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Aminomethylation Reaction of *ortho*-Pyridyl C−H Bonds Catalyzed by Group 3 Metal Triamido Complexes

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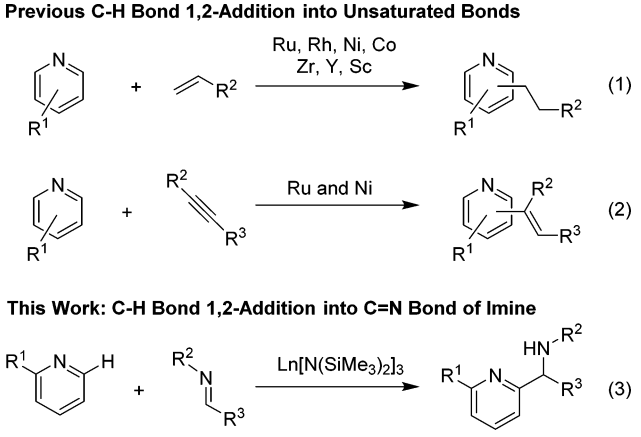
Supporting Information

ABSTRACT: Tris[*N*,*N*-bis(trimethylsilyl)amido] complexes of group 3 metals, especially yttrium and gadolinium, served as catalysts for *ortho*-C−H bond addition of pyridine derivatives and N-heteroaromatics into the C═N double bond of nonactivated imines to afford the corresponding aminomethylated products. Addition of catalytic amounts of secondary amines, such as dibenzylamine, dramatically improved the catalytic activity through the formation of a mixed ligated complex such as $[(Me_3Si)_2N]_2Y(NBn_2)(THF)$ (**4**). Furthermore, kinetic studies using the isolated complex **4** provided a plausible reaction mechanism by which coordination of two pyridine derivatives afforded a penta-coordinated species as a key step.

Pyridine derivatives are important structural motifs that exist in a number of natural products, medicinal agents, ligands, and functional materials.[1] Despite the development of several synthetic methods to date, the recent trend toward transition-metal-catalyzed C−H bond activation followed by functionalization is regarded as the most direct synthetic protocol to introduce functional groups on the pyridine skeleton in terms of atom and step economical processes.[2] Upon applying late transition-metal catalysts, the first step is typical oxidative addition of the C−H bond of the pyridine onto a coordinatively unsaturated low-valent metal center to generate a pyridyl-hydride-metal species, (py)M(H), to which sequential 1,2-addition reaction of nonpolar C═C double bonds and C≡C triple bonds to a hydride-metal moiety affords pyridyl-metal species with M-alkyl and alkenyl bonds, respectively, and then reductive elimination produces alkyl- and alkyenyl-substituted pyridine derivatives (Scheme 1).[2−6] Similarly, some early transition-metal complexes are reported to proceed via a σ-bond metathesis reaction with pyridine to give the corresponding pyridyl-metal species, to which a nonpolar C═C double bond is inserted to give alkylpyridine compounds catalytically (Scheme 1, eq 1).[7,8]

In contrast, although it is perceived that the C−H bond addition to C═X bond (X = N, O) of imines and carbonyl compounds expands the substrate scope to provide heteroatom-containing pyridine derivatives, no such catalytic coupling reaction has been achieved.[9−11] Such limitation is attributed to the undesired regioselectivity of C═X bond insertion into the hydride-metal moiety to form new C−C bonds for late transition-metal complexes. On the other hand, although it was reported that a M−N bond of groups 3 and 4 metals activates the C−H bond of pyridines through a σ-bond metathesis mechanism in a stoichiometric manner,[12] an addition reaction of the resulting pyridyl-metal species of groups 3 and 4 metals into a polar C═N double bond of imines in both a stoichiometric and catalytic manner has not been achieved and remains particularly challenging. We thus anticipated that amido complexes of group 3 metals could potentially act as catalysts by activating the *ortho*-C−H bond of pyridine derivatives by their M−N bonds and reproducing the M−N bonds by subsequent insertion of the resulting pyridyl-metal species into the C═N double bond of imines. Herein, we report the first catalytic addition reaction of pyridine derivatives to nonactivated imines as mediated by triamido complexes of group 3 metals (Scheme 1, eq 3).

Scheme 1. Catalytic Pyridyl C−H Bond Addition Reactions into Unsaturated Bonds



When 2-phenylpyridine (**1a**) was treated with *N*,1-dicyclohexylmethanimine (**2a**) (2 equiv) in the presence of $Y[N(SiMe_3)_2]_3$ (10 mol %) in C_6D_6 at 100 °C for 24 h, the corresponding pyridine aminomethylated product **3aa** was obtained in 46% yield (entry 1). In this aminomethylation reaction, the phenyl ring of 2-phenylpyridine did not react, but the *ortho*-position of the pyridine ring of 2-phenylpyridine was regioselectively activated.[13] A noteworthy difference was that late transition-metal complexes predominantly assisted the catalytic aminomethylation reaction with imines at the *ortho*-position of the phenyl ring of 2-phenylpyridine, where the pyridine moiety worked as a directing group to the metal center.[14] For the test reaction under the same conditions, we examined various rare-

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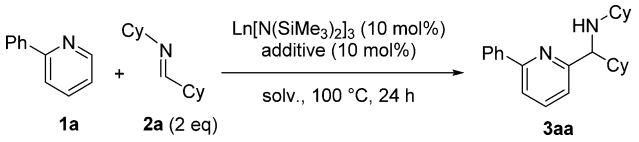
earth metal amidos, $M[N(SiMe_3)_2]_3$ (M = Yb, Gd, Sm, Nd, La), as catalysts. The ionic size of lanthanides affected the catalytic performance: lanthanide complexes of smaller (Yb) and larger (La) ionic size exhibited almost the same lower catalytic activities (16% and 20% yield, respectively), while complexes of ionic radii similar to yttrium ion exhibited moderate activities (41−59%, entries 3−5) equal to or better than that of the yttrium complex. Among them, $Gd[N(SiMe_3)_2]_3$ was the best catalyst (59%, entry 3). Thus, moderately sized lanthanide metals might be required to show enough catalytic activity.

We then investigated the additive effects of secondary amines because product **3aa** is one of secondary amines. Addition of tetramethylpiperidine (HTMP) and dicyclohexylamine ($HNCy_2$), both of which are bulky secondary amines typically used for activating C−H bonds,[12] to the reaction using $Gd[N(SiMe_3)_2]_3$ slightly increased the yield of **3aa** to 65% and 64%, respectively (entries 7 and 8). The addition of dibenzylamine ($HNBn_2$) to the reaction mixture of $Gd[N(SiMe_3)_2]_3$ effectively accelerated the aminomethylation reaction to produce **3aa** in 86% yield (entry 9). We further conducted the reaction under the conditions of $Gd[N(SiMe_3)_2]_3$ and dibenzylamine to reach 90% yield of **3aa** upon increasing the substrate concentration (entries 10 and 11). The same tendency was observed for the system of $Y[N(SiMe_3)_2]_3$ where $HNBn_2$ was the most effective.[13] Thus, dibenzylamine was selected as the best amine additive for this catalytic reaction.

Table 1. Screening of Catalysts

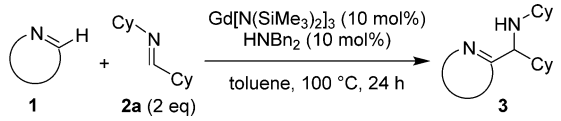


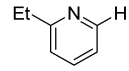
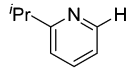
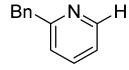
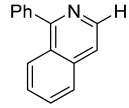
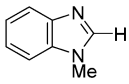
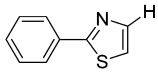
entry	Ln	solv.	conc., M	additive	yield[a] (%)
1	Y	C_6D_6	0.2	–	46
2	Yb	C_6D_6	0.2	–	16
3	Gd	C_6D_6	0.2	–	59
4	Sm	C_6D_6	0.2	–	43
5	Nd	C_6D_6	0.2	–	41
6	La	C_6D_6	0.2	–	20
7	Gd	C_6D_6	0.2	HTMP	65
8	Gd	C_6D_6	0.2	$HNCy_2$	64
9	Gd	C_6D_6	0.2	$HNBn_2$	86
10	Gd	Tol	0.2	$HNBn_2$	87
11	Gd	Tol	0.5	$HNBn_2$	90[b]

[a]^{1}H NMR yield 1,1,2,2-Cl_4-ethane was used as internal standard. [b]Isolated yield.

Under the optimized reaction conditions, we conducted the aminomethylation of heteroaromatic compounds **1b−1g** with the imine **2a**, and the results are summarized in Table 2. A series of 2-alkylpyridines **1b−1d** was converted to the corresponding coupling products **3ba−3da** in moderate to good yields (entries 1−3). In these cases, no coupling reaction was observed at the C(sp^3)-H bond of the alkyl moiety, even at the benzylic position.[8c,15] When 1-phenylisoquinoline was used as a substrate, a C−H bond of the isoquinoline ring was activated at the 3-position to afford **3ea** in 70% yield (entry 4). *N*-Methylbenzimidazole reacted efficiently at the 2-position to produce **3fa** in 94% yield (entry 5), whereas related benzoazoles, benzoxazole and benzothiazole, were not applicable in this reaction. The 4-position C−H bond of 2-phenylthiazole reacted with **2a** to form an aminomethylated product **3ga** in 67% yield (entry 6).

Table 2. Scope and Limitation of Pyridine Derivatives and N-Heteroaromatics

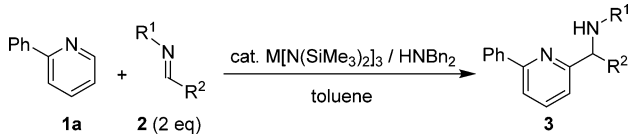


entry	*N*-heteroaromatics		product	yield[a]
1		(**1b**)	**3ba**	70
2		(**1c**)	**3ca**	81
3[b]		(**1d**)	**3da**	56
4[b]		(**1e**)	**3ea**	70
5[c]		(**1f**)	**3fa**	94
6		(**1g**)	**3ga**	67

[a]Isolated yield. [b]Reaction for 48 h. [c]5 mol % of [Gd] was used.

Secondary and tertiary alkyl groups as well as aryl groups were applicable as substituents at the imine-carbon and -nitrogen atoms of the substrates (Table 3). When isopropyl, 1-adamantyl, *tert*-butyl, 1-phenylethyl, and aryl groups were attached to the nitrogen atom of the imines, the corresponding aminoalkylated products **3ab−3af** were obtained in good yield (entries 1−5). Although the reaction with *N*-cyclohexylbenzylidenimine (**2j**) was slow and the product yield was moderate (entry 9), imines **2g−2i** having secondary alkyl groups at the imine carbon were

Table 3. Scope and Limitation of Imine Substrates



entry	R^1	R^2		product	yield[a] (%)
1[b,c]	^{i}Pr	Cy	(**2b**)	**3ab**	66
2[d,e]	Ad	Cy	(**2c**)	**3ac**	93
3[d,e]	^{t}Bu	Cy	(**2d**)	**3ad**	64
4[b,e]	CH(Me)Ph	Cy	(**2e**)	**3ae**	81
5[d,e]	4-OMe-2-Me-C_6H_3	Cy	(**2f**)	**3af**	81
6[d,e]	Cy	^{i}Pr	(**2g**)	**3ag**	57
7[d,e]	Cy	*c*-C_5H_9	(**2h**)	**3ah**	76
8[b,c]	Cy	$CHEt_2$	(**2j**)	**3ai**	60
9[d,e]	Cy	Ph	(**2j**)	***3aj***	35

[a]Isolated yield. [b]10 mol % of $Gd[N(SiMe_3)_2]_3/HNBn_2$ was used at 100 °C. [c]Reaction for 36 h. [d]20 mol % of $Y[N(SiMe_3)_2]_3/HNBn_2$ was used at 130 °C [e]Reaction for 96 h.

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efficiently transformed to the corresponding aminoalkylated products **3ag**–**3ai** (entries 6–8). In contrast, when imines having primary alkyl groups at the imine-nitrogen and -carbon atoms were applied to the reaction, the corresponding aminoalkylated products were obtained in low yield, probably due to the facile coordination of the reaction products to the metal center.

To gain insight into the reaction mechanism, yttrium complexes were used to monitor the reaction by ^{1}H NMR measurement,[13] as the Gd complex is paramagnetic. The reaction catalyzed by $Y[N(SiMe_3)_2]_3$ without any amine additives led to <10% yield of **3aa**, even after 10 h. In good accordance with the additive effects of $HNBn_2$ to enhance the catalytic activity, the reaction by $Y[N(SiMe_3)_2]_3$ and $HNBn_2$ proceeded smoothly even at the initial stage. Based on such clear evidence, we expected that a mixed-ligated yttrium amido complex might be generated as a catalytically active species. In fact, we mixed $Y[N(SiMe_3)_2]_3$ and $HNBn_2$ to give a complicated mixture, from which we could not isolate any identical yttrium compounds. Alternatively, when we treated $Y(CH_2SiMe_3)_3(THF)_2$ with 2 equiv of $HN(SiMe_3)_2$ and 1 equiv of $HNBn_2$, a mixed ligand complex, $[(Me_3Si)_2N]_2Y(NBn_2)(THF)$ (**4**), was isolated and crystallographically characterized (Figure 1). Remarkably, the

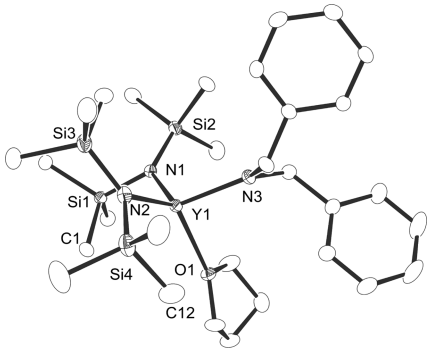


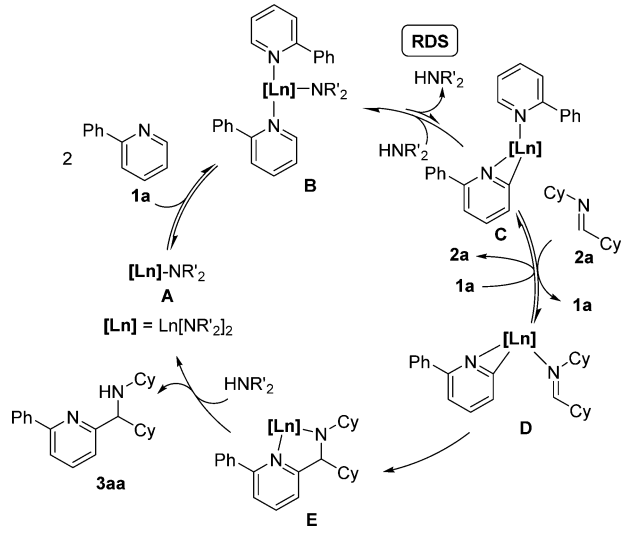
Figure 1. Molecular structure of complex **4** with 30% thermal ellipsoids. All H atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Y—N1, 2.251(2); Y—N2, 2.255(2); Y—N3, 2.1754(19); Y—Si1, 3.2559(15); Y—Si4, 3.3370(16); Y—N1—Si1, 109.59(10); Y—N1—Si2, 129.73(10); Y—N2—Si3, 123.41(11); Y—N2—Si4, 113.60(11).

isolated complex **4** became a catalyst with similar reaction profile as that of the in situ catalyst system of $Y[N(SiMe_3)_2]_3$ and $HNBn_2$.[13] While the presence of THF in the reaction mixture (up to 5 equiv based on catalyst) did not affect the product yield, the reaction in THF as the solvent resulted in low yield. Thus, the sterically less-hindered dibenzylamido ligand might open the active site by releasing THF, to which the substrates coordinated to induce the activation of the C–H bond followed by the insertion of imines.

With the isolated catalyst **4** in hand, we measured the reaction rate law in relation to the concentrations of catalyst **4**, 2-phenylpyridine (**1a**), and *N*,1-dicyclohexylmethanimine (**2a**). A first-order rate dependence on the catalyst concentration was observed over a 4-fold range, indicating that the active species was a monomeric species. The initial reaction rate did not depend on the concentration of imine **2a** in the range between 0.2 and 0.4 M, suggesting apparent zero-order dependence on the imine concentration up to half-lives; however, excess amounts of imine suppressed the reaction rate. Notably, the reaction showed a second-order rate dependence on the 2-phenylpyridine concentration. Thus, the reaction rate is presented as $[\mathbf{4}][\text{pyridines}]^2[\text{imine}]^0$. To gain insight into the mechanism, we performed a deuterium-labeling experiment using 2-phenylpyridine-d_9. The KIE value was 3.19, suggesting that C–H bond activation was involved at the rate-determining step. The rate of the consumption of 2-phenylpyridine catalyzed by **4** was also monitored by ^{1}H NMR spectroscopy over a temperature ranging from 89 to 110 °C under the optimized conditions shown in Table 2. Eyring kinetic analyses yielded the following activation parameters: $\Delta H^{\ddagger} = 48.8 \pm 1.5$ kJ mol^{-1}, $\Delta S^{\ddagger} = -153.9 \pm 4.0$ au, and $\Delta G^{\ddagger}(298\ \text{K}) = 94.6 \pm 2.7$ kJ mol^{-1}. The negative $\Delta S^{\ddagger}$ value is consistent with the highly ordered transition state involving the intrinsic coordination of two 2-phenylpyridine to the metal center.

Based on the isolation of $[(SiMe_3)_2N]_2YNBn_2(THF)$ (**4**) and kinetic study of the aminomethylation using the isolated complex **4**, we propose a plausible mechanism as shown in Scheme 2.

Scheme 2. Proposed Reaction Mechanism



Catalytic reaction of **1a** with **2a** using **4** is initiated by the coordination of 2 equiv of 2-phenylpyridine to the yttrium center of the mixed ligated triamido complex **A** derived by the dissociation of THF from **4** to form the penta-coordinated species **B**. The second-order rate dependence on the concentration of 2-phenylpyridine indicates the formation of **B** in this catalytic cycle. As model catalytically active species, we added pyridine (excess) and 2,2′-bipyridyl (1 equiv) to complex **4**. Isolation and structural characterization of tetra-coordinated and penta-coordinated $[(SiMe_3)_2N]_2YNBn_2(L)$ complexes (**5**: L = py, **6**: L = 2,2′-bipyridyl) suggests the coordination of 2 equiv of substrates to the metal center just before *ortho*-C–H bond activation.[13] *Ortho*-C–H bond activation of the pyridine moiety of **1a** by the amidometal moiety proceeds to form a η^2-pyridylmetal species **C** as the rate-determining step. The zero-order kinetics of the imine **2a** suggests that precoordination of **2a** is essential for the formation of **D**. The C–C bond formation between the η^2-pyridylmetal and the coordinated imine rapidly occurs to form **E**, and subsequent protonation by the amine regenerates the mixed ligated triamido complex species **A** and yields the aminomethylated product **3aa**. When the amino-alkylated product **3aa** was added to the reaction mixture (same amount to catalyst), the reaction rate was almost the same as that under normal conditions, suggesting that the catalytic cycle did

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not involve product inhibition. Bulky substituents at the nitrogen and carbon atoms of the aminoalkyl chain might lead to irreversible dissociation of the aminoalkylated products from the metal center.

In summary, we developed the first catalytic C−H bond addition of pyridine derivatives coupled with a nonactivated C═N double bond to afford aminomethylated products of pyridines using rather simple homoleptic rare-earth metal triamides. The catalytic activity was dramatically improved by adding a catalytic amount of dibenzylamine to generate a mixed ligated triamido complex that opened the coordination site for the substrate. Furthermore, several kinetic studies as well as the isolation of a mixed ligand triamido complex, $[(SiMe_3)_2N]_2YNBn_2(THF)$ (**4**) as a catalytically active species, provided a plausible reaction mechanism in which precoordination of two pyridine derivatives generating penta-coordinated species is assumed to be involved as a key step. Further development of this new catalytic reaction is ongoing in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, catalysts screening, NMR spectra, kinetics data and deuterium labeling experiments; CIF file giving for complexes **4**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) See some reviews (a) Bull, J. A.; Mousseau, J. J.; Pelletier, G.; Charette, A. B. *Chem. Rev.* **2012**, *112*, 2642−2713. (b) Hill, M. D. *Chem.—Eur. J.* **2010**, *16*, 12052−12062. (c) Campeau, L.-C.; Fagnou, K. *Chem. Soc. Rev.* **2007**, *36*, 1058−1068. (d) Schlosser, M.; Mongin, F. *Chem. Soc. Rev.* **2007**, *36*, 1161−1172. (e) Holliday, B. J.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 2022−2043. (f) Yamaguchi, J.; Muto, K.; Itami, K. *Eur. J. Org. Chem.* **2013**, 19−30. (g) Engle, K. M.; Yu, J.-Q. *J. Org. Chem.* **2013**, *78*, 8927−8955.

(2) For some examples of Ru-catalyzed pyridyl C−H bond addition into unsaturated bonds (a) Grigg, R.; Savic, V. *Tetrahedron Lett.* **1997**, *38*, 5737−5740. (b) Murakami, M.; Hori, S. *J. Am. Chem. Soc.* **2003**, *125*, 4720−4721. (c) Johnson, D. G.; Lynam, J. M.; Mistry, N. S.; Slattery, J. M.; Thatcher, R. J.; Whitwood, A. C. *J. Am. Chem. Soc.* **2013**, *135*, 2222−2234.

(3) For some examples of Rh-catalyzed pyridyl C−H bond addition into unsaturated bonds (a) Lewis, J. C.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2007**, *129*, 5332−5333. (b) Yotphan, S.; Bergman, R. G.; Ellman, J. A. *Org. Lett.* **2010**, *12*, 2978−2981.

(4) For some examples of Ni-catalyzed pyridyl C−H bond addition into unsaturated bonds (a) Nakao, Y.; Yamada, Y.; Kashihara, N.; Hiyama, T. *J. Am. Chem. Soc.* **2010**, *132*, 13666−13668. (b) Nakao, Y.; Kanyiva, K. S.; Hiyama, T. *J. Am. Chem. Soc.* **2008**, *130*, 2448−2449. (c) Tsai, C.-C.; Shih, W.-C.; Fang, C.-H.; Li, C.-Y; Ong, T.-G.; Yap, G. P. A. *J. Am. Chem. Soc.* **2010**, *132*, 11887−11889.

(5) For an example of Co-catalyzed quinolyl C−H bond addition into unsaturated bonds Yamamoto, S.; Saga, Y.; Ando, T.; Matsunaga, S. *Adv. Synth. Catal.* **2014**, *356*, 401−405.

(6) For an example of Zr-catalyzed pyridyl C−H bond addition into unsaturated bonds Jordan, R. F.; Taylor, D. F. *J. Am. Chem. Soc.* **1989**, *111*, 778−779.

(7) For recent reviews of σ-bond metathesis and catalytic reaction mediated by early transition metals (a) Waterman, R. *Organometallics* **2013**, *32*, 7249−7263. (b) Tsurugi, H.; Yamamoto, K.; Nagae, H.; Kaneko, H.; Mashima, K. *Dalton Trans.* **2014**, *43*, 2331−2343.

(8) For some examples of Sc and Y-catalyzed pyridyl C−H bond addition into unsaturated bonds (a) Deelman, B.-J.; Stevels, W. M.; Teuben, J. H.; Lakin, M. T.; Spek, A. L. *Organometallics* **1994**, *13*, 3881−3891. (b) Guan, B.-T.; Hou, Z. *J. Am. Chem. Soc.* **2011**, *133*, 18086−18089. (c) Kaneko, H.; Nagae, H.; Tsurugi, H.; Mashima, K. *J. Am. Chem. Soc.* **2011**, *133*, 19626−19629.

(9) For some reviews of C−H bond addition into C═X multiple bonds (a) Colby, D. A.; Tsai, A. S.; Bergman, R. G.; Ellman. *Acc. Chem. Res.* **2012**, *45*, 814−825. (b) Yan, G.; Wu, X.; Yang, M. *Org. Biomol. Chem.* **2013**, *11*, 5558−5578. (c) Zhang, X.-S.; Chen, K.; Shi, Z.-J. *Chem. Sci.* **2014**, *5*, 2146−2159.

(10) For an example of catalytic C−H bond addition of *N*-heteroaromatics into C═O double bond by using Et_3SiH (a) Fukumoto, Y.; Sawada, K.; Hagihara, M.; Chatani, N.; Murai, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2779−2781. (b) Li, B.-J.; Shi, Z.-J. *Chem. Sci.* **2011**, *2*, 488−493.

(11) For rare examples of catalytic C−H bond addition into C≡X triple bond (a) Moore, E. J.; Pretzer, W. R.; O'Connell, T. J.; Harris, J.; LaBounty, L.; Chou, L.; Grimmer, S. S. *J. Am. Chem. Soc.* **1992**, *114*, 5888−5890. (b) Wicker, B. F.; Scott, J.; Fout, A. R.; Pink, M.; Mindiola, D. J. *Organometallics* **2011**, *30*, 2453−2456.

(12) For two examples of pyridyl C−H bond activation by early transition amido complexes (a) Jeganmohan, M.; Knochel, P. *Angew. Chem., Int. Ed.* **2010**, *49*, 8520−8524. (b) Wunderlich, S. H.; Knochel, P. *Chem.—Eur. J.* **2010**, *16*, 3304−3307.

(13) See Supporting Information.

(14) For some examples of hydroarylation of imines (a) Tsai, A. S.; Tauchert, M. E.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2011**, *133*, 1248−1250. (b) Li, Y.; Li, B.-J.; Wang, W.-H.; Huang, W.-P.; Zhang, X.-S.; Chen, K.; Shi, Z.-J. *Angew. Chem., Int. Ed.* **2011**, *50*, 2115−2119. (c) Tauchert, M. E.; Incarvito, C. D.; Rheingold, A. L.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2012**, *134*, 1482−1485. (d) Li, Y.; Zhang, X.-S.; Li, H.; Wang, W.-H.; Chen, K.; Li, B.-J.; Shi, Z.-J. *Chem. Sci.* **2012**, *3*, 1634−1639. (e) Gao, K.; Yoshikai, N. *Chem. Commun.* **2012**, *48*, 4305−4307. (f) Yoshino, T.; Ikemoto, H.; Matsunaga, S.; Kanai, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 2207−2211.

(15) For some examples of benzylic C(sp^3)−H bond activation reactions (a) Tsurugi, H.; Yamamoto, K.; Mashima, K. *J. Am. Chem. Soc.* **2011**, *133*, 732−735. (b) Guan, B.-T.; Wang, B.; Nishiura, M.; Hou, Z. *Angew. Chem., Int. Ed.* **2013**, *52*, 4418−4421.

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