C–H Alkylation

DOI: 10.1002/ange.201208867

Yttrium-Catalyzed Addition of Benzylic C–H Bonds of Alkyl Pyridines to Olefins**

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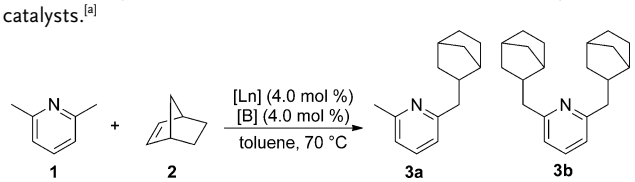
It is well-known that the benzylic C–H bonds of α-alkyl pyridines react with electrophiles to form C–C bonds in a nucleophilic fashion.[1–6] However, the substrate scope reported so far for this transformation is mostly limited to highly reactive polar electrophiles, such as halides,[2,3] carbonyl groups,[1,4] imines,[5] and enones.[6] Reactions of simple olefins with the benzylic C–H bonds of alkyl pyridines remain scarce. In particular, the catalytic addition of the benzylic C–H bond of alkyl pyridines to a simple olefin has not been reported previously.[7,8] Therefore, the search for new catalysts for this reaction is of much interest and importance because it would provide a useful protocol for the efficient synthesis of various alkylated pyridine derivatives, which are important structural motifs often found in natural products, pharmaceuticals, ligands, and functional materials. We report herein that cationic half-sandwich yttrium alkyl complexes can catalyze the addition of benzylic C–H bonds of various 2,6-dialkyl-substituted pyridines to a variety of olefins such as ethylene, 1-hexene, styrenes, and 1,3-conjugated dienes,[9,10] to afford new alkylated and allylated pyridine derivatives.

From our previous studies on rare-earth-catalyzed alkylation of the C_{sp^2}–H bond of pyridines with olefins,[9] it occurred to us that the scandium catalyst $[C_5Me_5ScR_2]$/$B(C_6F_5)_3$ ($R = Me_2N\text{-}2\text{-}CH_2C_6H_4$), which showed excellent activity and selectivity for the *ortho*-C_{sp^2}–H alkylation of 2-methylpyridine, could catalyze the benzylic C_{sp^3}–H alkylation of 2,6-lutidine in the reaction with norbornene. This reaction occurred under similar reaction conditions to the C_{sp^2}–H alkylation although the conversion was rather low (ca. 5%; Table 1, entry 1). To achieve the benzylic C–H alkylation more efficiently, we then examined the use of various catalysts in this reaction (Scheme 1), and we were pleased to find that the yttrium-based catalyst $[C_5Me_5YR_2]$/$[Ph_3C][B(C_6F_5)_4]$ showed much higher activity than $[C_5Me_5ScR_2]$/$B(C_6F_5)_3$, thus affording the benzylic C–H alkylation product **3a** in 65% yield (Table 1 entry 5). When $[C_5Me_5YR_2]$ was replaced by the smaller complex $[C_5H_5YR_2]$, an even higher yield (89%) was obtained (Table 1, entry 15). More remarkably, when 4 equivalents of norbornene were used, the alkylation took place at both methyl groups to give 2,6-bis(norbornylmethyl)pyridine **3b** quantitatively (Table 1, entry 16).

The reaction of 2,6-lutidine with various olefins was then examined, and some representative results are summarized in Table 2. In the presence of $[C_5H_5YR_2]$/$[Ph_3C][B(C_6F_5)_4]$, the

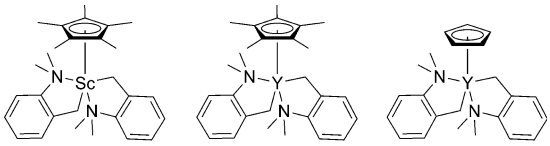
Table 1: Benzylic C–H addition of 2,6-lutidine to norbornene by various catalysts.[a]



1 + 2 → 3a + 3b

Entry	[Ln][b]	[B]	*t* [h]	Yield **3a** [%][c]	Yield **3b** [%]
1	$[C_5Me_5ScR_2]$	$B(C_6F_5)_3$	24	5	–
2	$[C_5Me_5YR_2]$	$B(C_6F_5)_3$	24	0	–
3	$[C_5Me_5ScR_2]$	$[Ph_3C][B(C_6F_5)_4]$	24	5	–
4	$[C_5Me_5YR_2]$	$[Ph_3C][B(C_6F_5)_4]$	24	40	–
5	$[C_5Me_5YR_2]$	$[Ph_3C][B(C_6F_5)_4]$	48	65	–
6	$[C_5Me_5YR_2]$	–	24	0	–
7	–	$[Ph_3C][B(C_6F_5)_4]$	24	0	–
8	$[C_5Me_5LaR_2]$	$[Ph_3C][B(C_6F_5)_4]$	24	0	–
9	$[C_5Me_5SmR_2]$	$[Ph_3C][B(C_6F_5)_4]$	24	10	–
10	$[C_5Me_5GdR_2]$	$[Ph_3C][B(C_6F_5)_4]$	24	23	–
11	$[C_5Me_5LuR_2]$	$[Ph_3C][B(C_6F_5)_4]$	24	8	–
12[d]	$[C_5Me_5YR_2]$	$[Ph_3C][B(C_6F_5)_4]$	24	25	–
13	$[C_5Me_5SiMe_3YR_2]$	$[Ph_3C][B(C_6F_5)_4]$	24	31	–
14	$[C_5Me_4HYR_2]$	$[Ph_3C][B(C_6F_5)_4]$	24	49	–
15	$[C_5H_5YR_2]$	$[Ph_3C][B(C_6F_5)_4]$	24	89(85)[e]	–
16[f]	$[C_5H_5YR_2]$	$[Ph_3C][B(C_6F_5)_4]$	24	–	99

[a] Reactions were carried out with 0.75 mmol of 2,6-lutidine and 0.5 mmol of norbornene in 2 mL of toluene at 70°C, unless otherwise noted. [b] [Ln] = Half-sandwich rare-earth dialkyl complex; $R = Me_2N\text{-}2\text{-}CH_2C_6H_4$. [c] Yields of **3a** were determined by GC with tridecane as an internal standard. [d] Reaction was carried out at 50°C. [e] Yield of the isolated product in parentheses. [f] Reaction was carried out with 0.5 mmol of 2,6-lutidine and 2 mmol of norbornene.



$[C_5Me_5ScR_2]$ $[C_5Me_5YR_2]$ $[C_5H_5YR_2]$

Scheme 1. Some representative half-sandwich rare-earth dialkyl complexes.

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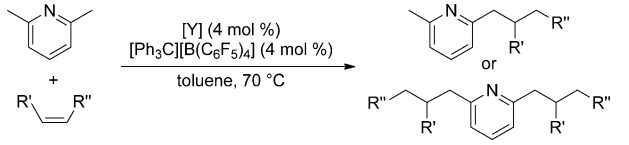
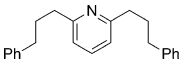
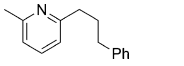
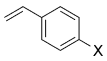
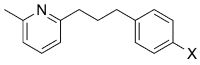
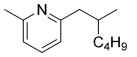
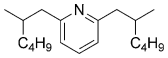
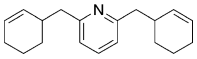
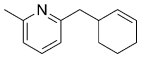
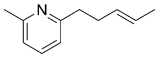
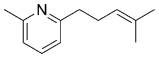
[**] This work was partly supported by a Grant-in-Aid for Scientific Research (S) (21225004) from JSPS and the Key Project of International Cooperation of NSFC (20920102030). Dr. Jianhua Cheng and Dr. Masanori Takimoto are gratefully appreciated for helpful discussions.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201208867.

Table 2: Catalytic benzylic C–H bond addition of 2,6-lutidine to various olefins.[a]



Entry	Olefin	[Y]	*t* [h]	Product	Yield [%][b]
1		$[C_5H_5YR_2]$	24		79
2		$[C_5Me_5YR_2]$	24		70
					
3	X = Me	$[C_5Me_5YR_2]$	24	X = Me	67
4	X = *t*Bu	$[C_5Me_5YR_2]$	24	X = *t*Bu	67
5	X = F	$[C_5Me_5YR_2]$	24	X = F	63
6	X = Cl	$[C_5Me_5YR_2]$	24	X = Cl	74
7[c]		$[C_5Me_5YR_2]$	24		69
8[c]		$[C_5Me_5YR_2]$	72		92
9		$[C_5H_5YR_2]$	24		97
10[d]		$[C_5H_5YR_2]$	24		65
11[d]		$[C_5H_5YR_2]$	24		41
12[d]		$[C_5H_5YR_2]$	24		51

[a] Reactions were carried out with 0.5 mmol of 2,6-lutidine and 2 mmol of olefin in 2 mL of toluene, unless otherwise noted. R = Me_2N-2-$CH_2C_6H_4$. [b] Yield of the isolated product. [c] 15 mmol of 1-hexene was used. [d] 0.5 mmol of olefin and 0.75 mmol of 2,6-lutidine were used.

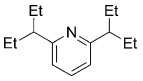
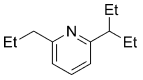
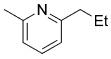
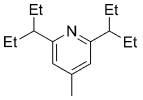
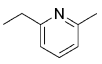
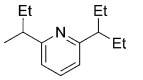
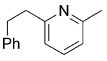
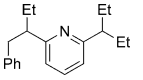
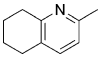
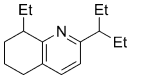
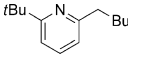
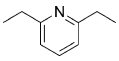
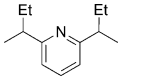
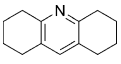
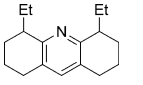
reaction between 2,6-lutidine and 4 equivalents of styrene gave the dialkylation product in 79% yield upon isolation (Table 2, entry 1). Interestingly, when the more sterically demanding complex $[C_5Me_5YR_2]$ was used, the monoalkylation product was obtained as the major product (70%; Table 2, entry 2). Substituted styrenes are also suitable for this reaction (Table 2, entries 3–6); both fluoro- and chloro-substituents are compatible with the catalyst. In all of these reactions, only the linear alkylation products were obtained.

In the reaction of 2,6-lutidine with 1-hexene catalyzed by $[C_5Me_5YR_2]/[Ph_3C][B(C_6F_5)_4]$, the monoalkylation product was isolated in 69% yield when the reaction was quenched after 24 h (Table 2, entry 7). However, when the reaction time was extended to 72 h, the dialkylation product was obtained in 92% yield (Table 2, entry 8). In this case, the branched alkylation products were obtained exclusively. A large excess amount of 1-hexene was required to obtain high yields of the alkylation products, probably because of the low activity of α-olefins toward the yttrium catalyst, as observed previously in polymerization studies.[10]

The addition of the benzylic C–H bond of 2,6-lutidine to 1,3-cyclohexadiene could also take place in the presence of $[C_5H_5YR_2]/[Ph_3C][B(C_6F_5)_4]$. The diallylation product was obtained almost quantitatively, when an excess amount of 1,3-cyclohexadiene (4 equivalents) was used (Table 2, entry 9). If a smaller amount of 1,3-cyclohexadiene (0.67 equivalents) was used, the monoallylation product could be isolated as the major product (65%; Table 2, entry 10). Under similar reaction conditions, the reaction of 2,6-lutidine with butadiene or isoprene gave the monoallylation product as the only separable product (Table 2, entries 11–12). Formation of oligomer products was also observed, obviously owing to successive insertion of the dienes.

Representative results of the reactions between ethylene and various pyridine substrates are summarized in Table 3. In the presence of 4 mol% of $[C_5H_5YR_2]/[Ph_3C][B(C_6F_5)_4]$ under 1.5 atm. ethylene, diethylation at each of the two methyl groups in 2,6-lutidine occurred selectively to afford the tetraethylation product in 97% yield upon isolation (Table 3, entry 1). In contrast, when the more sterically demanding catalyst $[C_5Me_5YR_2]$ was used instead of $[C_5H_5YR_2]$, the triethylation product was obtained in 92% yield under the same reaction conditions (Table 3, entry 2). When a smaller amount of ethylene (injected by syringe) was added to 2,6-lutidine (molar ratio = 0.5:0.75) in the presence

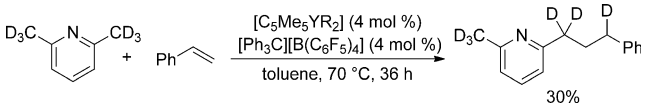
Table 3: Catalytic benzylic C–H bond addition of alkyl pyridines to ethylene.[a]

Entry	Alkyl Pyridine	[Y]	*t* [h]	Product	Yield [%][b]
1		$[C_5H_5YR_2]$	6		97
2		$[C_5Me_5YR_2]$	4		92
3[c]		$[C_5Me_5YR_2]$	24		68
4		$[C_5H_5YR_2]$	6		98
5		$[C_5H_5YR_2]$	3		99
6		$[C_5H_5YR_2]$	12		95
7		$[C_5H_5YR_2]$	12		95
8		$[C_5Me_5YR_2]$	12		58
9		$[C_5H_5YR_2]$	2		93
10[d]		$[C_5H_5YR_2]$	1		97

[a] Reactions were carried out with 4 mol% of [Y], 4 mol% of $[Ph_3C][B(C_6F_5)_4]$, 0.5 mmol of an alkyl pyridine in 2 mL of toluene at 70 °C under 1.5 atm. of ethylene, unless otherwise noted. R = Me_2N-2-$CH_2C_6H_4$. [b] Yield of the isolated product. [c] 0.5 mmol of ethylene and 0.75 mmol of 2,6-lutidine were used. [d] Mixture of *cis*- and *trans*-ethylation products with a ratio of 1.6:1.

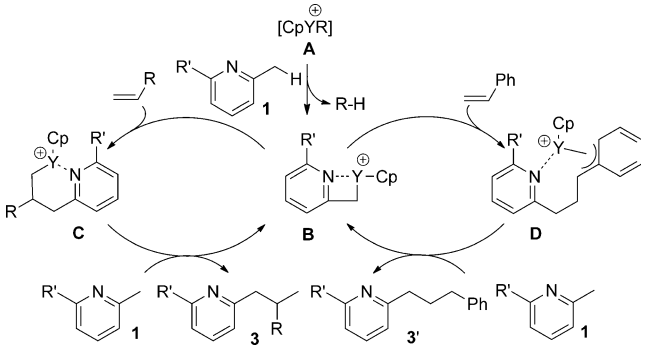
of $[C_5Me_5YR_2]/[Ph_3C][B(C_6F_5)_4]$, the monoethylation product was obtained in 68% yield (Table 3, entry 3). In the case of 2,4,6-trimethylpyridine, the ethylation took place only at the *ortho*-methyl C–H bonds to give the tetraethylation product in 98% isolated yield upon isolation (Table 3, entry 4); no reaction was observed at the more acidic *para*-methyl group. These results suggest that an interaction between the nitrogen atom in the pyridine ring and the catalyst metal center is essential for the present regioselective C–H alkylation reaction. In the reaction of a pyridine compound having one methyl group and one methylene unit at the *ortho* positions, diethylation took place at the methyl group, whereas the monoethylation occurred selectively at the methylene unit (Table 3, entries 5–7). In the case of 2-*tert*-butyl-6-methylpyridine, successive insertion of ethylene at the methyl group took place to give a mixture of multi-insertion products, from which the butylation product was isolated in 58% yield (Table 3, entry 8). The ethylations of 2,6-diethylpyridine and octahydroacridine with ethylene catalyzed by $[C_5H_5YR_2]/[Ph_3C][B(C_6F_5)_4]$ took place selectively at the two *ortho* methylene units (Table 3, entries 9–10).

The reaction of $[D_6]$2,6-lutidine with styrene afforded the corresponding deuterated alkylation product (Scheme 2). A kinetic isotope effect of $k_H/k_D = 3.7$ was observed (in comparison with 2,6-lutidine, see the Supporting Information), thus suggesting that the C–H bond cleavage (deprotonation) could be the rate-determining step in the present catalytic reaction.



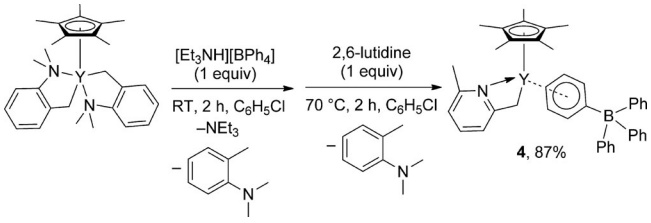
Scheme 2. Benzylic C–D bond addition of $[D_6]$2,6-lutidine to styrene.

A possible reaction mechanism is shown in Scheme 3. A cationic alkyl species such as **A** could be easily generated by treatment of $[CpYR_2]$ with one equivalent of $[Ph_3C][B(C_6F_5)_4]$.[10] Coordination of a 2,6-dialkyl pyridine **1** to the yttrium atom in **A** would assist C–H activation (deprotonation) of an *ortho* benzylic C–H bond of the pyridine compound to give **B**. Insertion of a 1-alkene into the $Y–CH_2$ bond in **B** in a 1,2-fashion should afford **C**, which upon deprotonation of another molecule of the pyridine compound would give the branched alkylation product **3** and regenerate **B**. In the case of styrene, the 2,1-insertion could be favored to give the benzylic species **D**, thus affording the linear alkylation product **3′** after protonation with pyridine **1**.



Scheme 3. A possible reaction mechanism.

In an attempt to isolate a possible reaction intermediate such as **B**, the reaction of 2,6-lutidine with a 1:1 mixture of $[C_5H_5Y(Me_2N\text{-}2\text{-}CH_2C_6H_4)_2]$ and $[Ph_3C][B(C_6F_5)_4]$ was performed, and after filtration and washing with benzene we obtained a yellow powder, which was determined to be the cationic species $[C_5H_5Y(2\text{-}CH_2\text{-}6\text{-}CH_3C_5H_3N)][B(C_6F_5)_4]$ by ^{1}H NMR spectroscopy.[11] The isolated yellow powder also catalyzed the addition of 2,6-lutidine to norbornene (see Table 1, entry 15). No decomposition was observed in $[D_8]$toluene at 70 °C in 24 h. In an analogous reaction using a 1:1 mixture of $[C_5Me_5Y(Me_2N\text{-}2\text{-}CH_2C_6H_4)_2]$ and $[Et_3NH][BPh_4]$, the structurally characterizable ion-pair complex $[C_5Me_5Y(2\text{-}CH_2\text{-}6\text{-}CH_3C_5H_3N)][(\mu\text{-}\eta^6\text{-}Ph)BPh_3]$ (**4**) was isolated (Scheme 4; Figure 1).[11]



Scheme 4. Isolation of a cationic yttrium picolyl complex.

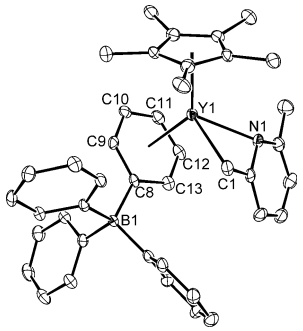


Figure 1. ORTEP drawing of **4** with thermal ellipsoids set at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances [Å]: Y1–C1 2.439(5), Y1–N1 2.343(4), Y1–C8 2.921(7), Y1–C9 2.804(6), Y1–C10 2.761(5), Y1–C11 2.763(6), Y1–C12 2.792(5), Y1–C13 2.855(6).[12]

In summary, the combination of a half-sandwich yttrium dialkyl complex such as $[C_5H_5YR_2]$ or $[C_5Me_5YR_2]$ with $[Ph_3C][B(C_6F_5)_4]$ can serve as an excellent catalyst for the *ortho*-selective benzylic C–H addition of various dialkyl pyridines to a variety of olefins such as ethylene, 1-hexene, styrenes, and 1,3-conjugated dienes, leading to formation of a new family of alkylated and allylated pyridine derivatives. The cationic half-sandwich yttrium picolyl species, such as $[CpY(2\text{-}CH_2\text{-}6\text{-}CH_3C_5H_3N)]^+$, has been confirmed to be a key active species in this transformation.

Received: November 5, 2012
Revised: December 2, 2012
Published online: March 19, 2013

Keywords: alkenes · alkyl pyridines · C–H alkylation · homogeneous catalysis · yttrium

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[11] See the Supporting Information for details.

[12] CCDC 924178 (**4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

