, *44*, 20352. (d) Zhang, Y.; Sun, Q.; Wang, Y.; Yuan, D.; Yao, Y.; Shen, Q. Intramolecular Hydroamination Reactions Catalyzed by Zirconium Complexes Bearing Bridged Bis(phenolato) Ligands. *RSC Adv.* **2016**, *6*, 10541.

(17) (a) Lim, Y.; Kim, Y. H.; Kang, J. Rhodium-catalysed regioselective alkylation of the phenyl ring of 2-phenylpyridines with olefins. *J. Chem. Soc., Chem. Commun.* **1994**, 2267. (b) Hull, K. L.; Anani, W. Q.; Sanford, M. S. Palladium-Catalyzed Fluorination of Carbon−Hydrogen Bonds. *J. Am. Chem. Soc.* **2006**, *128*, 7134. (c) Tsai, A. S.; Tauchert, M. E.; Bergman, R. G.; Ellman, J. A. Rhodium(III)-Catalyzed Arylation of Boc-Imines via C−H Bond Functionalization. *J. Am. Chem. Soc.* **2011**, *133*, 1248. (d) Thongpaen, J.; Schmid, T. E.; Toupet, L.; Dorcet, V.; Mauduit, M.; Baslé, O. Directed *ortho* C-H Borylation Catalyzed using Cp*Rh(III)-NHC Complexes. *Chem. Commun.* **2018**, *54*, 8202.

(18) Zhai, D.-D.; Zhang, X.-Y.; Liu, Y.-F.; Zheng, L.; Guan, B.-T. Potassium Amide-Catalyzed Benzylic C-H Bond Addition of Alkylpyridines to Styrenes. *Angew. Chem., Int. Ed.* **2018**, *57*, 1650.

(19) (a) Bochmann, M.; Lancaster, S. J. Base-free cationic zirconium benzyl complexes as highly active polymerization catalysts. *Organometallics* **1993**, *12*, 633. (b) Bochmann, M.; Lancaster, S. J.; Hursthouse, M. B.; Malik, K. M. A. Synthesis of Base-Free Cationic Zirconium Methyl and Benzyl Complexes. The Crystal and Molecular Structure of $\{C_5H_3(SiMe_3)_2\text{-}1,3\}_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$. *Organometallics* **1994**, *13*, 2235. (c) Carpentier, J.-F.; Martin, A.; Swenson, D. C.; Jordan, R. F. Synthesis, Stereochemistry, and Reactivity of Group 4 Metal Complexes That Contain a Chiral Tetradentate Diamine-Diamide Ligand. *Organometallics* **2003**, *22*, 4999. (d) Ackermann, L.; Bergman, R. G.; Loy, R. N. Use of Group 4 Bis(sulfonamido) Complexes in the Intramolecular Hydroamination of Alkynes and Allenes. *J. Am. Chem. Soc.* **2003**, *125*, 11956. (e) Knight, P. D.; Munslow, I.; O'Shaughnessy, P. N.; Scott, P. Zirconium Catalysed Enantioselective Hydroamination/Cyclisation. *Chem. Commun.* **2004**, 894. (f) Gribkov, D. V.; Hultzsch, K. C. Hydroamination/Cyclization of Aminoalkenes Using Cationic Zirconocene and Titanocene Catalysts. *Angew. Chem., Int. Ed.* **2004**, *43*, 5542. (g) Lavanant, L.; Silvestru, A.; Faucheux, A.; Toupet, L.; Jordan, R. F.; Carpentier, J.-F. Electron-Deficient Group 4 Metal Complexes of Sulfur-Bridged Dialkoxide Ligands: Synthesis, Structure, and Polymerization Activity Studies. *Organometallics* **2005**, *24*, 5604. (h) Beckerle, K.; Manivannan, R.; Spaniol, T. P.; Okuda, J. Living Isospecific Styrene Polymerization by Chiral Benzyl Titanium Complexes That Contain a Tetradentate [OSSO]-Type Bis(phenolato) Ligand. *Organometallics* **2006**, *25*, 3019. (i) Lian, B.; Beckerle, K.; Spaniol, T. P.; Okuda, J. Regioselective 1-Hexene Oligomerization Using Cationic Bis(phenolato) Group 4 Metal Catalysts: Switch from 1,2- to 2,1-Insertion. *Angew. Chem., Int. Ed.* **2007**, *46*, 8507. (j) Agapie, T.; Henling, L. M.; DiPasquale, A. G.; Rheingold, A. L.; Bercaw, J. E. Zirconium and Titanium Complexes Supported by Tridentate LX_2 Ligands Having Two Phenolates Linked to Furan, Thiophene, and Pyridine Donors: Precatalysts for Propylene Polymerization and Oligomerization. *Organometallics* **2008**, *27*, 6245. (k) Lee, H.; Nienkemper, K.; Jordan, R. F. Synthesis and Reactivity of a Sterically Crowded Tris(pyrazolyl)borate Hafnium Benzyl Complex. *Organometallics* **2008**, *27*, 5075. (l) Nienkemper, K.; Lee, H.; Jordan, R. F.; Ariafard, A.; Dang, L.; Lin, Z. Synthesis of Double-End-Capped Polyethylene by a Cationic Tris(pyrazolyl)borate Zirconium Benzyl Complex. *Organometallics* **2008**, *27*, 5867. (m) Chen, C.; Lee, H.; Jordan, R. F. Synthesis, Structures, and Ethylene Polymerization Behavior of Bis(pyrazolyl)borate Zirconium and Hafnium Benzyl Complexes. *Organometallics* **2010**, *29*, 5373. (n) Munha, R. F.; Antunes, M. A.; Alves, L. G.; Veiros, L. F.; Fryzuk, M. D.; Martins, A. M. Structure and Reactivity of Neutral and Cationic *trans-N,N'*-Dibenzylcyclam Zirconium Alkyl Complexes. *Organometallics* **2010**, *29*, 3753. (o) Manna, K.; Ellern, A.; Sadow, A. D. A Zwitterionic Zirconium Complex that Catalyzes Hydroamination of Aminoalkenes at Room Temperature. *Chem. Commun.* **2010**, *46*, 339. (p) Wang, X.; Chen, Z.; Sun, X.; Tang, Y.; Xie, Z. Intramolecular Hydroamination of

DOI: 10.1021/acs.inorgchem.8b01959
Inorg. Chem. XXXX, XXX, XXX−XXX

Aminoalkenes Catalyzed by a Cationic Zirconium Complex. *Org. Lett.* **2011**, *13*, 4758. (q) Mukherjee, A.; Nembenna, S.; Sen, T. K.; Sarish, S. P.; Ghorai, P. Kr.; Ott, H.; Stalke, D.; Mandal, S. K.; Roesky, H. W. Assembling Zirconium and Calcium Moieties through an Oxygen Center for an Intramolecular Hydroamination Reaction: A Single System for Double Activation. *Angew. Chem., Int. Ed.* **2011**, *50*, 3968. (r) Dagorne, S.; Bellemin-Laponnaz, S.; Romain, C. Neutral and Cationic N-Heterocyclic Carbene Zirconium and Hafnium Benzyl Complexes: Highly Regioselective Oligomerization of 1-Hexene with a Preference for Trimer Formation. *Organometallics* **2013**, *32*, 2736. (s) Luconi, L.; Rossin, A.; Tuci, G.; Germain, S.; Schulz, E.; Hannedouche, J.; Giambastiani, G. Intramolecular Hydroamination Reactions Catalyzed by Neutral and Cationic Group IV Pyridylamido Complexes. *ChemCatChem* **2013**, *5*, 1142.

(20) (a) Jantunen, K. C.; Scott, B. L.; Gordon, J. C.; Kiplinger, J. L. Reactivity of $(C_5Me_5)Lu(CH_2SiMe_3)_2(THF)$ with Pyridine Ring Systems: Synthesis and Structural Characterization of an η^2-(N,C)-Pyridyl (Mono)pentamethylcyclopentadienyl Lutetium(III) Complex. *Organometallics* **2007**, *26*, 2777. (b) Arndt, S.; Elvidge, B. R.; Zeimentz, P. M.; Spaniol, T. P.; Okuda, J. Formation of a Dicationic Yttrium η^2-Pyridyl Complex from an Yttrium Methyl Dication by C-H Activation of Pyridine. *Organometallics* **2006**, *25*, 793.

DOI: 10.1021/acs.inorgchem.8b01959
Inorg. Chem. XXXX, XXX, XXX−XXX