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C(sp^3)−H Alkenylation Catalyzed by Cationic Alkylhafnium Complexes: Stereoselective Synthesis of Trisubstituted Alkenes from 2,6-Dimethylpyridines and Internal Alkynes

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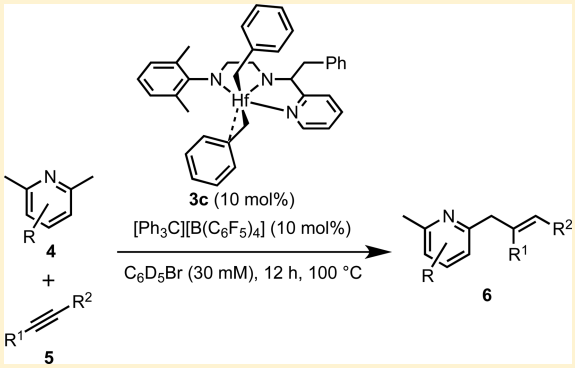
Supporting Information

ABSTRACT: Dibenzylhafnium complexes **3a−d**, supported by dianionic bidentate or tridentate ligands, upon activation via abstraction by either $[Ph_3C][B(C_6F_5)_4]$ or $B(C_6F_5)_3$ served as catalysts for the C(sp^3)−H alkenylation of 2,6-dimethylpyridines with dialkylalkynes to give corresponding C(sp^3)−H alkenylated products **6**. Complex **3c**, containing a pyridine arm in the ligand skeleton, exhibited the highest catalytic activity among **3a−d**; initial addition of 2,6-dimethylpyridine (**4a**) to the C_6D_5Br solution of **3c** followed by $[Ph_3C][B(C_6F_5)_4]$ and 3-hexyne (**5a**) produced trisubstituted alkene **6aa** in stereoselective manner in up to 50% yield without any byproducts, while the addition of **5a** prior to **4a** and $[Ph_3C][B(C_6F_5)_4]$ to the C_6D_5Br solution of **3c** generated **6aa**, together with the formation of byproduct (*E*)-(2-ethylpent-2-en-1-yl)benzene (**7**). When an asymmetrical pyridine, 3-bromo-2,6-dimethylpyridine, was used as the coupling partner, the corresponding trisubstituted alkene was obtained selectively. Catalytically active cationic benzylhafnium complexes **8a−d**, which were prepared by the reactions of **3a−d** and $B(C_6F_5)_3$, respectively, were characterized by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy. Kinetic studies of the catalytic reaction between **4a** and 4-octyne (**5b**) using **3c** and $[Ph_3C][B(C_6F_5)_4]$ in C_6D_5Br revealed that the catalytic reaction was zero-order for both **4a** and **5b**, indicating that the rate-determining step involved the C(sp^3)−H bond activation of **4a** by vinylhafnium intermediate **11c**.



INTRODUCTION

Functionalization of C−H bonds has recently attracted great interest in terms of its versatility as one of the most straightforward and atom-economical synthetic protocols to introduce various functional groups into the unreactive hydrocarbon skeletons, in sharp contrast to the standard strategies to use prefunctionalized organometallic reagents as well as halogenated and pseudohalogenated substrates, which inevitably form wasteful byproducts.[1] In the last two decades, various transition metal complexes, especially those of noble transition metals such as Ru, Rh, Pd, Ir, and Pt as well as base transition metals, were developed to efficiently catalyze direct C−H bond functionalization reactions.[2−14] Beyond the well-developed direct C(sp^2)−H bond functionalization of aromatic and vinylic compounds, a recent research target was devoted to achieving direct functionalization of C(sp^3)−H bonds under mild reaction conditions without any specific directing groups.[15,16]

Notably, it has been reported that early transition metal complexes such as metallocene and half-metallocene alkyl complexes of group 3 and 4 metals serve as stoichiometric reagents and catalysts for functionalizing not only C(sp^2)−H bonds but also C(sp^3)−H bonds of simple organic compounds.[17−21] The highly Lewis acidic early transition metal centers cleaved the C(sp^3)−H bonds of methane and a methyl group adjacent to *N*-heterocycles through a σ-bond metathesis pathway under neutral conditions, leading to the formation of new organometallic species. Further insertion of alkenes and alkynes into the newly generated metal−carbon bond afforded the C(sp^3)−H alkylated and alkenylated metallacyclic complexes, as initially demonstrated stoichiometrically by Jordan et al. for the reaction with 2,6-dimethylpyridine by a cationic methylzirconocene complex (Scheme 1a).[20b] In a seminal work for catalytic C(sp^3)−H bond functionalization, Tilley et al. reported the catalytic C(sp^3)−H alkylation of methane via C(sp^3)−H activation of methane and subsequent insertion of alkenes by Cp*$_2$ScMe (Scheme 1b).[20d,e] Recently, Hou and co-workers achieved catalytic C(sp^3)−H alkylation of *ortho*-methylated *N*-heterocycles via C(sp^3)−H bond activation of the methyl group and further insertion of alkenes by half-metallocene group 3 metal alkyl complexes (Scheme 1c).[20g,h] Although catalytic C(sp^3)−H alkenylation was recently achieved by late transition metal catalysts,[22] the related transformation of the C(sp^3)−H bond in early transition metal complexes has been considered difficult due to formation of the stable metallacycle, as shown in Scheme 1a.[20b,c] In a related report, our group has recently shown the catalytic

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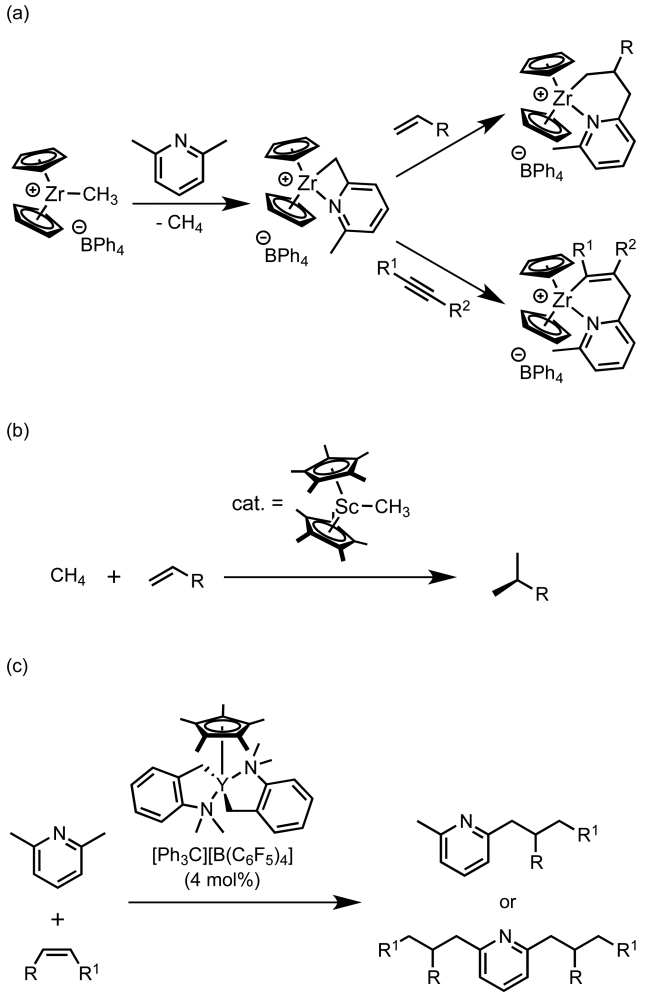
Scheme 1. C(sp^3)−H Bond Alkylation and Alkenylation by Group 3 and 4 Metal Alkyl Complexes[a]



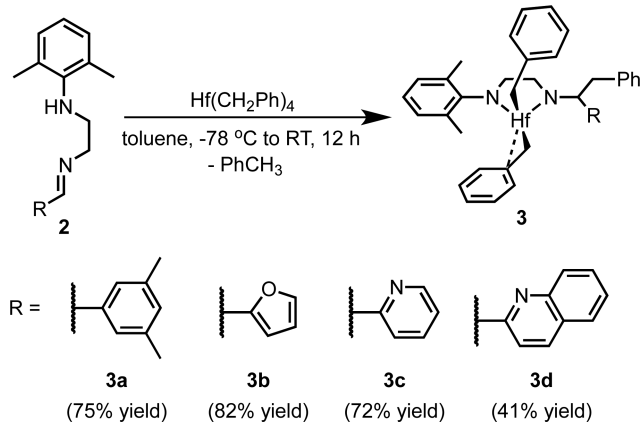
[a](a) Cationic zirconocene-mediated stoichiometric C(sp^3)−H alkylation and alkenylation.[20b] (b) Scandocene-catalyzed C(sp^3)−H alkylation of methane.[20d,e] (c) Half-metallocene yttrium-catalyzed C(sp^3)−H alkylation of *ortho*-methylated *N*-heterocycles.[20g,h]

formation of carbocycles by a cationic alkylhafnium complex, in which four-membered (pyridylmethyl)hafnium species was formed via C(sp^3)−H bond activation of 2,6-dimthylpyridine followed by insertion of 2 equiv of internal alkynes into the hafnium−carbon bond.[23] Herein, we report the first catalytic example of an early transition metal complex for C(sp^3)−H alkenylation of 2,6-dimethylpyridine via C(sp^3)−H bond activation of the methyl group by cationic alkylhafnium complexes, giving 1 to 1 coupling products of internal alkynes and 2,6-dimethylpyridine derivatives. Based on the characterization of the cationic intermediate together with reaction kinetics, the rate-determining step was assigned to be a C(sp^3)−H bond activation of 2,6-dimethylpyridine bound to the six-membered metallacycle complex in the catalytic cycle.

RESULTS AND DISCUSSION

Synthesis and Characterization of Dibenzylhafnium Complexes with Bidentate and Tridentate Diamido Ligands. Dibenzylhafnium complexes **3a−d** were synthesized by treating Hf(CH$_2$Ph)$_4$ with pro-ligands **2a−d**, which were prepared from 1-(2,6-dimethylphenyl)-2-aminoethane (**1**) and the corresponding aldehyde, in toluene at −78 °C, followed by allowing the reaction mixture to warm to room temperature to give the analytically pure complexes **3a−d** as red-orange microcrystalline solids upon recrystallization from a mixture of toluene and hexane (4:1) (Scheme 2). One benzyl group

Scheme 2. Preparation of Dibenzylhafnium Complexes 3a−d



3a (75% yield) **3b** (82% yield) **3c** (72% yield) **3d** (41% yield)

migrated from the hafnium center to the imine carbon of the pro-ligands, and the other benzyl group was protonated by the secondary amine moiety to eliminate toluene, resulting in the formation of the corresponding dianionic ligands. The benzyl group migration to the ligand backbone of imine-based ligands was one of the methodology to introduce the supporting ligand into the metal center.[23,24] Consequently, the dibenzylhafnium complexes **3a−d** were supported by the dianionic *N*,*N*-bidentate ligands.

Complexes **3a−d** were characterized by ^{1}H and ^{13}C NMR spectroscopies, elemental analyses, and X-ray crystallography studies (*vide infra*). Representative of the dibenzylhafnium series **3a−d**, the ^{1}H NMR spectrum of **3c** in C$_6$D$_6$ displayed nonequivalent benzyl groups as two AB*q* resonances at δ 1.14 and 1.94 (^2J = 11.4 Hz) and δ 1.41 and 1.61 (^2J = 10.3 Hz) due to the C_1 symmetry of **3c**. In addition, the ABX signals at δ 2.66, 2.77, and 4.42 (^2J = 13.7 Hz, ^3J = 5.6 and 3.0 Hz) corresponded to the methylene and methine protons in the NC*H*C*H*$_2$Ph fragment, and the ABXY signals at δ 3.59, 3.88, 4.02, and 4.25 (^2J = 11.0, 10.4 Hz, ^3J = 6.7, 6.4, 5.6, 4.7 Hz) were assigned as the methylene protons in the NC*H*$_2$C*H*$_2$N fragment. The ^{13}C NMR spectrum of **3c** in C$_6$D$_6$ showed the methylene carbon of one benzyl group at δ 66.4 ($^1J_{C-H}$ = 119 Hz) as an η^1 coordination and the other at δ 69.4 ($^1J_{C-H}$ = 129 Hz) as an η^2 coordination based on its J_{C-H} coupling constants. The characteristic of η^1 versus η^2 benzyl group coordination modes are commonly observed in coordinatively unsaturated metal complexes, in which higher $^1J_{C-H}$ coupling constants are ascribed to an increase in the sp^2 character of the benzyl carbon and thus typically assigned as η^2-coordination.[23−25] A similar trend occurred across the series of hafnium complexes **3a−d**, in which the methylene carbon of one benzyl group has a higher $^1J_{C-H}$ coupling constant ($^1J_{C-H}$ = 126−131 Hz) assigned to the η^2 coordination mode, while that of the second benzyl group with the lower coupling constant ($^1J_{C-H}$ = 117−121 Hz) is assigned as the η^1 coordination mode.

The molecular structures of all dibenzylhafnium complexes **3a−d** were clarified by X-ray analyses as shown in Figure 1, and their respective selected bond distances and angles are summarized in Table 1. The hafnium center in complex **3a**

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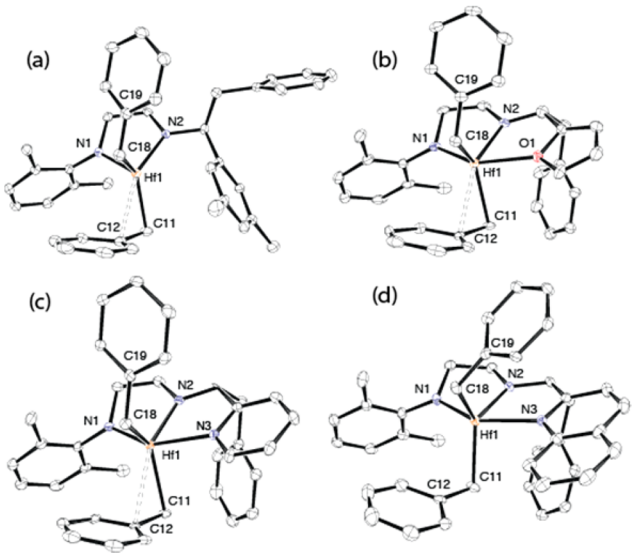

Figure 1. Molecular structures of neutral dibenzylhafnium complexes **3a–d**. Thermal ellipsoids are set to 30% probability level. Hydrogen atoms have been omitted for clarity.

adopts a distorted tetrahedral geometry, in which the small bite angle of the diamido ligand (81.83(17)°) induced coordinative unsaturation around the hafnium center, resulting in one benzyl group as the η^2 coordination based on the shorter Hf1–C12 distance (2.589(6) Å) and the acute Hf1–C11–C12 angle (84.3(4)°) and the other benzyl group as the η^1 coordination depicted by the longer Hf1–C19 distance (3.185(6) Å) and the obtuse Hf1–C18–C19 angle (113.6(3)°).[23,24d,e] Thus, the η^2 benzyl coordination persists in both solid-state and solution (*vide supra*). The Hf–N(amido) distances (2.013(5) and 2.022(4) Å) are slightly shorter than those (2.070(3)–2.867(12) Å) found in our previous hafnium complexes, consistent with a more electron-deficient hafnium center relative to the hafnium-amido complexes reported by us and Waele et al.[23,24d,e]

Complexes **3b–d** largely share bond distances and angles comparable to those of **3a**, albeit pentacoordinate due to the coordination of the extra heteroatom of the ligand. Thus, all complexes **3b–d** adopt a distorted trigonal bipyramidal geometry where the two benzyl groups (C11 and C18) and N2 occupy the equatorial positions, while the N1 and either O1 (complex **3b**) or N3 (complexes **3c–d**) define the axial positions. The hafnium-heteroatom distances in **3b** (Hf1–O1 = 2.372(5) Å) and in **3c** and **3d** (Hf1–N3 = 2.344(5) Å and 2.384(4) Å, respectively) are comparable to those reported for Hf–O and Hf–N(sp^2) distances.[23,24d,e] The other notable feature is that **3d** has two η^1-coordinated benzyl moieties (Hf1–C12 = 2.979(6) Å and Hf1–C19 = 3.153(5) Å) due to strong donation of the nitrogen atom of the quinoline moiety, values that are sufficiently elongated relative to **3a–c** thereby supporting an η^1 over η^2 coordination in the solid-state (Table 1).

Catalytic Coupling Reaction of 2,6-Dimethylpyridine and 3-Hexyne. In our initial trials, we used 2,6-dimethylpyridine (**4a**) as a substrate for C(sp^3)–H alkenylation with 3-hexyne (**5a**) using a 3:1 ratio of **4a**/**5a**. In a typical experiment, we added **4a** to a solution containing one of the complexes **3a–d** (10 mol %) in C_6D_5Br followed by sequentially adding $[Ph_3C][B(C_6F_5)_4]$ (10 mol %) and **5a** at room temperature; then, the reaction mixture was allowed to heat at 100 °C for 12 h (Table 2, entries 1–4). Gratifyingly, complex **3c** was found to serve as a precatalyst, exclusively giving C(sp^3)–H alkenylated product **6aa** as a single stereoisomer in 50% yield (46% isolated yield). The moderate yield of the product was due to the moderate conversion of 3-hexyne: We did not observe any other byproducts or insoluble materials in the reaction mixture. Notably, when we added **5a** first to the solution of **3c** in C_6D_5Br at room temperature followed by the addition of $[Ph_3C][B(C_6F_5)_4]$ (10 mol %) and **4a**, the yield of **6aa** was essentially the same, while (*E*)-(2-ethylpent-2-en-1-yl)benzene (**7**) was obtained in equimolar amounts to the catalyst **3c** (entry 5), indicating that the insertion of 3-hexyne into the benzyl-hafnium bond proceeded before the C(sp^3)–H activation of **4a**. We thus fixed the addition order of **4a** first, then $[Ph_3C][B(C_6F_5)_4]$ second before adding **5a** to the reaction mixture to avoid the formation of byproduct **7**. Next, we conducted the reaction using other catalyst precursors, **3a**,**b** and **3d**, under the same reaction conditions: The yields of **6aa** were very low in all cases. Accordingly, we selected **3c** as the best catalyst precursor, whose catalytic activity upon activation by $[Ph_3C][B(C_6F_5)_4]$ was attributed to the enhanced stability of the *N*,*N*,*N*-tridentate manifold. In addition, the sterically less-encumbered environment of the pyridyl moiety of **3c** compared to the quinolinyl group of **3d** allowed for the coordination of **4a** to release the product **6aa**. This is in contrast to our previous report using a bidentate diamido-supported cationic alkylhafnium complex; under similar reaction condition, the double insertion of alkyne was allowed following C–H activation of 2,6-dimethylpyridine, giving the 2-to-1 coupled product.[23] It was disfavored a second alkyne insertion for **3c** due to the sterically congested tridentate ligand system, thus forming the

Table 1. Selected Bond Distances (Å) and Angles (deg) in Complexes 3a–d

	3a	**3b** (X = O1)	**3c** (X = N3)	**3d** (X = N3)
Hf1–N1	2.013(5)	2.046(5)	2.063(5)	2.066(4)
Hf1–N2	2.022(4)	2.045(6)	2.047(5)	2.045(4)
Hf1–C11	2.280(7)	2.272(6)	2.287(5)	2.277(6)
Hf1–C12	2.589(6)	2.655(7)	2.702(6)	2.979(6)
Hf1–C19	3.185(6)	3.242(7)	3.261(6)	3.153(5)
Hf1–X	n.a.	2.372(5)	2.344(5)	2.384(4)
N1–Hf1–N2	81.83(17)	81.6(2)	79.06(18)	78.39(17)
C11–Hf1–C18	123.1(2)	117.2(2)	117.37(18)	120.3(2)
N2–Hf1–X	n.a.	69.54(17)	70.12(16)	71.26(16)
Hf1–C11–C12	84.3(4)	87.9(4)	88.8(3)	102.5(4)
Hf1–C18–C19	113.6(3)	116.6(4)	118.2(3)	111.4(3)

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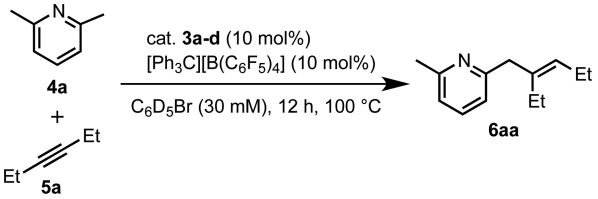
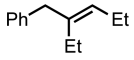
Table 2. Optimization of C(sp^3)−H Alkenylation of 2,6-Dimethylpyridine with 3-Hexyne Catalyzed by Hafnium Complexes 3a−d



entry	cat.	2,6-lutidine	3-hexyne	6aa[b]
1	3a	3	1	<10%
2	3b	3	1	14%
3	3c	3	1	50% (46%)[c]
4	3d	3	1	<10%
5[d,f]	3c	3	1	47%
6[e]	3c	3	1	14%
7[f]	3c	2	1	33%
8[f]	3c	1	1	32%
9[f]	3c	1	2	27%
10	3c	1	3	0%
11[g]	3c	3	1	42%

[a]Reaction conditions: hafnium complex (15 μmol) and **4a** was dissolved in C_6D_5Br, followed by $[Ph_3C][B(C_6F_5)_4]$ (15 μmol) and **5a**. [b]NMR yield reported using the phenanthrene as internal standard. [c]Isolated yield. [d]**5a** was added prior to **4a**. [e]Loading of calatyst and [Ph3C][$B(C_6F_5)_4$] was 5 mol %. [f]Alkene **7** was formed. [g]Used $B(C_6F_5)_3$ and increased reaction time to 27 h.



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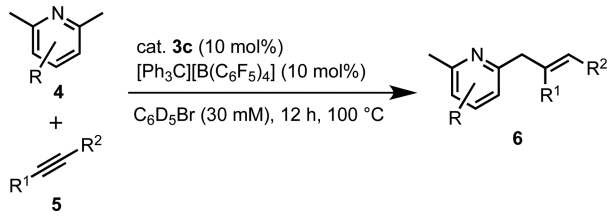
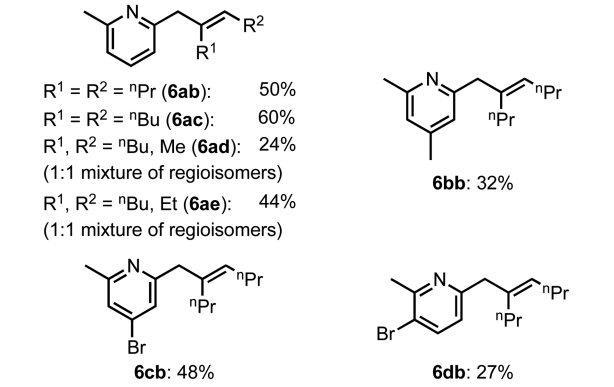
1-to-1 coupled product. Lowering the catalytic loading of **3c** down to 5 mol % resulted in a reduced yield (14%) of **6aa** (entry 6). The ratio of **4a** and **5a** was also sensitive to the yield: When the 3:1 ratio of **4a**/**5a** was changed to 2:1, 1:1, and 1:2, the yield of **6aa** was reduced to ∼30% yield along with the production of **7** (entries 7−9). Further decreasing the ratio of **4a** over **5a** (**4a**/**5a** = 1:3) completely suppressed the reaction (entry 10). Thus, we rationalized that the cationic species from **3c** first reacted with 3-hexyne under this reaction condition to give an alkenylhafnium species that possessed stronger affinity to 3-hexyne relative to 2,6-dimethylpyridine under the reaction condition. Upon activation with $B(C_6F_5)_3$, **6aa** was obtained in a yield comparable to that of the reaction using $[Ph_3C][B(C_6F_5)_4]$, albeit only after 27 h (entry 11), suggesting that benzylborate anion $[PhCH_2B(C_6F_5)_3]^-$ competed with the substrate to coordinate with the cationic hafnium center (*vide infra*). In this catalytic reaction, the maximum turnover number (TON) reached 5: The low TON was probably due to the product inhibition via coordination of **6aa** to the metal center.

With the optimized reaction conditions in hand, we screened substrates for the reactions between **4a** and dialkylalkynes (**5b**−**e**) together with other 2,6-dimethylpyridines (**4b**−**d**) (Table 3). When 4-octyne (**5b**, bp 131 °C) was used for the reaction with **4a**, the isolated yield of C(sp^3)−H alkenylated product **6ab** was 50%, while the reaction between **4a** and 5-decyne (**5c**, bp 177 °C) gave **6ac** in 60% yield. In both cases, single stereoisomers were obtained from the reaction mixture. Although unsymmetrical alkynes, such as 2-heptyne (**5d**) and 3-octyne (**5e**), were applicable to the C(sp^3)−H alkenylation reaction, trisubstituted alkenes **6ad** and **6ae** were obtained in 24

Table 3. Substrate Scope for C(sp^3)−H Alkenylation of 2,6-Dimethylpyridines with Both Internal Symmetric and Unsymmetric Dialkylalkynes Catalyzed by Hafnium Complex 3c[a]





[a] Isolated yield.

[a]Isolated yield.

and 44% yield as a mixture of regioisomers, respectively, suggesting that the small steric differences, *n*-butyl versus methyl for **5d** as well as ethyl groups for **5e**, were difficult to distinguish by this hafnium catalyst. We further examined the coupling reaction with trisubstituted pyridine derivatives: electron-rich pyridine, 2,4,6-trimethylpyridine (**4b**), was operative for the coupling reaction with 4-octyne (**5b**) to give the C(sp^3)−H alkenylated product **6bb** in 32% yield, while the coupling reaction of **5b** with electron-deficient pyridines such as 4-bromo-2,6-dimethylpyridine (**4c**) resulted in the formation of **6cb** in 48% yield. An unsymmetrical pyridine, 3-bromo-2,6-dimethylpyridine (**4d**), selectively formed the C-(sp^3)−H alkenylated product **6db** in 27% yield upon reacting with **5b**, where the sterically less-hindered methyl group was alkenylated.

Characterization and Reactions of Cationic Benzylhafnium Complexes. To gain additional insight into the reaction mechanism, we carried out benzyl abstraction reactions of **3a−c** with both of $[Ph_3C][B(C_6F_5)_4]$ and $B(C_6F_5)_3$. Reactions of **3a−c** with $B(C_6F_5)_3$ quantitatively generated thermally stable cationic hafnium species **8a−c** (Scheme 3), whereas treatment of **3a−c** with $[Ph_3C][B(C_6F_5)_4]$ resulted in decomposition. Due to difficulties isolating the highly reactive cationic species **8a−c**, *in situ* generated cationic species **8a−c** were characterized by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopies. The ^{1}H NMR spectrum of **8c**, as a representative of the cationic species **8a−c**, displayed only one set of AB*q* resonances for the benzyl protons at δ 1.85 and 2.16 (^2J = 11.7 Hz), indicating successful benzyl-abstraction by $B(C_6F_5)_3$. Signals for the methylene and methine protons in the NC*H*C*H*$_2$Ph fragment were observed at δ 2.78 (^3J = 3.4 Hz) and 4.49 as a broad doublet and broad singlet, respectively. It was noteworthy that four upfield-shifted signals due to the phenyl group of the benzylborate anion were detected at δ 5.30, 6.00, 6.14, and

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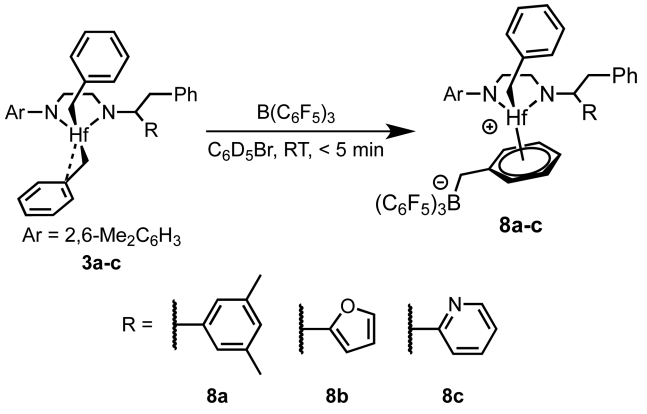
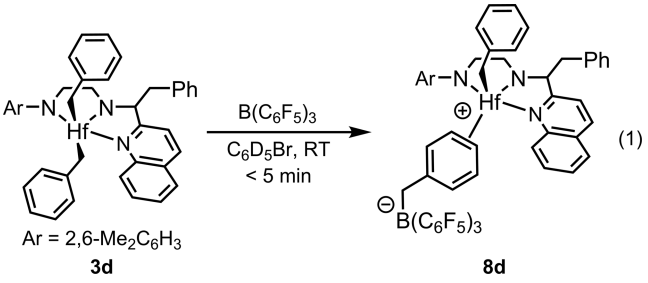
Scheme 3. Preparation of Cationic Monobenzylhafnium Complexes 8a−c



6.27, as typically observed for the η^6-coordinated benzylborate anion.[25] In the ^{13}C NMR spectrum, the methylene resonance of the benzylhafnium moiety was observed as a triplet at δ 61.6 ($^1J_{C-H}$ = 118 Hz), which was best represented as an η^1-coordination to the hafnium center. The difference between *meta*- and *para*-fluorine resonances in the ^{19}F NMR spectrum of **8c** ($\Delta\delta$(*m*-,*p*-F) = 3.7) also suggested η^6-benzylborate coordination through the abstracted benzyl group,[25] resulting in the η^1-fashion of the remaining benzylhafnium moiety. A similar coordination mode of the benzylhafnium moiety was observed for complexes **8a** (δ 62.2, $^1J_{C-H}$ = 118 Hz) and **8b** (δ 61.7, $^1J_{C-H}$ = 119 Hz), and in all cases, the signals for the phenyl protons of the benzylborate anion were shifted upfield.

Similar to the cationic hafnium species series **8a−c**, we generated the cationic hafnium species **8d** quantitatively through the benzyl abstraction reaction using $B(C_6F_5)_3$, since the reaction with $[Ph_3C][B(C_6F_5)_4]$ resulted in decomposition. Analogous to series **8a−c**, we characterized the *in situ* generated **8d** by ^1H, ^{13}C, and ^{19}F NMR spectroscopies. In sharp contrast, a triplet signal with a large coupling constant was observed at δ 62.3 ($^1J_{C-H}$ = 134 Hz) for the methylene carbon of the benzylhafnium moiety in **8d** in the ^{13}C NMR spectrum, which was typical for the η^2-fashion of the benzylhafnium moiety (eq 1).



Although the more sterically congested quinoline-tethered ligand attached to the hafnium in **8d**, the difference between the *meta*- and *para*-fluorine resonances in the ^{19}F NMR was 3.8 ppm, suggesting that the benzylborate anion interacted with the hafnium center, similar to the zwitterionic species **8a−c**. In the ^1H NMR spectrum at −20 °C in C_6D_5Br, an unusually upfield-shifted phenyl resonance was observed at δ 4.21 for the *para*-proton together with four other signals at δ 5.26 and 5.89 for the *meta*-protons and 5.41 and 7.28 for the *ortho*-protons. The upfield-shifted resonance for the *para*-position and the downfield-shifted signal for one *ortho*-position were consistent with those found for the η^2-coordination of the phenyl ring of the borate anion to cationic metal species: Horton et al. observed similar upfield- and downfield-shifted resonances for one phenyl group of the tetraphenylborate anion bound in an η^2-fashion to a cationic bis(indenyl)zirconium center, while Floriani et al. reported the structurally characterized cationic copper complex with an η^2-coordinated phenyl ring of the tetraphenylborate anion (Figure 2).[26]

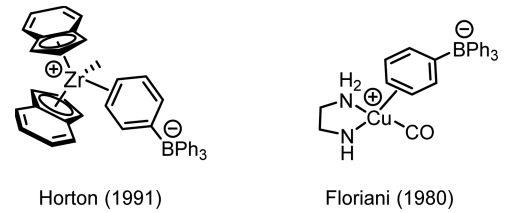
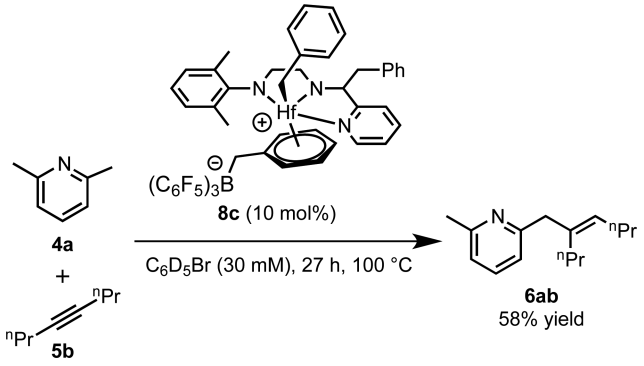


Figure 2. Examples of η^2-coordination of borate anion to the metal center.

We tested the catalytic activity of **8c** for the C(sp^3)−H alkenylation of 2,6-dimethylpyridine (**4a**) with 4-octyne (**5b**), as **3c** exhibited the best catalytic performance (Scheme 4).

Scheme 4. *In Situ* Generation of 8c Followed by Subsequent Addition of 2,6-Dimethylpyridine and 3-Hexyne



Addition of large excess amounts (30 equiv) of **4a** to the solution of **8c** in C_6D_5Br followed by the addition of 10 equiv of **5b** the reaction mixture and heating at 100 °C for 12 h led to the formation of target compound **6ab** in 58% yield (based on the amount of 4-octyne) without any byproducts, suggesting that the cationic benzylhafnium complex was an active species.

Reaction Kinetics. We monitored the progress of the reaction by ^1H NMR spectroscopy and calculated the thermodynamic parameters for the formation of the C(sp^3)−H alkenylated product **6**. According to the conditions used for the C(sp^3)−H alkenylation reaction of 2,6-dimethylpyridine (**4a**) with 4-octyne (**5b**) (Table 3, entry for **6ab**), we monitored the overall reaction rates at four different temperatures. The yield of **6ab** increased linearly in the temperature range of 353−368 K,[27] indicating that the reaction was zero-order for both substrates **4a** and **5b** under the condition of excess **4a** (3 equiv). In fact, even in the presence of 4.5 equiv of **4a**, the reaction rate was almost the same as that under the standard conditions (3 equiv of **4a**), in good accordance with C(sp^3)−H activation of **4a** being the rate-determining step.[28] Eyring analysis of the reaction rate provided a high free activation energy of 27.1 ± 1.2 kcal/mol (at 368 K) for the C(sp^3)−H activation step to release the product.[27] In the

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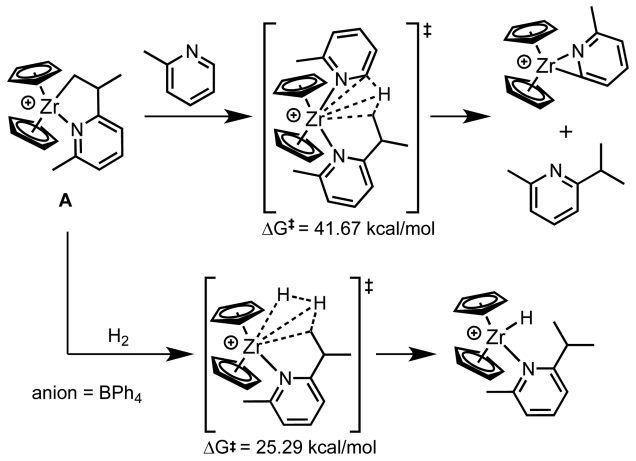
related system of a cationic zirconocene-catalyzed C(sp^2)−H alkylation, Jordan et al. reported density functional theory calculations for the C(sp^2)−H alkylation of 2-methylpyridine with propene: after the formation of a five-memberd chelating structure, $Cp_2Zr\{\eta^2$-C,N−CH_2CHMe-(2-Me-6-pyridyl)$\}^+$ (**A**), the activation free energy for the C(sp^2)−H activation of 2-picoline was 41.67 kcal/mol to release the C(sp^2)−H alkylated product (Scheme 5).[28] Because the barrier for this C(sp^2)−H

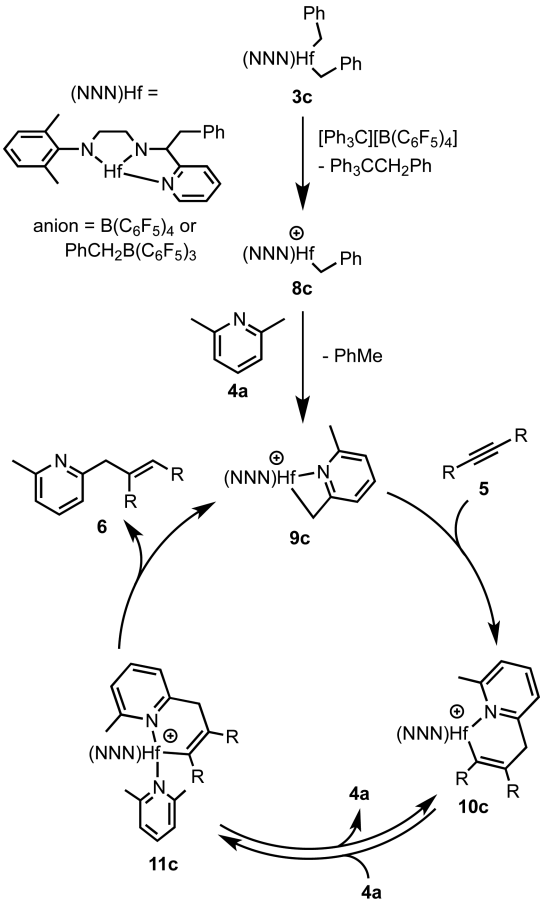
Scheme 5. Activation Energy for the Transformation of 5-Membered Metallacycle $Cp_2Zr\{\eta^2$-C,N−CH_2CHMe-(2-Me-6-pyridyl)$\}^+$ Reported by Jordan et al.[28a]



bond activation process was inaccessibly high, H_2 gas was necessary to afford the C(sp^2)−H alkylated product with a small activation free energy (25.29 kcal/mol). The activation energy for the C(sp^3)−H activation in our system was low enough to produce the C(sp^3)−H alkenylated compound without H_2 gas. In addition, the negative entropic value of −24.0 ± 1.7 e.u. suggests an ordered transition state of the C−H bond activation.

Proposed Reaction Mechanism. Scheme 6 describes a plausible reaction mechanism of the C(sp^3)−H alkenylation of **4a** with **5** catalyzed by **3c**. The activation step of **3c** is a benzyl abstraction to produce the cationic species **8c**, which directly activates the C(sp^3)−H bond of **4a** to form a four-membered metallacycle **9c**. Complex **9c** selectively allows insertion of only 1 equiv of internal alkyne **5** to give a six-membered metallacycle **10c** due to the steric congestion of the supporting ligand, which is in sharp contrast to the double insertion of internal alkynes into the four-membered metallacycle for the related hafnium complex having a *N*,*N*′-dialkylethylenediamido ligand.[23] In the next step, we hypothesize that further coordination of one equivalent of **4a** to the hafnium center produces six-coordinated species **11c**, which is in an equilibrium with the five-coordinated species **10c**. In the above-mentioned zirconocene-catalyzed C(sp^2)−H alkylation by Jordan et al., coordination of pyridine derivatives to the metallacycle intermediate before C(sp^2)−H bond activation is proposed for H_2-free system, based on the density functional theory calculation.[28a] Zero-order dependence for **4a** and **5b** in the kinetic study in the presence of excess **4a** suggests that the rate-determining step is a C(sp^3)−H activation of the precoordinated substrate **4a** along with the release of the trisubstituted alkene **6** in a stereoselective manner.

Scheme 6. Proposed Reaction Mechanism for the C(sp^3)−H Alkenylation of 2,6-Dimethylpyridine (4a) with Alkynes (5) Catalyzed by 3c/$[Ph_3C][B(C_6F_5)_4]$



CONCLUSIONS

We demonstrated the catalytic and stereoselective C(sp^3)−H alkenylation of 2,6-dimethylpyridine derivatives with internal dialkylalkynes by cationic hafnium complexes. After screening a series of four neutral dibenzyl hafnium complexes **3a**−**d** supported by nitrogen-based dianionic multidentate ligands in combination with $[Ph_3C][B(C_6F_5)_4]$, **3c** proved to be the only catalytically active hafnium complex. Addition of 2,6-dimethylpyridine to the reaction mixture prior to 3-hexyne led to selective formation of the C(sp^3)−H alkenylated product **6aa**. In contrast, when the reagent addition order of 2,6-dimethylpyridine and 3-hexyne was reversed, the C(sp^3)−H alkenylated product **6aa** was obtained together with byproduct **7**. Kinetic analysis of the reaction progress revealed zero-order dependence on both 2,6-dimethylpyridine and alkyne, suggesting that the C(sp^3)−H activation of precoordinated 2,6-dimethylpyridine accompanied by release of the product was the rate-determining step in the overall catalytic cycle.

By increasingly the steric congestion around the hafnium center relative to our previous report of hafnium-catalyzed carbocycle synthesis (tridentate versus bidentate ligand frameworks),[23] we can control the insertion of either 1 equiv of alkyne (tridentate ligand) or 2 equiv of alkyne (bidentate ligand). Furthermore, in our current system, selectivity of the reaction was high for the 1:1 coupling product due to the limited coordination environment around the metal center. We are currently working on the further applications of early

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transition metal alkyl complexes for C−H activation and coupling reactions by small modifications of the nitrogen-based supporting ligand system.

EXPERIMENTAL SECTION

General Remarks. All manipulations involving air- and moisture-sensitive organometallic compounds were carried out under argon using the standard Schlenk technique or argon-filled glovebox. $Hf(CH_2Ph)_4$ was prepared according to the literature.[29] 2,6-Dimethylpyridines and dialkylacetylenes were purchased and purified by distillation over CaH_2. $B(C_6F_5)_3$ and $[Ph_3C][B(C_6F_5)_4]$ were purchased and used as received. Hexane and toluene were dried and deoxygenated by distillation over sodium benzophenone ketyl under argon or by using Grubbs purification system. Chlorobenzene, benzene-d_6, and bromobenzene-d_5 were distilled from CaH_2 and thoroughly degassed by trap-to-trap distillation before use. ^1H NMR (400 MHz), ^{13}C NMR (100 MHz), and ^{19}F NMR (376 MHz) spectra were measured on BRUKER AVANCEIII-400 spectrometer. Assignments for ^1H and ^{13}C NMR peaks for some of the complexes were aided by 2D $^1H-^1H$ COSY, 2D $^1H-^{13}C$ HMQC, and 2D $^1H-^{13}C$ HMBC spectra. GC-MS measurement was carried out using a DB-1 capillary column (0.25 mm × 30 m) on a Shimadzu GCMS-QP2010Plus. All melting points were measured in sealed tubes under argon atmosphere. Mass spectra were recorded on a JEOL JMS-700 spectrometer. The elemental analyses were recorded by using PerkinElmer 2400 at the Faculty of Engineering Science, Osaka University.

Synthesis of ***1***. To a solution of bromoethylamine hydrobromide (2.66 g, 13.0 mmol, 1.0 equiv) in water (8.0 mL) was added 2,6-dimethylaniline (3.03 g, 25.0 mmol, 2.0 equiv). The reaction mixture was allowed to warm to 95 °C and vigorously stirred for 12 h. After cooling to room temperature, water (7 mL) was added, and the solution was washed (3 × 15 mL) with EtOAc. The aqueous phase was evaporated to dryness. The resulting solid was recrystallized from a MeOH/hexane mixture. The crystals were quenched using 10% aqueous KOH, extracted with CH_2Cl_2 (3 × 5 mL) and dried under vacuum giving a pale yellow oil in 45% yield. ^1H NMR (400 MHz, $CDCl_3$, 30 °C, δ) 2.32 (s, 6H, 2,6-$(CH_3)_2C_6H_3$), 2.91 (br t, ^3J = 5.6 Hz, 2H, $HNCH_2CH_2NH_2$), 3.03 (br t, ^3J = 5.6 Hz, 2H, $HNCH_2CH_2NH_2$), 6.81 (t, ^3J = 7.4 Hz, 1H, *p*-H of 2,6-$(CH_3)_2C_6H_3$), 6.90 (d, ^3J = 7.4 Hz, 2H, *m*-H of 2,6-$(CH_3)_2C_6H_3$). The three amine protons ($HNCH_2CH_2NH_2$) were not observed in the ^1H NMR spectrum due to the fast exchange. ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C, δ) 18.5 (2,6-$(CH_3)_2C_6H_3$), 42.5, ($NCH_2CH_2NH_2$), 50.9 ($NCH_2CH_2NH_2$), 121.7 (*p*-C of 2,6-$(CH_3)_2C_6H_3$), 128.8 (*m*-C of 2,6-$(CH_3)_2C_6H_3$), 129.4, 146.1. HRMS (EI) *m*/*z* calcd for $C_{10}H_{16}N_2$ 164.1313, found 164.1313.

Synthesis of ***2a***. 3,5-Dimethylbenzaldehyde (2.00 g, 12.2 mmol, 1 equiv) and 1-(2,6-dimethylphenyl)-2-aminoethane (**1**) (1.29 g, 12.2 mmol, 1 equiv) were sequentially added at room temperature to a stirred mixture of diethyl either (ca. 20 mL) and $MgSO_4$ (18.0 g, 149 mmol, 8 equiv). The reaction mixture was vigorously stirred overnight. The $MgSO_4$ was filtered, and the solvent was removed under reduced pressure to give amine-imine compound **2a** as an off-white oil in 65% yield. ^1H NMR (400 MHz, $CDCl_3$, 30 °C): δ 2.30 (s, 6H, 2,6-$(CH_3)_2C_6H_3$), 2.36 (s, 6H, 3,5-$(CH_3)_2C_6H_3$), 3.34 (t, ^3J = 5.7 Hz, 2H, $CH_2N{=}CH$), 3.76 (br t, ^3J = 5.7 Hz, 2H, $NHCH_2$), 6.83 (t, ^3J = 7.4 Hz, 1H, *p*-H of 2,6-$(CH_3)_2C_6H_3$), 6.98 (d, ^3J = 7.4 Hz, 2H, *m*-H of 2,6-$(CH_3)_2C_6H_3$), 7.08 (s, 1H, *p*-H of 3,5-$(CH_3)_2C_6H_3$), 7.37 (s, 2H, *o*-H of 3,5-$(CH_3)_2C_6H_3$), 8.24 (s, 1H, N=CH). The amine proton ($NHCH_2$) was not observed in the ^1H NMR spectrum due to the fast exchange. ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 18.8 (2,6-$(CH_3)_2C_6H_3$), 21.2 (3,5-$(CH_3)_2C_6H_3$), 49.4 (NC_2H_4N), 61.5 (NC_2H_4N), 122.0, 126.6, 129.3, 129.6, 137.0, 128.2, 146.7, 162.3 (N=CH). HRMS (EI) *m*/*z* calcd for $C_{19}H_{24}N_2$ 280.1939, found 280.1944. Amine-imine compounds **2b**−**d** was prepared using a similar procedure as **2a**.

2b. 82% yield, ^1H NMR (400 MHz, C_6D_6, 30 °C:) δ 2.24 (s, 6H, 2,6-$(CH_3)_2C_6H_3$), 3.15 (dd, ^3J = 6.0, 4.7 Hz, 2H, $CH_2N{=}CH$), 3.37 (br t, ^3J = 6.0 Hz, 2H, $NHCH_2$), 6.00 (dd, ^3J = 3.4 Hz, ^3J = 1.4 Hz, 1H, 4-franyl), 6.57 (d, ^3J = 3.4 Hz, 1H, 3-franyl), 6.84 (t, ^3J = 7.5 Hz, 1H, *p*-H of 2,6-$(CH_3)_2C_6H_3$), 6.98 (d, ^3J = 7.5 Hz, 2H, *m*-H of 2,6-$(CH_3)_2C_6H_3$), 7.02 (d, ^3J = 1.4 Hz, 1H, 5-franyl), 7.74 (s, 1H, N=CH). The amine proton ($NHCH_2$) was not observed in the ^1H NMR spectrum due to the fast exchange. ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 18.3 (2,6-$(CH_3)_2C_6H_3$), 48.8 (NC_2H_4N), 61.1 (NC_2H_4N), 111.3, 112.0, 121.6, 128.8, 129.2, 144.0, 146.2, 150.4, 152.5. HRMS (EI) *m*/*z* calcd for $C_{15}H_{18}N_2O$ 242.1419, found 242.1419.

2c. 85% yield, ^1H NMR (400 MHz, C_6D_6, 30 °C): δ 2.21 (s, 6H, 2,6-$(CH_3)_2C_6H_3$), 3.12 (t, ^3J = 5.5 Hz, 2H, $CH_2N{=}CH$), 3.44 (t, ^3J = 5.5 Hz, 2H, $NHCH_2$), 3.54 (br s, 1H, $NHCH_2$), 6.63 (br dd, ^3J = 6.3 Hz, 1H, 5-py), 6.87 (t, ^3J = 7.3 Hz, 1H, *p*-H of 2,6-$(CH_3)_2C_6H_3$), 6.97 (d, ^3J = 7.3 Hz, 2H, *m*-H of 2,6-$(CH_3)_2C_6H_3$), 7.07 (br dd, ^3J = 7.8 Hz, 1H, 4-py), 8.03 (dd, ^3J = 7.8 Hz, ^4J = 1.0 Hz, 1H, 3-py), 8.44 (s, 1H, N=CH), 8.46 (d, ^3J = 6.3 Hz, 1H, 6-py). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C): δ 18.7 (2,6-$(CH_3)_2C_6H_3$), 49.2 (NC_2H_4N), 61.2 (NC_2H_4N), 120.7 (3-py), 122.2 (*p*-C of 2,6-$(CH_3)_2C_6H_3$), 124.6 (5-py), 129.3, 129.6, 136.1, 146.6, 149.7, 155.5, 163.8 (N=CH). HRMS (EI) *m*/*z* calcd for $C_{16}H_{19}N_3$ 253.1579, found 253.1579.

2d. 85% yield, ^1H NMR (400 MHz, C_6D_6, 30 °C): δ 2.23 (s, 6H, 2,6-$(CH_3)_2C_6H_3$), 3.15 (t, ^3J = 5.6 Hz, 2H, $CH_2N{=}CH$), 3.49 (t, ^3J = 5.6 Hz, 2H, $NHCH_2$), 3.56 (br s, 1H, $NHCH_2$), 6.87 (t, ^3J = 7.4 Hz, 1H, *p*-H of 2,6-$(CH_3)_2C_6H_3$), 6.98 (d, ^3J = 7.4 Hz, 2H, *m*-H of 2,6-$(CH_3)_2C_6H_3$), 7.13−7.16 (m, 1H, quinolinyl), 7.32−7.37 (m, 2H, quinolinyl), 7.59 (d, ^3J = 8.5 Hz, 1H, 4-quinolinyl), 8.21 (d, ^3J = 8.5 Hz, 1H, 3-quinolinyl), 8.27 (d, ^3J = 8.3 Hz, 1H, 8-quinolinyl), 8.59 (s, 1H, N=CH). ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 18.3 (2,6-$(CH_3)_2C_6H_3$), 48.8 (NC_2H_4N), 60.9 (NC_2H_4N), 118.0, 121.8, 127.0, 128.6, 128.8, 129.2, 129.3, 130.0, 135.9, 146.2, 148.2, 155.0, 163.7 (N=CH). HRMS (EI) *m*/*z* calcd for $C_{20}H_{21}N_3$ 303.1735, found 303.1737.

*Synthesis and Characterization of Dibenzylhafnium Complex Series (**3a**).* To a solution of $Hf(CH_2Ph)_4$ (2.25 g, 4.15 mmol, 1 equiv) in toluene (20 mL), a solution of amine-imine pro-ligand **2a** (1.16 g, 4.15 mmol, 1 equiv) in toluene (20 mL) was added via a syringe at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. After removing all the volatiles under reduced pressure, the resulting residue was washed with hexanes (3 × 5 mL) to give **3a** as yellow powders in 75% yield, mp 82−83 °C (dec). The analytically pure complexes were crystallized from a toluene/hexanes (4:1) solution placed overnight at −20 °C. ^1H NMR (400 MHz, C_6D_6, 30 °C): δ 0.76 (d, ^2J = 10.1 Hz, 1H, Hf(CH*H*Ph)), 1.24 (d, ^2J = 11.5 Hz, 1H, Hf(C*H*HPh)), 1.47 (d, ^2J = 10.1 Hz, 1H, Hf(CH*H*Ph)), 1.78 (d, ^2J = 11.5 Hz, 1H, Hf(C*H*HPh)), 2.06 (s, 6H, 3,5-$(CH_3)_2C_6H_3$), 2.32 (s, 6H, 2,6-$(CH_3)_2C_6H_3$), 2.68 (dd, ^2J = 12.0 Hz, ^3J = 8.5 Hz, 1H, NCH(CH*H*Ph)Ar), 2.98 (dd, ^2J = 12.0 Hz, ^3J = 4.3 Hz, 1H, NCH(C*H*HPh)Ar), 3.34 (dd, ^3J = 8.5, 4.3 Hz, 1H, NC*H*(CH_2Ph)Ar), 3.77−3.83 (m, 1H, NCH_2CHHNH), 3.93−3.98 (m, 1H, NCH_2CHHNH), 4.10 (br ddd, ^2J = 10.8 Hz, ^3J = 6.2 Hz, 1H, $NCHHCH_2NH$), 4.27 (br dd, ^2J = 10.8 Hz, ^3J = 4.5 Hz, 1H, $NCHHCH_2NH$), 6.27 (d, ^3J = 7.1 Hz, 2H, Ar), 6.66 (s, 1H, Ar), 6.77 (t, ^3J = 7.6 Hz, 1H, Ar), 6.88−7.30 (17H, aromatic protons overlapped with a residual proton signal of C_6D_6). ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 19.4, 21.5, 41.4, 50.1, 54.3, 66.9 ($^1J_{C-H}$ = 118 Hz, Hf(CH_2Ph)), 71.1 ($^1J_{C-H}$ = 131 Hz, Hf(CH_2Ph)), 71.3, 121.7, 123.6, 124.0, 124.9, 126.1, 126.7, 127.2, 128.3, 128.7, 128.8, 130.8, 131.6, 134.6, 139.5, 141.1, 141.3, 143.3, 149.4, 152.3. Anal. Calcd for $C_{40}H_{44}HfN_2$: C, 65.70; H, 6.06; N, 3.83. Found: C, 65.26; H, 6.37; N, 3.87. Small deviation of found E.A. values is probably due to high sensitivity of **3a** to air. Dibenzylhafnium complexes **3b**−**d** was prepared using a similar procedure as **3a**.

3b. 82% yield, mp 79−81 °C (dec). ^1H NMR (400 MHz, C_6D_6, 30 °C): δ 1.07 (d, ^2J = 11.3 Hz, 1H, Hf(CH*H*Ph)), 1.33 (d, ^2J = 11.3 Hz, 1H, Hf(CH*H*Ph)), 1.68 (d, ^2J = 11.2 Hz, 1H, Hf(CH*H*Ph)), 1.79 (d, ^2J = 11.2 Hz, 1H, Hf(CH*H*Ph)), 2.40 (dd, ^2J = 13.3 Hz, ^3J = 6.2 Hz, 1H, NCH(C*H*HPh)Ar), 2.49 (s, 6H, 2,6-$(CH_3)_2C_6H_3$), 2.66 (dd, ^2J = 13.3 Hz, ^3J = 3.2 Hz, 1H, NCH(CH*H*Ph)Ar), 3.38 (dt, ^2J = 10.6 Hz, ^3J = 6.4 Hz, 1H, $NCHHCH_2NH$), 3.70 (dt, ^2J = 11.1 Hz, ^3J = 6.4 Hz, 2H, NCH_2CHHN), 3.83 (dt, ^2J = 10.6 Hz, ^3J = 5.6 Hz, 1H,

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NCH*H*CH$_2$N), 3.98 (dt, ^2J = 11.1 Hz, ^3J = 5.6 Hz, 1H NCH$_2$C*H*HN), 4.16 (dd, ^3J = 6.2, 3.2 Hz, 1H, NC*H*(CH$_2$Ph)Ar), 5.37 (d, ^3J = 3.2 Hz, 1H, 3-franyl), 5.78 (dd, ^3J = 3.2, 1.9 Hz, 1H, 4-franyl), 6.42 (d, ^3J = 7.6 Hz, 2H, Ar), 6.53 (d, ^3J = 7.6 Hz, 2H, Ar), 6.74 (br s, 1H, 5-franyl), 6.77−7.14 (14H, aromatic protons). ^{13}C NMR (100 MHz, C$_6$D$_6$, 30 °C): δ 40.2, 55.1, 55.2, 55.9, 66.0 ($^1J_{C-H}$ = 121 Hz, Hf(*C*H$_2$Ph)), 69.1 ($^1J_{C-H}$ = 127 Hz, Hf(*C*H$_2$Ph)), 120.6, 121.3, 121.5, 122.1, 120.0, 126.6, 127.9, 128.0, 128.1, 128.4, 128.6, 128.7, 129.3, 130.3, 137.1, 142.7, 146.1, 146.2, 148.1, 169.0. Anal. Calcd for C$_{36}$H$_{38}$HfN$_2$O: C, 62.38; H, 5.53; N, 4.04. Found: C, 61.94; H, 5.91; N, 4.11. Small deviation of found E.A. values is probably due to high sensitivity of **3b** to air.

3c. 72% yield, mp 67−68 °C (dec). ^{1}H NMR (400 MHz, C$_6$D$_6$, 30 °C, δ) 1.14 (d, ^2J = 11.4 Hz, 1H, Hf(CH*H*Ph)), 1.41 (d, ^2J = 10.3 Hz, 1H, Hf(CH*H*Ph)), 1.61 (d, ^2J = 10.3 Hz, 1H, Hf(C*H*HPh)), 1.94 (d, ^2J = 11.4 Hz, 1H, Hf(C*H*HPh)), 2.60 (s, 6H, 2,6-(C*H*$_3$)$_2$C$_6$H$_3$), 2.66 (dd, ^2J = 13.7 Hz, ^3J = 3.0 Hz, 1H, NCH(CH*H*Ph)Ar), 2.77 (dd, ^2J = 13.7 Hz, ^3J = 5.6 Hz, 1H, NCH(CH*H*Ph)Ar), 3.59 (ddd, ^2J = 10.4 Hz, ^3J = 6.4, 4.7 Hz, 1H, NCH*H*CH$_2$NH), 3.88 (ddd, ^2J = 11.0 Hz, ^3J = 6.7, 4.7 Hz, 1H, NCH$_2$CH*H*NH), 4.02 (ddd, ^2J = 10.4 Hz, ^3J = 6.7, 5.6 Hz, 1H, NCH$_2$CH*H*NH), 4.25 (ddd, ^2J = 11.0 Hz, ^3J = 6.4, 5.6 Hz, 1H, NCH*H*CH$_2$NH), 4.42 (dd, ^3J = 5.6, 3.0 Hz, 1H, NC*H*(CH$_2$Ph)-Ar), 6.20 (t, ^3J = 6.5 Hz, 1H, Ar), 6.34 (d, ^3J = 7.3 Hz, 2H, Ar), 6.38 (d, ^3J = 7.3 Hz, 2H, Ar), 6.51 (d, ^3J = 8.0 Hz, 1H, Ar), 6.60 (t, ^3J = 7.3 Hz, 1H, Ar), 6.77−7.08 (12H, aromatic protons), 7.21 (d, ^3J = 7.6 Hz, 2H, Ar), 7.57 (d, ^3J = 5.5 Hz, 1H, Ar). ^{13}C NMR (100 MHz, C$_6$D$_6$, 30 °C): δ 18.2, 38.5, 55.0, 55.1, 66.4 ($^1J_{C-H}$ = 119 Hz, Hf(*C*H$_2$Ph)), 69.4 ($^1J_{C-H}$ = 129 Hz, Hf(*C*H$_2$Ph)), 118.7, 120.1, 120.6, 120.7, 123.4, 124.2, 124.9, 125.1, 127.6, 128.8, 129.1, 135.3, 135.4, 143.2, 143.8, 148.6, 150.3. Anal. Calcd for C$_{37}$H$_{39}$HfN$_3$: C, 63.11; H, 5.58; N, 5.97. Found: C, 62.62; H, 5.33; N, 5.92. Small deviation of found E.A. values is probably due to high sensitivity of **3c** to air.

3d. 41% yield, mp 117−118 °C (dec). ^{1}H NMR (400 MHz, C$_6$D$_6$, 30 °C) δ: 1.57 (d, ^2J = 12.3 Hz, 1H, Hf(CH*H*Ph)), 1.61 (d, ^2J = 12.2 Hz, 1H, Hf(C*H*HPh)), 1.76 (d, ^2J = 12.2 Hz, 1H, Hf(CH*H*Ph)), 2.19 (d, ^2J = 12.3 Hz, 1H, Hf(C*H*HPh)), 2.67 (s, 6H, 2,6-(C*H*$_3$)$_2$C$_6$H$_3$), 2.81 (br d, ^2J = 4.4 Hz, 2H, NCH(C*H*$_2$Ph)Ar), 3.48 (ddd, ^2J = 10.2 Hz, ^3J = 6.5, 4.5 Hz, 1H, NCH*H*CH$_2$NH), 3.77 (ddd, ^2J = 11.2 Hz, ^3J = 6.9, 3.7 Hz, 1H, NCH$_2$CH*H*NH), 4.18 (ddd, ^2J = 10.2 Hz, ^3J = 6.9, 3.7 Hz, 1H, NCH$_2$CH*H*NH), 4.42 (ddd, ^2J = 11.2 Hz, ^3J = 6.5, 4.5 Hz, 1H, NCH*H*CH$_2$NH), 4.54 (dd, ^3J = 4.7, 4.4 Hz, 1H, NC*H*(CH$_2$Ph)-Ar), 6.22 (d, ^3J = 7.1 Hz, 2H, Ar), 6.48 (t, ^3J = 7.3 Hz, 1H, Ar), 6.62−7.26 (19H, aromatic protons overlapped with a residual proton signal of C$_6$D$_6$), 7.35 (d, ^3J = 8.5 Hz, 1H, Ar), 7.75 (d, ^3J = 8.5 Hz, 1H, Ar). ^{13}C NMR (100 MHz, C$_6$D$_6$, 30 °C): δ 19.5, 39.7, 55.8, 57.3, 69.8 ($^1J_{C-H}$ = 117 Hz, Hf(*C*H$_2$Ph)), 72.4 ($^1J_{C-H}$ = 126 Hz, Hf(*C*H$_2$Ph)), 74.2, 119.4, 119.9, 121.3, 124.4, 125.5, 126.3, 126.4, 126.5, 126.8, 126.9, 127.7, 128.8, 128.9, 129.3, 129.4, 135.2, 136.1, 137.5, 144.5, 145.3, 148.4, 152.4, 170.4. Anal. Calcd for C$_{41}$H$_{41}$HfN$_3$: C, 65.29; H, 5.48; N, 5.57. Found: C, 65.61; H, 5.70; N, 5.57.

*Synthesis and Characterization of Cationic Monobenzylhafnium Complex Series (**8a**).* A yellow solution of dibenzylhafnium complex **3a** (15.0 mg, 0.02 mmol) in bromobenzene-d_5 (0.5 mL) was added to B(C$_6$F$_5$)$_3$ (10.5 mg, 0.02 mmol) at room temperature to quantitatively generate the orange solution of monobenzylhafnium complex **8a**. ^{1}H NMR (400 MHz, C$_6$D$_5$Br, 30 °C): δ 1.99 (s, 6H, 3,5-(C*H*$_3$)$_2$C$_6$H$_3$), 2.03 (s, 3H, 2,6-(C*H*$_3$)$_2$C$_6$H$_3$), 2.16 (d, ^2J = 11.4 Hz, 1H, Hf(C*H*HPh)), 2.22 (s, 3H, 2,6-(C*H*$_3$)$_2$C$_6$H$_3$), 2.40 (d, ^2J = 11.4 Hz, 1H, Hf(CH*H*Ph)), 2.59 (dd, ^2J = 10.7 Hz, ^3J = 5.6 Hz, 1H, NCH(CH*H*Ph)Ar), 2.80 (dd, ^3J = 8.0 Hz, 4.5 Hz, 1H, NCH*H*CH$_2$N), 2.84 (dd, ^3J = 10.7 Hz, 4.6 Hz, 1H, NCH(CH*H*Ph)Ar), 3.01 (br, 1H, PhC*H*HBAr$^F_3$), 3.26 (br, 1H, PhCH*H*BAr$^F_3$), 3.98 (br dd, ^3J = 6.6 Hz, 4.5 Hz, 1H, NCH$_2$CH*H*N), 4.02 (dd, ^3J = 5.6 Hz, 4.6 Hz, 1H, NC*H*(CH$_2$Ph)Ar), 4.16 (dd, ^2J = 10.7 Hz, ^3J = 8.0 Hz, 1H, NCH$_2$CH*H*N), 4.36 (m, 1H, NCH*H*CH$_2$N), 5.70 (t, ^3J = 7.3 Hz, 1H, *m*-H of *Ph*CH$_2$BAr$^F_3$), 5.81 (d, ^3J = 7.3 Hz, 1H, *o*-H of *Ph*CH$_2$BAr$^F_3$), 5.98 (d, ^3J = 7.3 Hz, 1H, *o*-H of *Ph*CH$_2$BAr$^F_3$), 6.26 (t, ^3J = 7.3 Hz, 1H, *m*-H of *Ph*CH$_2$BAr$^F_3$), 6.43 (t, ^3J = 7.3 Hz, 1H, *p*-H of *Ph*CH$_2$BAr$^F_3$), 6.52 (s, 2H, Ar), 6.64−7.30 (aromatic protons overlapped with residual proton signals of C$_6$D$_5$Br). ^{13}C NMR (100 MHz, C$_6$D$_5$Br, 30 °C): δ 18.5, 19.7, 21.0, 40.5, 48.6, 55.3, 62.2 ($^1J_{C-H}$ = 118 Hz, Hf(*C*H$_2$Ph)), 70.7, 123.1, 124.4, 125.1, 127.6, 128.3, 128.9, 129.1, 129.2, 130.6, 131.6, 133.0, 135.6, 137.5, 138.1, 139.7, 141.5, 142.2, 146.9, 149.3, 154.6, 160.9. ^{19}F NMR (376 MHz, C$_6$D$_5$Br, 30 °C): δ −164.0 (t, $^3J_{F-F}$ = 20.1 Hz, 2F, *m*-F of Ar$^F_3$), −160.1 (t, $^3J_{F-F}$ = 21.1 Hz, 1F, *p*-F of Ar$^F_3$), −129.9 (t, $^3J_{F-F}$ = 21.5 Hz, 2F, *o*-F of Ar$^F_3$). Cationic monobenzylhafnium complexes **8b−d** were prepared using a procedure similar to that for **8a**.

8b. ^{1}H NMR (400 MHz, C$_6$D$_5$Br, 30 °C): δ 1.75 (d, ^2J = 12.1 Hz, 1H, Hf(CH*H*Ph)), 2.08 (s, 3H, 2,6-(C*H*$_3$)$_2$C$_6$H$_3$), 2.15 (d, ^2J = 12.1 Hz, 1H, Hf(C*H*HPh)), 2.20 (s, 3H, 2,6-(C*H*$_3$)$_2$C$_6$H$_3$), 2.52−2.53 (m, 1H, NCH(CH*H*Ph)Ar), 2.58 (dd, ^2J = 13.7 Hz, ^2J = 4.3 Hz, 1H, NCH(C*H*HPh)Ar), 2.68 (dd, ^2J = 11.4 Hz, ^3J = 5.9 Hz, 1H, NCH*H*CH$_2$N), 2.84 (dd, ^3J = 11.4 Hz, ^3J = 5.2 Hz, 1H, NCH$_2$CH*H*N), 3.32−3.46 (br m, 2H, PhC*H*$_2$BAr$^F_3$), 4.21 (br s, 1H, NC*H*(CH$_2$Ph)Ar), 4.23−4.30 (m, 1H, NCH$_2$CH*H*N), 4.34−4.41 (m, 1H, NCH*H*CH$_2$N), 5.47 (t, ^3J = 7.4 Hz, 1H, *p*-H of *Ph*CH$_2$BAr$^F_3$), 5.88 (d, ^3J = 3.4 Hz, 1H, *m*-H of Hf(CH$_2$*Ph*)), 6.00−6.02 (m, 2H, *o*-H of *Ph*CH$_2$BAr$^F_3$ and *p*-H of Hf(CH$_2$*Ph*)), 6.19 (m, 2H, *m*-H of *Ph*CH$_2$BAr$^F_3$ and Ar), 6.48 (d, ^3J = 7.5 Hz, 2H, Ar), 6.53 (d, ^3J = 7.2 Hz, 2H, Ar), 6.63 (d, ^3J = 1.4 Hz, 1H, *m*-H of Hf(CH$_2$*Ph*)), 6.69 (t, ^3J = 7.3 Hz, 1H, Ar), 6.93−7.15 (aromatic protons overlapped with residual proton signals of C$_6$D$_5$Br). ^{13}C NMR (100 MHz, C$_6$D$_5$Br, 30 °C): δ 18.6, 19.7, 40.7, 55.6, 59.2, 61.7 ($^1J_{C-H}$ = 119 Hz, Hf(*C*H$_2$Ph)), 63.2, 104.7, 114.3, 118.9, 121.9, 125.4, 125.6, 127.4, 127.8, 128.2, 128.9, 129.0, 129.9, 133.7, 134.1, 135.9, 139.4, 148.0, 155.9, 159.6, 162.2. ^{19}F NMR (376 MHz, C$_6$D$_5$Br, 30 °C, δ) −164.0 (t, $^3J_{F-F}$ = 20.1 Hz, 2F, *m*-F of Ar$^F_3$), −160.2 (t, $^3J_{F-F}$ = 21.1 Hz, 1F, *p*-F of Ar$^F_3$), −130.0 (t, $^3J_{F-F}$ = 21.4 Hz, 2F, *o*-F of Ar$^F_3$).

8c. ^{1}H NMR (400 MHz, C$_6$D$_5$Br, 30 °C): δ 1.85 (d, ^2J = 11.7 Hz, 1H, Hf(C*H*HPh)), 2.16 (s, 3H, 2,6-(C*H*$_3$)$_2$C$_6$H$_3$), 2.17 (d, 1H, Hf(CH*H*Ph), partial overlap with 2,6-(C*H*$_3$)$_2$C$_6$H$_3$), 2.22 (s, 3H, 2,6-(C*H*$_3$)$_2$C$_6$H$_3$), 2.78 (d, ^3J = 3.4 Hz, 2H, NCH(C*H*$_2$Ph)Ar), 2.87 (dd, ^2J = 11.4 Hz, ^3J = 5.8 Hz, 1H, NCH*H*CH$_2$N), 3.00 (dd, ^3J = 11.4 Hz, 5.5 Hz, 1H, NCH$_2$CH*H*N), 3.34 (br s, 1H, PhCH*H*BAr$^F_3$), 3.49 (br s, 1H, PhCH*H*BAr$^F_3$), 4.27−4.32 (m, 1H, NCH$_2$CH*H*N), 4.38−4.45 (m, 1H, NCH*H*CH$_2$N), 4.49 (br t, 1H, NC*H*(CH$_2$Ph)Ar), 5.30 (t, ^3J = 7.3 Hz, 1H, *p*-H of *Ph*CH$_2$BAr$^F_3$), 6.00 (d, ^3J = 7.3 Hz, 1H, *o*-H of *Ph*CH$_2$BAr$^F_3$), 6.14 (t, ^3J = 7.3 Hz, 1H, *m*-H of *Ph*CH$_2$BAr$^F_3$), 6.27−6.32 (m, 4H, *m*-H of *Ph*CH$_2$BAr$^F_3$ and Ar), 6.50−6.57 (m, 2H, Ar), 6.72 (t, ^3J = 7.5 Hz, 2H, Ar), 6.92−7.35 (aromatic protons overlapped with residual proton signals of C$_6$D$_5$Br), 7.62 (d, ^3J = 5.5 Hz, 1H, Ar). ^{13}C NMR (100 MHz, C$_6$D$_5$Br, 30 °C): δ 18.8, 20.1, 21.4, 39.7, 58.5, 60.0, 61.6 ($^1J_{C-H}$ = 118 Hz, Hf(*C*H$_2$Ph)), 73.4, 118.5, 121.1, 122.8, 125.0, 125.1, 125.3, 127.2, 127.5, 128.0, 128.2, 128.8, 129.9, 131.4, 132.1, 133.1, 134.9, 135.2, 138.0, 146.7, 150.2, 157.0, 161.3, 166.6. ^{19}F NMR (376 MHz, C$_6$D$_5$Br, 30 °C): δ −164.1 (t, $^3J_{F-F}$ = 20.2 Hz, 2F, *m*-F of Ar$^F_3$), −160.4 (t, $^3J_{F-F}$ = 21.1 Hz, 1F, *p*-F of Ar$^F_3$), −130.0 (t, $^3J_{F-F}$ = 21.4 Hz, 2F, *o*-F of Ar$^F_3$).

8d. ^{1}H NMR (400 MHz, C$_6$D$_5$Br, 30 °C): δ 1.79−1.87 (m, 7H, Hf(CH*H*Ph) and 2,6-(C*H*$_3$)$_2$C$_6$H$_3$), 2.23 (d, ^2J = 12.8 Hz, 1H, Hf(C*H*HPh)), 2.60 (br m, 2H, NCH(CH*H*Ph)Ar and NCH*H*CH$_2$N), 2.80−2.83 (br m, 2H, NCH(CH*H*Ph)Ar and NCH*H*CH$_2$N), 4.15 (br dd, ^3J = 8.5 Hz, 2H, NC*H*$_2$CH$_2$N), 4.46 (s, 1H, NC*H*(CH$_2$Ph)Ar), 5.91−6.17 (aromatic protons overlapped with residual proton signals of C$_6$D$_5$Br), 6.62 (br s, 2H, Ar), 6.55−6.96 (aromatic protons overlapped with residual proton signals of C$_6$D$_5$Br), 7.04 (d, ^3J = 8.0 Hz, 1H, Ar), 7.40−7.48 (aromatic protons overlapped with residual proton signals of C$_6$D$_5$Br). ^{1}H NMR (400 MHz, C$_6$D$_5$Br, −20 °C): δ 1.83 (br s, 4H, 2,6-(C*H*$_3$)$_2$C$_6$H$_3$ and Hf(CH*H*Ph)), 1.93 (s, 3H, 2,6-(C*H*$_3$)$_2$C$_6$H$_3$), 2.34 (d, ^2J = 12.9 Hz, 1H, Hf(C*H*HPh)), 2.55 (br d, ^3J = 8.5 Hz, 2H, NCH*H*CH$_2$N and NCH(C*H*HPh)Ar), 2.71 (br s, 1H, PhCH*H*BAr$^F_3$), 2.79 (br m, 2H, NC*H*HCH$_2$N and NCH(CH*H*Ph)-Ar), 3.75 (br s, 1H, PhCH*H*BAr$^F_3$), 4.16−4.21 (br m, 3H, NCH$_2$C*H*$_2$N and *p*-H of *Ph*CH$_2$BAr$^F_3$), 4.46 (s, 1H, (NC*H*(CH$_2$Ph)-Ar), 5.26 (br s, 1H, *m*-H of *Ph*CH$_2$BAr$^F_3$), 5.41 (d, ^3J = 5.4 Hz, 1H, *o*-H of *Ph*CH$_2$BAr$^F_3$), 5.89 (br t, 1H, *m*-H of *Ph*CH$_2$BAr$^F_3$), 5.96−7.00 (aromatic protons overlapped with residual proton signals of C$_6$D$_5$Br), 7.30 (d, 1H, ^3J = 5.4 Hz, *o*-H of *Ph*CH$_2$BAr$^F_3$), 7.39 (d, ^3J = 8.3 Hz, 1H, Ar), 7.50 (s, 2H, Ar). ^{13}C NMR (100 MHz, C$_6$D$_5$Br, 30 °C): δ

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21.4, 34.3, 38.4, 57.6, 62.3 ($^1J_{C-H}$ = 134 Hz, Hf(CH_2Ph)), 74.0, 119.4, 125.3, 125.4, 127.2, 127.4, 127.8, 128.2, 128.3, 129.0, 129.1, 129.9, 135.6, 136.9, 138.0, 139.4, 139.8, 143.7, 147.1, 149.4, 157.9, 168.7. ^{19}F NMR (376 MHz, C_6D_5Br, 30 °C): δ −164.4 (br s, 2F, *m*-F of Ar^F_3), −160.6 (br s, 1F, *p*-F of Ar^F_3), −130.1 (t, $^3J_{F-F}$ = 21.3 Hz, 2F, *o*-F of Ar^F_3). ^{19}F NMR (376 MHz, C_6D_5Br, −20 °C): δ −164.2 (t, $^3J_{F-F}$ = 20.5 Hz, 2F, *m*-F of Ar^F_3), −160.3 (t, $^3J_{F-F}$ = 21.2 Hz, 1F, *p*-F of Ar^F_3), −130.5 (br s, 2F, *o*-F of Ar^F_3).

*Synthesis and Characterization of C(sp^3)−H Alkenylated Products (**6aa**).* In the glovebox, a solution of dibenzylhafnium complex **3c** (21.1 mg, 0.03 mmol) in bromobenzene-d_5 (1.0 mL) was added sequentially to 2,6-dimethylpyridine (96.4 mg, 0.90 mmol), $[Ph_3C][B(C_6F_5)_4]$ (27.7 mg, 0.03 mmol), and 3-hexyne (24.6 mg, 0.30 mmol) at room temperature. The reaction mixture was removed from the glovebox and heated to 100 °C in an oil bath for 12 h. The reaction was quenched with a saturated aqueous solution of $NaHCO_3$ (ca. 3 mL) and extracted with Et_2O (5 × 7 mL). Removing volatiles under reduced pressure gave an oily residue, which was grafted on silica. The alkenylated product was purified using flash column chromatography with 10% EtOAc in hexane as the eluent. Alkene 7 was detected by GC-MS measurement when the addition of 2,6-dimethylpyridines and 3-hexyne was reversed. ^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 0.92 (t, ^3J = 6.4 Hz, 3H, CH_2CH_3), 0.95 (t, ^3J = 6.4 Hz, 3H, CH_2CH_3), 1.94−2.08 (m, 4H, CH_2CH_3), 2.42 (s, 3H, pyCH_3), 3.59 (s, 2H, pyCH_2C = CH), 5.25 (t, ^3J = 7.1 Hz, 1H, pyCH_2C = C*H*), 6.59 (d, ^3J = 7.6 Hz, 1H, 3H of py), 6.83 (d, ^3J = 7.6 Hz, 1H, 5H of py), 7.08 (t, ^3J = 7.6 Hz, 1H, 4H of py). ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 12.9 (CH_2CH_3), 14.4 (CH_2CH_3), 20.9 (CH_2CH_3), 22.8 (CH_2CH_3), 24.1 (pyCH_3), 46.0 (pyCH_2C=CH), 119.4 (py), 119.8 (py), 128.7 (pyCH_2C=CH), 135.7 (4C of py), 139.0 (pyCH_2C=CH), 157.5 (py), 160.0 (py). HRMS (FAB) *m*/*z* calcd for $[C_{13}H_{19}N + H]$ 190.1596, found 190.1602. A similar procedure was conducted for the other C(sp^3)−H alkenylation reactions in Table 3.

6ab. ^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 0.84 (t, ^3J = 7.4 Hz, 3H, $CH_2CH_2CH_3$), 0.88 (t, ^3J = 7.4 Hz, 3H, $CH_2CH_2CH_3$), 1.31−1.40 (m, 2H, $CH_2CH_2CH_3$), 1.41−1.49 (m, 2H, $CH_2CH_2CH_3$), 1.98 (dd, ^3J = 14.6, 7.4 Hz, 2H, $CH_2CH_2CH_3$), 2.05 (dd, ^3J = 9.1, 7.3 Hz, 2H, $CH_2CH_2CH_3$), 2.42 (s, 3H, pyCH_3), 3.61 (br s, 2H, pyCH_2C=CH), 5.32 (t, ^3J = 7.3 Hz, 1H, pyCH_2C=C*H*), 6.59 (br d, ^3J = 7.6 Hz, 1H, 3H of py), 6.85 (br d, ^3J = 7.6 Hz, 1H, 5H of py), 7.09 (t, ^3J = 7.6 Hz, 1H, 4H of py). ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 13.6 ($CH_2CH_2CH_3$), 13.8 ($CH_2CH_2CH_3$), 21.3 (CH_2), 23.1 (CH_2), 24.2 (pyCH_3), 29.9 (CH_2), 31.8 (CH_2), 46.4 (pyCH_2C=CH), 119.3 (py), 119.8 (py), 127.6 (pyCH_2C=CH, overlap with solvent), 135.6 (4C of py), 137.8 (pyCH_2C=CH), 157.5 (py), 160.5 (py). HRMS (FAB) *m*/*z* calcd for $[C_{15}H_{23}N + H]$ 218.1909, found 218.1909.

6ac. ^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 0.83−0.89 (m, 6H, $CH_2CH_2CH_2CH_3$), 1.21−1.45 (m, 8H, $CH_2CH_2CH_2CH_3$), 2.03−2.12 (m, 4H, $CH_2CH_2CH_2CH_3$), 2.42 (s, 3H, pyCH_3), 3.62 (s, 2H, pyCH_2C=CH), 5.32 (t, ^3J = 7.1 Hz, 1H, pyCH_2C=C*H*), 6.60 (d, ^3J = 7.6 Hz, 1H, 3H of py), 6.87 (d, ^3J = 7.6 Hz, 1H, 5H of py), 7.10 (t, ^3J = 7.6 Hz, 1H, 4H of py). ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 13.8 ($CH_2CH_2CH_2CH_3$), 22.3 (CH_2), 22.6 (CH_2), 24.1 (pyCH_3), 27.6 (CH_2), 29.6 (CH_2), 30.4 (CH_2), 32.2 (CH_2), 46.4 (pyCH_2C=CH), 119.3 (py), 119.8 (py), 127.8 (pyCH_2C=CH), 135.6 (4C of py), 137.9 (pyCH_2C=CH), 157.5 (py), 160.5 (py). HRMS (FAB) *m*/*z* calcd for $[C_{17}H_{27}N + H]$ 246.2222, found 246.2224.

6ad. Product was isolated as a mixture of regioisomers (ca. 1:1). ^{1}H NMR assignment is separated into three catagories; major isomer, minor isomer, and overlapping (shared) peaks. Integration of nonoverlapping (not shared) peaks are reported as decimal values when setting the doublet at δ 1.55 (pyCH_2C=CCH_3) to 3H intensity, while the integration of overlapping (shared) peaks are reported as integrals.

6ad-A: ^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 1.55 (d, ^3J = 6.8 Hz, 3H, pyCH_2C=CCH_3), 2.08 (br dd, ^3J = 7.7 Hz, 2H, $CH_2CH_2CH_2CH_3$), 3.60 (s, 2H, pyCH_2C=CH).

6ad-B: ^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 1.62 (s, 2.3H, pyCH_2CH_3C=CH), 1.98 (br dt, ^3J = 14.3, 7.7 Hz, 2.3H, $CH_2CH_2CH_2CH_3$), 3.58 (s, 1.6H, pyCH_2C=CH). Overlapping (shared): ^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 0.84 (t, ^3J = 7.3 Hz, 3H, $CH_2CH_2CH_2CH_3$), 0.87 (t, ^3J = 7.3 Hz, 3H, $CH_2CH_2CH_2CH_3$), 1.19−1.43 (m, 8H, $CH_2CH_2CH_2CH_3$), 2.43 (s, 6H, pyCH_3), 5.32−5.37 (m, 2H, pyCH_2C=C*H*), 6.59 (d, ^3J = 7.6 Hz, 2H, 3H of py), 6.82 (d, ^3J = 7.6 Hz, 2H, 5H of py), 7.08 (t, ^3J = 7.6 Hz, 2H, 4H of py). ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 13.1 ($CH_2CH_2CH_2CH_3$), 13.8 ($CH_2CH_2CH_2CH_3$), 15.7 (pyCH_2C=CCH_3), 22.3 (CH_2), 22.4 (CH_2), 22.6 (CH_2), 24.2 (pyCH_3), 27.7 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 30.1 (CH_2), 30.2 (CH_2), 31.9 (CH_2), 32.0 (CH_2), 46.4 (pyCH_2C=CH), 48.9 (pyCH_2C=CH), 119.1 (py), 119.4 (py), 119.8, 119.9, 120.0, 121.2, 133.3 (pyCH_2C=CH), 135.6 (4C of py), 135.7 (4C of py), 138.8 (pyCH_2C=CH), 157.6 (py), 160.4 (py). HRMS (FAB) *m*/*z* calcd for $[C_{14}H_{21}N + H]$ 204.1752, found 204.1752.

6ae. Product was isolated as a mixture of regioisomers (ca. 1:1). Integration of nonoverlapping (not shared) peaks are reported as decimal values when setting the triplet at 0.85 ($CH_2CH_2CH_2CH_3$) to 3, while the integration of overlapping (shared) peaks are reported as integrals. ^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 0.83 (t, ^3J = 7.1 Hz, 2.9H, $CH_2CH_2CH_2CH_3$), 0.85 (t, ^3J = 7.3 Hz, 3H, $CH_2CH_2CH_2CH_3$), 0.92−0.99 (m, 6H, CH_2CH_3), 1.21−1.43 (m, 8H, $CH_2CH_2CH_2CH_3$), 2.01−2.09 (m, 8H, $CH_2CH_2CH_2CH_3$ and CH_2CH_3), 2.42 (s, 6H, pyCH_3), 3.61 (s, 4H, pyCH_2C=CH), 5.27−5.31 (m, 2H, pyCH_2C=C*H*), 6.59 (d, ^3J = 7.6 Hz, 2H, 3H of py), 6.85 (d, ^3J = 7.6 Hz, 2H, 5H of py), 7.09 (t, ^3J = 7.6 Hz, 2H, 4H of py). ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 12.9 ($CH_2CH_2CH_2CH_3$), 13.8 ($CH_2CH_2CH_2CH_3$), 14.3 (pyCH_2C=CCH_3), 21.1 (CH_2), 22.3 (CH_2), 22.6 (CH_2), 22.8 (CH_2), 24.1 (pyCH_3), 27.4 (CH_2), 29.5 (CH_2), 30.5 (CH_2), 32.2 (CH_2), 46.0 (pyCH_2C=CH), 46.4 (pyCH_2C=CH), 119.4 (py), 119.8 (py), 127.1 (pyCH_2C=CH), 129.3 (pyCH_2C=CH), 135.6 (4C of py), 137.4 (4C of py), 139.4 (pyCH_2C=CH), 157.5 (py), 160.4 (py). HRMS (FAB) *m*/*z* calcd for $[C_{15}H_{23}N + H]$ 218.1909, found 218.1901.

6bb. ^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 0.86 (t, ^3J = 7.3 Hz, 3H, $CH_2CH_2CH_3$), 0.89 (t, ^3J = 7.4 Hz, 3H, $CH_2CH_2CH_3$), 1.32 (br dq, ^3J = 14.7, 7.4 Hz, 2H, $CH_2CH_2CH_3$), 1.44 (br dq, ^3J = 15.1, 7.6 Hz, 2H, $CH_2CH_2CH_3$), 1.90 (s, 3H, 3-CH_3 of py), 2.00 (dd, ^3J = 14.7, 7.4 Hz, 2H, $CH_2CH_2CH_3$), 2.09 (br dd, ^3J = 7.3 Hz, 2H, $CH_2CH_2CH_3$), 2.44 (s, 3H, 6-CH_3 of py), 3.63 (s, 2H, pyCH_2C=CH), 5.37 (t, ^3J = 7.3 Hz, 1H, pyCH_2C=C*H*), 6.46 (s, 1H, 3H of py), 6.76 (s, 1H, 5H of py). ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 13.6 ($CH_2CH_2CH_3$), 13.8 ($CH_2CH_2CH_3$), 20.2 (3-CH_3 of py), 21.4 (CH_2), 23.1 (CH_2), 24.0 (6-CH_3 of py), 29.9 (CH_2), 31.9 (CH_2), 46.3 (pyCH_2C=CH), 120.4 (py), 121.0 (py), 127.7 (pyCH_2C=CH), 138.0 (4C of py), 146.3 (pyCH_2C=CH), 157.3 (py), 160.2 (py). HRMS (FAB) *m*/*z* calcd for $[C_{16}H_{25}N + H]$ 232.2065, found 232.2067.

6cb. ^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 0.79 (t, ^3J = 7.3 Hz, 3H, $CH_2CH_2CH_3$), 0.86 (t, ^3J = 7.4 Hz, 3H, $CH_2CH_2CH_3$), 1.26−1.42 (m, 4H, $CH_2CH_2CH_3$), 1.91−2.01 (m, 4H, $CH_2CH_2CH_3$), 2.21 (s, 3H, pyCH_3), 3.45 (s, 2H, pyCH_2C=CH), 5.24 (t, ^3J = 7.3 Hz, 1H, pyCH_2C=C*H*), 6.78 (s, 1H, 3H of py), 7.16 (s, 1H, 5H of py). ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 13.6 ($CH_2CH_2CH_3$), 13.7 ($CH_2CH_2CH_3$), 21.2 (CH_2), 23.0 (CH_2), 23.7 (pyCH_3), 29.8 (CH_2), 31.7 (CH_2), 45.9 (pyCH_2C=CH), 122.7 (py), 123.3 (py), 128.6 (pyCH_2C=CH), 132.6 (4C of py), 137.0 (pyCH_2C=CH), 159.1 (py), 162.1 (py). HRMS (FAB) *m*/*z* calcd for $[C_{15}H_{22}NBr + H]$ 296.1014, found 296.1017.

6db. ^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 0.87 (t, ^3J = 7.4 Hz, 3H, $CH_2CH_2CH_3$), 0.92 (t, ^3J = 7.4 Hz, 3H, $CH_2CH_2CH_3$), 1.30−1.41 (m, 2H, $CH_2CH_2CH_3$), 1.47−1.57 (m, 2H, $CH_2CH_2CH_3$), 1.96−2.02 (m, 2H, $CH_2CH_2CH_3$), 2.14−2.17 (m, 2H, $CH_2CH_2CH_3$), 2.23 (s, 3H, pyCH_3), 3.78 (s, 2H, pyCH_2C=CH), 5.25 (t, ^3J = 7.1 Hz, 1H, pyCH_2C=C*H*), 6.20 (d, ^3J = 8.1 Hz, 1H, 3H of py), 7.24 (d, ^3J = 8.1 Hz, 1H, 4H of py). ^{13}C NMR (100 MHz, C_6D_6, 30 °C): δ 13.6 ($CH_2CH_2CH_3$), 13.9 ($CH_2CH_2CH_3$), 21.4 (CH_2), 23.0 (CH_2), 23.4 (pyCH_3), 29.9 (CH_2), 32.5 (CH_2), 44.8 (pyCH_2C=CH), 121.7 (py), 127.5 (pyCH_2C=CH), 136.1 (4C of py), 139.8 (pyCH_2C=CH), 156.4 (py), 158.0 (py). HRMS (FAB) *m*/*z* calcd for $[C_{15}H_{22}NBr + H]$ 296.1014, found 296.1017.

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■ ASSOCIATED CONTENT

Supporting Information

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NMR spectra, kinetics and Eyring graphs, plot of yield of **6ab** as a function of 2,6-dimethylpyridine equivalents (PDF)

Crystallographic details for **3a−d** (CIF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Representative reviews for C−H activation/functionalization: (a) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507. (b) Godula, K.; Sames, D. *Science* **2006**, *312*, 67. (c) Jones, W. D. *Comprehensive Organometallic Chemistry III*; Crabtree, R. H., Mingos, M. P., Eds.; Elsevier Ltd.: Amsterdam, 2007; pp 699−723. Pfeffer, M.; Spencer, J. *Comprehensive Organometallic Chemistry III*; Crabtree, R. H., Mingos, M. P., Eds.; Elsevier Ltd.: Amsterdam, 2007; pp 101−166. (e) Davies, H. M. L.; Dai, X. *Comprehensive Organometallic Chemistry III*; Crabtree, R. H., Mingos, M. P., Eds.; Elsevier Ltd.: Amsterdam, 2007; pp 167−212. (f) Kitamura, T.; Fujiwara, Y. *Comprehensive Organometallic Chemistry III*; Crabtree, R. H., Mingos, M. P., Eds.; Elsevier Ltd.: Amsterdam, 2007; pp 213−250. (g) Giri, R.; Shi, B.; Engle, K. M.; Maugel, N.; Yu, J.-Q. *Chem. Soc. Rev.* **2009**, *38*, 3242. (h) Yamaguchi, J.; Yamaguchi, A. D.; Itami, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 8960. (i) Kuhl, N.; Hopkinson, M. N.; Wencel-Delord, J.; Glorius, F. *Angew. Chem., Int. Ed.* **2012**, *51*, 10236. (j) Girard, S. A.; Knauber, T.; Li, C.-J. *Angew. Chem., Int. Ed.* **2014**, *53*, 74. (k) Gensch, T.; Hopkinson, M. N.; Glorius, F.; Wencel-Delord, J. *Chem. Soc. Rev.* **2016**, *45*, 2900. (l) Hartwig, J. F. *J. Am. Chem. Soc.* **2016**, *138*, 2. (m) Hartwig, J. F.; Larsen, M. A. *ACS Cent. Sci.* **2016**, *2*, 281.

(2) Early examples of C−H functionalization using Ru, Pd, and Pt catalysts: (a) Moritanl, I.; Fujiwara, Y. *Tetrahedron Lett.* **1967**, *8*, 1119. (b) Goldshleger, N. F.; Tyabin, M. B.; Shilov, A. E.; Shteninman, A. A. *Russ. J. Phys. Chem.* **1969**, *43*, 1222. (c) Fujiwara, Y.; Moritani, I.; Danno, S.; Asano, R.; Teranishi, S. *J. Am. Chem. Soc.* **1969**, *91*, 7166. (d) Fujiwara, Y.; Kawauchi, T.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.* **1980**, 220. (e) Murai, S.; Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N. *Nature* **1993**, *366*, 529.

(3) Representative recent reviews for Ru-catalyzed C−H functionalization: (a) Arockiam, P. B.; Bruneau, C.; Dixneuf, P. H. *Chem. Rev.* **2012**, *112*, 5879. (b) Kozhushkov, S. I.; Ackermann, L. *Chem. Sci.* **2013**, *4*, 886. (c) Ackermann, L. *Acc. Chem. Res.* **2014**, *47*, 281. (d) De Sarkar, S.; Liu, W.; Kozhushkov, S. I.; Ackermann, L. *Adv. Synth. Catal.* **2014**, *356*, 1461.

(4) Representative recent examples for Ru-catalyzed C−H functionalization reactions: (a) Inoue, S.; Shiota, H.; Fukumoto, Y.; Chatani, N. *J. Am. Chem. Soc.* **2009**, *131*, 6898. (b) Kochi, T.; Urano, S.; Seki, H.; Mizushima, E.; Sato, M.; Kakiuchi, F. *J. Am. Chem. Soc.* **2009**, *131*, 2792. (c) Kakiuchi, F.; Kochi, T.; Mizushima, E.; Murai, S. *J. Am. Chem. Soc.* **2010**, *132*, 17741. (d) Flegeau, E. F.; Bruneau, C.; Dixneuf, P. H.; Jutand, A. *J. Am. Chem. Soc.* **2011**, *133*, 10161. (e) Klare, H. F. T.; Oestreich, M.; Ito, J.-I.; Nishiyama, H.; Ohki, Y.; Tatsumi, K. *J. Am. Chem. Soc.* **2011**, *133*, 3312. (f) Hofmann, N.; Ackermann, L. *J. Am. Chem. Soc.* **2013**, *135*, 5877. (g) Konigs, C. D. F.; Klare, H. F. T.; Oestreich, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 10076. (h) Stahl, T.; Muther, K.; Ohki, Y.; Tatsumi, K.; Oestreich, M. *J. Am. Chem. Soc.* **2013**, *135*, 10978. (i) Mehta, V. P.; Garcia-Lopez, J.-A.; Greaney, M. F. *Angew. Chem., Int. Ed.* **2014**, *53*, 1529. (j) Li, J.; Warratz, S.; Zell, D.; De Sarkar, S.; Ishikawa, E. E.; Ackermann, L. *J. Am. Chem. Soc.* **2015**, *137*, 13894. (k) Omann, L.; Oestreich, M. *Angew. Chem., Int. Ed.* **2015**, *54*, 10276. (l) Teskey, C. J.; Lui, A. Y. W.; Greaney, M. F. *Angew. Chem., Int. Ed.* **2015**, *54*, 11677. (m) Warratz, S.; Kornhaaß, C.; Cajaraville, A.; Niepotter, B.; Stalke, D.; Ackermann, L. *Angew. Chem., Int. Ed.* **2015**, *54*, 5513. (n) Simonetti, M.; Perry, G. J. P.; Cambeiro, X. C.; Julia-Hernandez, F.; Arokianathar, J. N.; Larrosa, I. *J. Am. Chem. Soc.* **2016**, *138*, 3596. (o) Fan, Z.; Ni, J.; Zhang, A. *J. Am. Chem. Soc.* **2016**, *138*, 8470.

(5) Representative recent reviews for Rh-catalyzed C−H functionalization: (a) Satoh, T.; Miura, M. *Chem. - Eur. J.* **2010**, *16*, 11212. (b) Davies, H. M. L.; Morton, D. *Chem. Soc. Rev.* **2011**, *40*, 1857. (c) Colby, D. A.; Tsai, A. S.; Bergman, R. G.; Ellman, J. A. *Acc. Chem. Res.* **2012**, *45*, 814. (d) Song, G.; Li, X. *Acc. Chem. Res.* **2015**, *48*, 1007. (e) Ye, B.; Cramer, N. *Acc. Chem. Res.* **2015**, *48*, 1308. (f) Li, S.-S.; Qin, L.; Dong, L. *Org. Biomol. Chem.* **2016**, *14*, 4554. (g) Motevalli, S.; Sokeirik, Y.; Ghanem, A. *Eur. J. Org. Chem.* **2016**, *2016*, 1459.

(6) Representative recent examples for Rh-catalyzed C−H functionalization reactions: (a) Umeda, N.; Tsurugi, H.; Satoh, T.; Miura, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 4019. (b) Kurokawa, T.; Kim, M.; Du Bois, J. *Angew. Chem., Int. Ed.* **2009**, *48*, 2777. (c) Ureshino, T.; Yoshida, T.; Kuninobu, Y.; Takai, K. *J. Am. Chem. Soc.* **2010**, *132*, 14324. (d) Patureau, F. W.; Besset, T.; Glorius, F. *Angew. Chem., Int. Ed.* **2011**, *50*, 1064. (e) Patureau, F. W.; Besset, T.; Kuhl, N.; Glorius, F. *J. Am. Chem. Soc.* **2011**, *133*, 2154. (f) Rakshit, S.; Grohmann, C.; Besset, T.; Glorius, F. *J. Am. Chem. Soc.* **2011**, *133*, 2350. (g) Tauchert, M. E.; Incarvito, C. D.; Rheingold, A. L.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2012**, *134*, 1482. (h) Wang, H.; Glorius, F. *Angew. Chem., Int. Ed.* **2012**, *51*, 7318. (i) Brasse, M.; Campora, J.; Ellman, J. A.; Bergman, R. G. *J. Am. Chem. Soc.* **2013**, *135*, 6427. (j) Duttwyler, S.; Chen, S.; Takase, M. K.; Wiberg, K. B.; Bergman, R. G.; Ellman, J. A. *Science* **2013**, *339*, 678. (k) Kuninobu, Y.; Yamauchi, K.; Tamura, N.; Seiki, T.; Takai, K. *Angew. Chem., Int. Ed.* **2013**, *52*, 1520. (l) Lian, Y.; Bergman, R. G.; Lavis, L. D.; Ellman, J. A. *J. Am. Chem. Soc.* **2013**, *135*, 7122. (m) Lian, Y.; Huber, T.; Hesp, K. D.; Bergman, R. G.; Ellman, J. A. *Angew. Chem., Int. Ed.* **2013**, *52*, 629. (n) Lian, Y.; Hummel, J. R.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2013**, *135*, 12548. (o) Shi, Z.; Suri, M.; Glorius, F. *Angew. Chem., Int. Ed.* **2013**, *52*, 4892. (p) Wang, H.; Schroder, N.; Glorius, F. *Angew. Chem., Int. Ed.* **2013**, *52*, 5386. (q) Zhang, G.; Yang, L.; Wang, Y.; Xie, Y.; Huang, H. *J. Am. Chem. Soc.* **2013**, *135*, 8850. (r) Zhao, D.; Shi, Z.; Glorius, F. *Angew. Chem., Int. Ed.* **2013**, *52*, 12426. (s) Bess, E. N.; DeLuca, R. J.; Tindall, D. J.; Oderinde, M. S.; Roizen, J. L.; Du Bois, J.; Sigman, M. S. *J. Am. Chem. Soc.* **2014**, *136*, 5783. (t) Cheng, C.; Hartwig, J. F. *Science* **2014**, *343*, 853. (u) Wangweerawong, A.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2014**, *136*, 8520. (v) Romanov-Michailidis, F.; Sedillo, K. F.; Neely, J. M.; Rovis, T. *J. Am. Chem. Soc.* **2015**, *137*, 8892. (w) Unoh, Y.; Satoh, T.; Hirano, K.; Miura, M. *ACS Catal.* **2015**, *5*, 6634. (x) Vaughan, B. A.; Webster-Gardiner, M. S.; Cundari, T. R.; Gunnoe, T. B. *Science* **2015**, *348*, 421. (y) Liao, K.; Negretti, S.; Musaev, D. G.; Bacsa, J.; Davies, H. M. L. *Nature* **2016**, *533*, 230.

(7) Representative recent reviews for Pd-catalyzed C−H functionalization: (a) Sigman, M. S.; Werner, E. W. *Acc. Chem. Res.* **2012**, *45*, 874. (b) Neufeldt, S. R.; Sanford, M. S. *Acc. Chem. Res.* **2012**, *45*, 936. (c) Engle, K. M.; Yu, J.-Q. *J. Org. Chem.* **2013**, *78*, 8927. (d) Wu, Y.; Wang, J.; Mao, F.; Kwong, F. Y. *Chem. - Asian J.* **2014**, *9*, 26. (e) Ye, J.; Lautens, M. *Nat. Chem.* **2015**, *7*, 863. (f) Dey, A.; Agasti, S.; Maiti, D. *Org. Biomol. Chem.* **2016**, *14*, 5440.

(8) Representative recent examples for Pd-catalyzed C−H functionalization reactions: (a) Mariampillai, B.; Alliot, J.; Li, M.; Lautens, M. *J.*

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Organometallics XXXX, XXX, XXX−XXX

Am. Chem. Soc. **2007**, *129*, 15372. (b) Stuart, D. R.; Fagnou, K. *Science* **2007**, *316*, 1172. (c) Desai, L. V.; Stowers, K. J.; Sanford, M. S. *J. Am. Chem. Soc.* **2008**, *130*, 13285. (d) Kakiuchi, F.; Kochi, T.; Mutsutani, H.; Kobayashi, N.; Urano, S.; Sato, M.; Nishiyama, S.; Tanabe, T. *J. Am. Chem. Soc.* **2009**, *131*, 11310. (e) Kalyani, D.; McMurtrey, K. B.; Neufeldt, S. R.; Sanford, M. S. *J. Am. Chem. Soc.* **2011**, *133*, 18566. (f) Musaev, D. G.; Kaledin, A.; Shi, B.-F.; Yu, J.-Q. *J. Am. Chem. Soc.* **2012**, *134*, 1690. (g) Baba, K.; Tobisu, M.; Chatani, N. *Angew. Chem., Int. Ed.* **2013**, *52*, 11892. (h) Dong, Z.; Dong, G. *J. Am. Chem. Soc.* **2013**, *135*, 18350. (i) Kuninobu, Y.; Iwanaga, T.; Omura, T.; Takai, K. *Angew. Chem., Int. Ed.* **2013**, *52*, 4431. (j) Rosen, B. R.; Simke, L. R.; Thuy-Boun, P. S.; Dixon, D. D.; Yu, J.-Q.; Baran, P. S. *Angew. Chem., Int. Ed.* **2013**, *52*, 7317. (k) Saget, T.; Cramer, N. *Angew. Chem., Int. Ed.* **2013**, *52*, 7865. (l) Wang, H.; Li, G.; Engle, K. M.; Yu, J.-Q.; Davies, H. M. L. *J. Am. Chem. Soc.* **2013**, *135*, 6774. (m) Liu, Y.-J.; Xu, H.; Kong, W.-J.; Shang, M.; Dai, H.-X.; Yu, J.-Q. *Nature* **2014**, *515*, 389. (n) Calleja, J.; Pla, D.; Gorman, T. W.; Domingo, V.; Haffemayer, B.; Gaunt, M. J. *Nat. Chem.* **2015**, *7*, 1009. (o) Chen, G.; Shigenari, T.; Jain, P.; Zhang, Z.; Jin, Z.; He, J.; Li, S.; Mapelli, C.; Miller, M. M.; Poss, M. A.; Scola, P. M.; Yeung, K.-S.; Yu, J.-Q. *J. Am. Chem. Soc.* **2015**, *137*, 3338. (p) Dastbaravardeh, N.; Toba, T.; Farmer, M. E.; Yu, J.-Q. *J. Am. Chem. Soc.* **2015**, *137*, 9877. (q) Dong, Z.; Wang, J.; Ren, Z.; Dong, G. *Angew. Chem., Int. Ed.* **2015**, *54*, 12664. (r) Thompson, S. J.; Thach, D. Q.; Dong, G. *J. Am. Chem. Soc.* **2015**, *137*, 11586. (s) Zhang, S.-Y.; Li, Q.; He, G.; Nack, W. A.; Chen, G. *J. Am. Chem. Soc.* **2015**, *137*, 531. (t) Prieto, A.; Melot, R.; Bouyssi, D.; Monteiro, N. *Angew. Chem., Int. Ed.* **2016**, *55*, 1885. (u) Topczewski, J. J.; Cabrera, P. J.; Saper, N. I.; Sanford, M. S. *Nature* **2016**, *531*, 220.

(9) Representative recent review for Ir-catalyzed C−H functionalization: Jongwook, C.; Goldman, A. S. In *Iridium Catalysis*; Andersson, P. G., Ed.; Topics in Organometallic Chemistry series, Vol. *34*; Springer-Verlag: Berlin, 2011; pp 139−167.

(10) Representative recent examples for Ir-catalyzed C−H functionalization reactions: (a) Cho, J.-Y.; Tse, M. K.; Holmes, D.; Maleczka, R. E., Jr.; Smith, M. R., III *Science* **2002**, *295*, 305. (b) Jo, T. S.; Kim, S. H.; Shin, J.; Bae, C. *J. Am. Chem. Soc.* **2009**, *131*, 1656. (c) Liskey, C. W.; Liao, X.; Hartwig, J. F. *J. Am. Chem. Soc.* **2010**, *132*, 11389. (d) Robbins, D. W.; Boebel, T. A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2010**, *132*, 4068. (e) Roosen, P. C.; Kallepalli, V. A.; Chattopadhyay, B.; Singleton, D. A.; Maleczka, R. E., Jr.; Smith, M. R., III. *J. Am. Chem. Soc.* **2012**, *134*, 11350. (f) Chang, Y.; Lee, H. H.; Kim, S. H.; Jo, T. S.; Bae, C. *Macromolecules* **2013**, *46*, 1754. (g) Preshlock, S. M.; Ghaffari, B.; Maligres, P. E.; Krska, S. W.; Maleczka, R. E., Jr.; Smith, M. R., III. *J. Am. Chem. Soc.* **2013**, *135*, 7572. (h) Sharma, A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2013**, *135*, 17983. (i) Ghaffari, B.; Preshlock, S. M.; Plattner, D. L.; Staples, R. J.; Maligres, P. E.; Krska, S. W.; Maleczka, R. E., Jr.; Smith, M. R., III. *J. Am. Chem. Soc.* **2014**, *136*, 14345. (j) Hwang, H.; Kim, J.; Jeong, J.; Chang, S. *J. Am. Chem. Soc.* **2014**, *136*, 10770. (k) Larsen, M. A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2014**, *136*, 4287. (l) Saito, Y.; Segawa, Y.; Itami, K. *J. Am. Chem. Soc.* **2015**, *137*, 5193.

(11) Representative recent review for Pt-catalyzed C−H functionalization: Labinger, J. A.; Bercaw, J. E. In *Higher Oxidation State Organopalladium and Platinum Chemistry*; Canty, A. J., Ed.; Topics in Organometallic Chemistry series, Vol. *35*; Springer-Verlag: Berlin, 2011; p 29−59.

(12) Representative recent examples for Pt-catalyzed C−H functionalization reactions: (a) Wagner, A. M.; Hickman, A. J.; Sanford, M. S. *J. Am. Chem. Soc.* **2013**, *135*, 15710. (b) Furukawa, T.; Tobisu, M.; Chatani, N. *J. Am. Chem. Soc.* **2015**, *137*, 12211.

(13) Representative recent reviews for base transition metal-catalyzed C−H functionalization: (a) Sun, C.-L.; Li, B.-J.; Shi, Z.-J. *Chem. Rev.* **2011**, *111*, 1293. (b) Yamaguchi, J.; Muto, K.; Itami, K. *Eur. J. Org. Chem.* **2013**, *2013*, 19. (c) Gao, K.; Yoshikai, N. *Acc. Chem. Res.* **2014**, *47*, 1208. (d) Tasker, S. Z.; Standley, E. A.; Jamison, T. F. *Nature* **2014**, *509*, 299. (e) Castro, L. C. M.; Chatani, N. *Chem. Lett.* **2015**, *44*, 410. (f) Guo, X.-X.; Gu, D.-W.; Wu, Z.; Zhang, W. *Chem. Rev.* **2015**, *115*, 1622. (g) Moselage, M.; Li, J.; Ackermann, L. *ACS Catal.* **2016**, *6*, 498.

(14) Representative recent examples for base transition metal-catalyzed C−H functionalization reactions: (a) Nakao, Y.; Kanyiva, K. S.; Oda, S.; Hiyama, T. *J. Am. Chem. Soc.* **2006**, *128*, 8146. (b) Kanyiva, K. S.; Nakao, Y.; Hiyama, T. *Angew. Chem., Int. Ed.* **2007**, *46*, 8872. (c) Li, Y.-Z.; Li, Bi. -J.; Lu, X.-Y.; Lin, S.; Shi, Z.-J. *Angew. Chem.* **2009**, *121*, 3875. (d) Gao, K.; Lee, P.-S.; Fujita, T.; Yoshikai, N. *J. Am. Chem. Soc.* **2010**, *132*, 12249. (d1) Lee, P.-S.; Fujita, T.; Yoshikai, N. *J. Am. Chem. Soc.* **2011**, *133*, 17283. (e) Li, B.; Wu, Z.-H.; Gu, Y.-F.; Sun, C.-L.; Wang, B.-Q.; Shi, Z.-J. *Angew. Chem., Int. Ed.* **2011**, *50*, 1109. (f) Shiota, H.; Ano, Y.; Aihara, Y.; Fukumoto, Y.; Chatani, N. *J. Am. Chem. Soc.* **2011**, *133*, 14952. (g) Zhao, C.; Toste, F. D.; Bergman, R. G. *J. Am. Chem. Soc.* **2011**, *133*, 10787. (h) Amaike, K.; Muto, K.; Yamaguchi, J.; Itami, K. *J. Am. Chem. Soc.* **2012**, *134*, 13573. (i) Ding, Z.; Yoshikai, N. *Angew. Chem., Int. Ed.* **2012**, *51*, 4698. (j) Muto, K.; Yamaguchi, J.; Itami, K. *J. Am. Chem. Soc.* **2012**, *134*, 169. (k) Aihara, Y.; Chatani, N. *J. Am. Chem. Soc.* **2013**, *135*, 5308. (l) Hennessy, E. T.; Betley, T. A. *Science* **2013**, *340*, 591. (m) Muto, K.; Yamaguchi, J.; Lei, A.; Itami, K. *J. Am. Chem. Soc.* **2013**, *135*, 16384. (n) Zhou, B.; Chen, H.; Wang, C. *J. Am. Chem. Soc.* **2013**, *135*, 1264. (o) Ikemoto, H.; Yoshino, T.; Sakata, K.; Matsunaga, S.; Kanai, M. *J. Am. Chem. Soc.* **2014**, *136*, 5424. (p) Obligacion, J. V.; Semproni, S. P.; Chirik, P. J. *J. Am. Chem. Soc.* **2014**, *136*, 4133. (q) Shang, R.; Ilies, L.; Asako, S.; Nakamura, E. *J. Am. Chem. Soc.* **2014**, *136*, 14349. (r) Hummel, J. R.; Ellman, J. A. *J. Am. Chem. Soc.* **2015**, *137*, 490. (s) Moselage, M.; Sauermann, N.; Richter, S. C.; Ackermann, L. *Angew. Chem., Int. Ed.* **2015**, *54*, 6352. (t) Shang, R.; Ilies, L.; Nakamura, E. *J. Am. Chem. Soc.* **2015**, *137*, 7660. (v) Iovan, D. A.; Betley, T. A. *J. Am. Chem. Soc.* **2016**, *138*, 1983. (w) Yu, R. P.; Hesk, D.; Rivera, N.; Pelczer, I.; Chirik, P. L. *Nature* **2016**, *529*, 195. (x) Zell, D.; Bu, Q.; Feldt, M.; Ackermann, L. *Angew. Chem., Int. Ed.* **2016**, *55*, 7408. (u) Boerth, J. A.; Hummel, J. R.; Ellman, J. A. *Angew. Chem., Int. Ed.* **2016**, *55*, 12650.

(15) Review for C(sp^3)−H functionalization by late transition metals: He, G.; Wang, B.; Nack, W. A.; Chen, G. *Acc. Chem. Res.* **2016**, *49*, 635.

(16) Examples of C(sp^3)−H Functionalization by late transition metals: (a) Qian, B.; Guo, S.; Shao, J.; Zhu, Q.; Yang, L.; Xia, C.; Huang, H. *J. Am. Chem. Soc.* **2010**, *132*, 3650. (b) Aihara, Y.; Chatani, N. *J. Am. Chem. Soc.* **2014**, *136*, 898. (c) Aihara, Y.; Tobisu, M.; Fukumoto, Y.; Chatani, N. *J. Am. Chem. Soc.* **2014**, *136*, 15509. (d) Chen, K.; Shi, B.-F. *Angew. Chem., Int. Ed.* **2014**, *53*, 11950. (e) Gong, W.; Zhang, G.; Liu, T.; Giri, R.; Yu, J.-Q. *J. Am. Chem. Soc.* **2014**, *136*, 16940. (f) McNally, A.; Haffemayer, B.; Collins, B. S. L.; Gaunt, M. J. *Nature* **2014**, *510*, 129. (g) Mo, F.; Dong, G. *Science* **2014**, *345*, 68. (h) Tsukano, C.; Muto, N.; Enkhtaivan, I.; Takemoto, Y. *Chem. - Asian J.* **2014**, *9*, 2628. (i) Zhu, R.-Y.; He, J.; Wang, X.-C.; Yu, J.-Q. *J. Am. Chem. Soc.* **2014**, *136*, 13194. (j) Du, W.; Gu, Q.; Li, Z.; Yang, D. *J. Am. Chem. Soc.* **2015**, *137*, 1130. (k) He, J.; Takise, R.; Fu, H.; Yu, J.-Q. *J. Am. Chem. Soc.* **2015**, *137*, 4618. (l) Lee, M.; Sanford, M. S. *J. Am. Chem. Soc.* **2015**, *137*, 12796. (m) Liu, T.; Mei, T.-S.; Yu, J.-Q. *J. Am. Chem. Soc.* **2015**, *137*, 5871. (n) Spangler, J. E.; Kobayashi, Y.; Verma, P.; Wang, D.-H.; Yu, J.-Q. *J. Am. Chem. Soc.* **2015**, *137*, 11876. (o) Zhang, J.; Chen, H.; Lin, C.; Liu, Z.; Wang, C.; Zhang, Y. *J. Am. Chem. Soc.* **2015**, *137*, 12990. (p) Cook, A. K.; Schimler, S. D.; Matzger, A. J.; Sanford, M. S. *Science* **2016**, *351*, 1421. (q) Jiang, H.; He, J.; Liu, T.; Yu, J.-Q. *J. Am. Chem. Soc.* **2016**, *138*, 2055. (r) Lee, T.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **2016**, *55*, 8723. (s) Palmer, W. N.; Obligacion, J. V.; Pappas, I.; Chirik, P. J. *J. Am. Chem. Soc.* **2016**, *138*, 766. (t) Smith, K. T.; Berritt, S.; Gonzalez-Moreiras, M.; Ahn, S.; Smith, M. R., III; Baik, M.-H.; Mindiola, D. J. *Science* **2016**, *351*, 1424.

(17) Review of early transition mediated C−H functionalization: (a) Waterman, R. *Organometallics* **2013**, *32*, 7249. (b) Tsurugi, H.; Yamamoto, K.; Nagae, H.; Kaneko, H.; Mashima, K. *Dalton Trans.* **2014**, *43*, 2331. (c) Arnold, P. L.; McMullon, M. W.; Rieb, J.; Kuhn, F. E. *Angew. Chem., Int. Ed.* **2015**, *54*, 82. (d) Nishiura, M.; Guo, F.; Hou, Z. *Acc. Chem. Res.* **2015**, *48*, 2209.

(18) Early reports of group 3 metal mediated C−H activation: (a) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491. (b) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1983**, 276. (c) Thompson, M. E.;

DOI: 10.1021/acs.organomet.6b00655
Organometallics XXXX, XXX, XXX−XXX

Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203. (d) Bunel, E.; Burger, B. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 976. (e) Booij, M.; Kiers, N. H.; Meetsma, A.; Teuben, J. H.; Smeets, W. J. J.; Spek, A. L. *Organometallics* **1989**, *8*, 2454.

(19) Early transition metal catalyzed C(sp^2)−H functionalization: (a) Jordan, R. F.; Taylor, D. F. *J. Am. Chem. Soc.* **1989**, *111*, 778. (b) Deelman, B.-J.; Stevels, W. M.; Teuben, J. H.; Lakin, M. T.; Spek, A. L. *Organometallics* **1994**, *13*, 3881. (c) Ringelberg, S. N.; Meetsma, A.; Hessen, B.; Teuben, J. H. *J. Am. Chem. Soc.* **1999**, *121*, 6082. (d) Guan, B.-T.; Hou, Z. *J. Am. Chem. Soc.* **2011**, *133*, 18086. (e) Kaneko, H.; Nagae, H.; Tsurugi, H.; Mashima, K. *J. Am. Chem. Soc.* **2011**, *133*, 19626. (f) Oyamada, J.; Nishiura, M.; Hou, Z. *Angew. Chem., Int. Ed.* **2011**, *50*, 10720. (g) Song, G.; O, W. W. N.; Hou, Z. *J. Am. Chem. Soc.* **2014**, *136*, 12209. (h) Nagae, H.; Shibata, Y.; Tsurugi, H.; Mashima, K. *J. Am. Chem. Soc.* **2015**, *137*, 640. (i) Song, G.; Wang, B.; Nishiura, M.; Hou, Z. *Chem. - Eur. J.* **2015**, *21*, 8394. (j) Shi, X.; Nishiura, M.; Hou, Z. *J. Am. Chem. Soc.* **2016**, *138*, 6147. (k) Song, G.; Luo, G.; Oyamada, J.; Luo, Y.; Hou, Z. *Chem. Sci.* **2016**, *7*, 5265.

(20) Early transition metal mediated and catalyzed C(sp^3)−H alkylation: (a) Heeres, H. J.; Heeres, A.; Teuben, J. H. *Organometallics* **1990**, *9*, 1508. (b) Guram, A. S.; Jordan, R. F.; Taylor, D. F. *J. Am. Chem. Soc.* **1991**, *113*, 1833. (c) Guram, A. S.; Swenson, D. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1992**, *114*, 8991. (d) Sadow, A. D.; Tilley, T. D. *J. Am. Chem. Soc.* **2003**, *125*, 7971. (e) Fontaine, F.-G.; Tilley, T. D. *Organometallics* **2005**, *24*, 4340. (f) Norambuena, V. F. Q.; Heeres, A.; Heeres, H. J.; Meetsma, A.; Teuben, J. H.; Hessen, B. *Organometallics* **2008**, *27*, 5672. (g) Oyamada, J.; Hou, Z. *Angew. Chem., Int. Ed.* **2012**, *51*, 12828. (h) Guan, B.-T.; Wang, B.; Nishiura, M.; Hou, Z. *Angew. Chem., Int. Ed.* **2013**, *52*, 4418.

(21) Early transition metal catalyzed aminoalkylation via C(sp^3)−H bond activation: (a) Herzon, S. B.; Hartwig, J. F. *J. Am. Chem. Soc.* **2007**, *129*, 6690. (b) Eisenberger, P.; Ayinla, R. O.; Lauzon, J. M. P.; Schafer, L. L. *Angew. Chem., Int. Ed.* **2009**, *48*, 8361. (c) Prochnow, I.; Zark, P.; Muller, T.; Doye, S. *Angew. Chem., Int. Ed.* **2011**, *50*, 6401. (d) Dorfler, J.; Doye, S. *Angew. Chem., Int. Ed.* **2013**, *52*, 1806. (e) Garcia, P.; Lau, Y. Y.; Perry, M. R.; Schafer, L. L. *Angew. Chem., Int. Ed.* **2013**, *52*, 9144. (f) Chong, E.; Brandt, J. W.; Schafer, L. L. *J. Am. Chem. Soc.* **2014**, *136*, 10898. (g) Dorfler, J.; Preuß, T.; Schischko, A.; Schmidtmann, M.; Doye, S. *Angew. Chem., Int. Ed.* **2014**, *53*, 7918. (h) Manßen, M.; Lauterbach, N.; Dorfler, J.; Schmidtmann, M.; Saak, W.; Doye, S.; Beckhaus, R. *Angew. Chem., Int. Ed.* **2015**, *54*, 4383. (i) Nako, A. E.; Oyamada, J.; Nishiura, M.; Hou, Z. *Chem. Sci.* **2016**, *7*, 6429.

(22) Catalytic C(sp^3)−H alkenylation by late transition metals: (a) Liu, B.; Zhou, T.; Li, B.; Xu, S.; Song, H.; Wang, B. *Angew. Chem., Int. Ed.* **2014**, *53*, 4191. (b) Li, M.; Yang, Y.; Zhou, D.; Wan, D.; You, J. *Org. Lett.* **2015**, *17*, 2546. (c) Maity, S.; Agasti, S.; Earsad, A. M.; Hazra, A.; Maiti, D. *Chem. - Eur. J.* **2015**, *21*, 11320. (d) Sen, M.; Emayavaramban, B.; Barsu, N.; Premkumar, J. R.; Sundararaju, B. *ACS Catal.* **2016**, *6*, 2792. (e) Xu, J.-W.; Zhang, Z.-Z.; Rao, W.-H.; Shi, B.-F. *J. Am. Chem. Soc.* **2016**, *138*, 10750. Intermolecular C(sp^3)−H alkenylation at the α-position to nitrogen: (f) Sakaguchi, S.; Kubo, T.; Ishii, Y. *Angew. Chem., Int. Ed.* **2001**, *40*, 2534. (g) Tsuchikama, K.; Kasagawa, M.; Endo, K.; Shibata, T. *Org. Lett.* **2009**, *11*, 1821. Intramolecular C(sp^3)−H alkenylation: (h) Odedra, A.; Datta, S.; Liu, R.-S. *J. Org. Chem.* **2007**, *72*, 3289. (i) Tobisu, M.; Nakai, H.; Chatani, N. *J. Org. Chem.* **2009**, *74*, 5471. (j) Vadola, P. A.; Sames, D. *J. Am. Chem. Soc.* **2009**, *131*, 16525. (k) Jurberg, I. D.; Odabachian, Y.; Gagosz, F. *J. Am. Chem. Soc.* **2010**, *132*, 3543.

(23) Tsurugi, H.; Yamamoto, K.; Mashima, K. *J. Am. Chem. Soc.* **2011**, *133*, 732.

(24) Previous examples of benzyl migration from a group 4 metal center to imine-based ligands: (a) Knight, P. D.; Clarke, A. J.; Kimberley, B. S.; Jackson, R. A.; Scott, P. *Chem. Commun.* **2002**, 352. (b) Tsurugi, H.; Yamagata, T.; Tani, K.; Mashima, K. *Chem. Lett.* **2003**, *32*, 756. (c) Tsurugi, H.; Matsuo, Y.; Yamagata, T.; Mashima, K. *Organometallics* **2004**, *23*, 2797. (d) Mashima, K.; Ohnishi, R.; Yamagata, T.; Tsurugi, H. *Chem. Lett.* **2007**, *36*, 1420. (e) De Waele, P.; Jazdzewski, B. A.; Klosin, J.; Murray, R. E.; Theriault, C. N.; Vosejpka, P. C.; Petersen, J. L. *Organometallics* **2007**, *26*, 3896. (f) Tsurugi, H.; Ohnishi, R.; Kaneko, H.; Panda, T. K.; Mashima, K. *Organometallics* **2009**, *28*, 680. (g) Thomson, R. K.; Schafer, L. L. *Organometallics* **2010**, *29*, 3546.

(25) Examples of cationic group 4 benzyl complexes (also including characterization of insertion reactions into cationic group 4 alkyl bonds): (a) Bochmann, M.; Lancaster, S. J. *Organometallics* **1993**, *12*, 633. (b) Bochmann, M.; Lancaster, S. J.; Hursthouse, M. B.; Malik, K. M. A. *Organometallics* **1994**, *13*, 2235. (c) Pellecchia, C.; Grassi, A.; Zambelli, A. *Organometallics* **1994**, *13*, 298. (d) Bei, X.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1997**, *16*, 3282. (e) Horton, A. D.; de With, J. *Organometallics* **1997**, *16*, 5424. (f) Amor, F.; Butt, A.; du Plooy, K. E.; Spaniol, T. P.; Okuda, J. *Organometallics* **1998**, *17*, 5836. (g) Bouwkamp, M.; van Leusen, D.; Meetsma, A.; Hessen, B. *Organometallics* **1998**, *17*, 3645. (h) Warren, T. H.; Schrock, R. R.; Davis, W. M. *Organometallics* **1998**, *17*, 308. (i) Gauvin, R. M.; Osborn, J. A.; Kress, J. *Organometallics* **2000**, *19*, 2944. (j) Carpentier, J.-F.; Martin, A.; Swenson, D. C.; Jordan, R. F. *Organometallics* **2003**, *22*, 4999. (k) Lavanant, L.; Silvestru, A.; Faucheux, A.; Toupet, L.; Jordan, R. F.; Carpentier, J.-F. *Organometallics* **2005**, *24*, 5604. (l) Beckerle, K.; Manivannan, R.; Spaniol, T. P.; Okuda, J. *Organometallics* **2006**, *25*, 3019. (m) Lian, B.; Beckerle, K.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **2007**, *46*, 8507. (n) Agapie, T.; Henling, L. M.; DiPasquale, A. G.; Rheingold, A. L.; Bercaw, J. E. *Organometallics* **2008**, *27*, 6245. (o) Lee, H.; Nienkemper, K.; Jordan, R. F. *Organometallics* **2008**, *27*, 5075. (p) Nienkemper, K.; Lee, H.; Jordan, R. F.; Ariafard, A.; Dang, L.; Lin, Z. *Organometallics* **2008**, *27*, 5867. (q) Chen, C.; Lee, H.; Jordan, R. F. *Organometallics* **2010**, *29*, 5373. (r) Munha, R. F.; Antunes, M. A.; Alves, L. G.; Veiros, L. F.; Fryzuk, M. D.; Martins, A. M. *Organometallics* **2010**, *29*, 3753. (s) Dagorne, S.; Bellemin-Laponnaz, S.; Romain, C. *Organometallics* **2013**, *32*, 2736.

(26) Examples of borate anion coordination to a cationic metal center: (a) Horton, A. D.; Frijns, J. H. G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1152. (b) Horton, A. D.; de With, J. *Chem. Commun.* **1996**, 1375. (c) Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A. *Inorg. Chem.* **1980**, *19*, 1191.

(27) See the Supporting Information.

(28) Calculations of Jordan's C−H hydroarylation of propene with 2-picoline with and without H_2: (a) Bi, S.; Lin, Z.; Jordan, R. F. *Organometallics* **2004**, *23*, 4882. Related group 3 system for C−H hydroarylation of olefins with pyridines via C(sp^2)−H activation: (b) Luo, G.; Luo, Y.; Qu, J.; Hou, Z. *Organometallics* **2012**, *31*, 3930.

(29) (a) Zucchini, U.; Albizzati, E.; Giannini, U. *J. Organomet. Chem.* **1971**, *26*, 357. (b) Felten, J. J.; Anderson, W. P. *J. Organomet. Chem.* **1972**, *36*, 87.

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