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Direct *ortho*-C—H Aminoalkylation of 2-Substituted Pyridine Derivatives Catalyzed by Yttrium Complexes with *N,N'*-Diarylethylenediamido Ligands

Abhinanda Kundu, Mariko Inoue, Haruki Nagae, Hayato Tsurugi,* and Kazushi Mashima*

Department of Chemistry, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan

C-H activation, Aminoalkylation, diamine ligand, asymmetric reaction

ABSTRACT: A mixed ligated amidoyttrium complex, Y(NBn_2)(**L1**)$(THF)_2$ (**8**, **L1** = *N,N'*-bis(2,6-diisopropylphenyl)ethylenediamine), served as a catalyst for addition of the *ortho*-pyridyl C(sp^2)—H bond of 2-substituted pyridines to non-activated imines; complex **8** showed superior catalytic performance compared with Y[$N(SiMe_3)_2]_3$ (**1**) and Y[$N(SiMe_3)_2]_2(NBn_2)(THF)$ (**2**). Concerning the reaction mechanism, we conducted a stoichiometric reaction of an alkylyttrium complex, Y(CH_2SiMe_3)(**L1**)$(THF)_2$ (**7**), with 2-ethylpyridine (**4e**), giving a mixture of (η^3-pyridylmethyl)yttrium complex **9** and (η^2-pyridyl)yttrium complex **10** along with elimination of $SiMe_4$. Furthermore, addition of *N*-(*tert*-butyl)-2-methylpropan-1-imine (**5i**) to the mixture of **9** and **10** afforded (pyridylmethylamido)yttrium complex **11** as a single product, and the catalytic activity of **11** was comparable to that of complex **8**. Kinetic analysis of the aminoalkylation reaction in the presence/absence of $HNBn_2$ revealed that the reaction rate in the presence of $HNBn_2$ was four times faster than that without $HNBn_2$ due to acceleration of the product-eliminating step from complex **11** by $HNBn_2$ to regenerate amidoyttrium complex **8** and the product. In addition, we determined that the catalytic reaction obeyed a first-order rate dependence on the catalyst concentration, independent of the imine concentration, and a second–order rate dependence on the concentration of the pyridine substrate in the reaction system, both with and without $HNBn_2$. An enantiomerically pure *N,N'*-diaryl-1,2-diphenylethylenediamido ligand was applied for the C(sp^2)—H aminoalkylation reaction in combination with $Lu(CH_2SiMe_3)_3(THF)_2$ to give chiral aminoalkylated products in moderate yield with good enantioselectivity.

Functionalized *N*-heteroaromatic compounds are among the most important skeletons of bio-active molecules often used in pharmaceuticals and agrochemicals.[1] Although various synthetic protocols to introduce any functional group in *N*-heteroaromatics have been intensively developed, metal catalyzed C—H bond activation followed by functionalization is one of the most atom-economical and cost-effective synthetic tools in terms of excluding the pre-functionalization step of any substrates and minimizing the formation of byproducts. In fact, the insertion of non-polar C=C (alkene) and C≡C bonds (alkyne) into a C—H bond of pyridine and its derivatives is catalyzed by various transition metal complexes to give *ortho*-, *meta*-, and *para*-substituted alkyl and alkenyl pyridine derivatives, respectively.[2-8] Typically, low-valent late-transition metal catalyst systems such as nickel(0) complexes combined with Lewis acid activators as well as $[RhCl(coe)_2]_2$ supported by PCy_3 work in alkylation and alkenylation reactions (Figure 1(a)), while alkyl and hydride complexes of d^0 lanthanide metals and early-transition metals serve as catalysts for *ortho*-alkylation through the σ-bond metathesis pathway, in which η^2-pyridine species are key intermediates prior to insertion of the C=C bond (Figure 1(b)).[9-11] Although insertion of non-polar unsaturated substrates into a C—H bond of pyridine derivatives has been widely demonstrated, the catalytic insertion of polar multiple bonds,[12] such as C=N,[13a-d] C≡N,[13e] and C=O,[13f-h] is still considered to be a difficult task, and only a few catalytic reactions have been successfully established. Relevantly, Bergman and Ellman reported that the electrophilic rhodium(III) system of $[Cp^*RhCl_2]_2/AgSbF_6$ is a catalyst for the C—H bond activation of the arene ring of 2-arylpyridines followed by insertion of *Boc*-protected imines, leading to the selective aminoalkylation at the arene ring of 2-arylpyridines,[13a] and Shi *et al.* reported that a dicationic rhodium catalyst, $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$, assists in the activation of the C—H bond of the aryl ring of 2-phenylpyridine, followed by the addition to *N*-sulfonyl aldimines to give the corresponding *N*-sulfonyl arylmethylamines.[13b] After these rhodium catalyst systems appeared, alkylcobalt and dicationic cobalt catalysts were also applied to the same regioselective C—H aminoalkylation of 2-arylpyridines with *N*-arylbenzaldimines and *N*-sulfonyl benzaldimies, respectively.[13c,d]

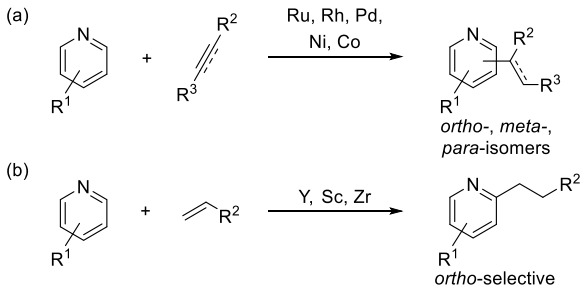
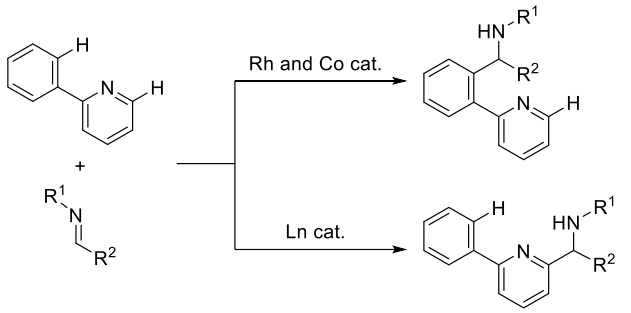


Figure 1. (a) Late transition metal catalysts for alkylation and alkenylation of pyridine derivatives; (b) Lanthanide and early transition metal catalysts for *ortho*-selective alkylation of pyridine derivatives.

In contrast to these successful insertion reactions of an activated C=N double bond and a C≡N triple bond, we recently

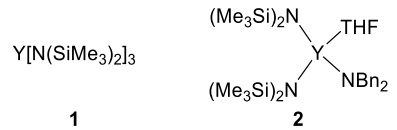
found that homoleptic triamido complexes of group 3 metals and lanthanides, $M[N(SiMe_3)_2]_3$, act as catalysts in the presence of $HNBn_2$ for selective insertion of non-activated imines into the *ortho*-C—H bond of the pyridine ring of 2-arylpyridines.[14] Noteworthy is that the achieved regioselectivity for C—H bond functionalization of the *ortho*-C—H bond of the pyridine moiety of 2-arylpyridines differed from the electrophilic late-transition metal catalyst systems that selectively aminomethylate at the aryl ring of 2-arylpyridines, as schematically outlined in Scheme 1. As part of our continuing interest, we herein report that application of both chelating *N,N'*-diarylethylenediamido ligands and $HNBn_2$ onto yttrium complexes produces bidentate ligand-supported catalysts for aminoalkylation of the *ortho*-C—H bond of *N*-heteroaromatic compounds with non-activated imines. Based on the results for screening the effective achiral bidentate nitrogen-based ligand series, we achieved the first example, to the best of our knowledge, for asymmetric C—H aminoalkylation of 2-phenylpyridine using a *C*2-symmetric (1*S*,2*S*)-*N*,*N'*-dimesityl-1,2-diphenylethane-1,2-diamido-supported lutetium complex, although Cramer[15] and Ellman[16] reported asymmetric C—H alkoxymethylation and aminomethylation of aromatic compounds catalyzed by rhodium complexes, respectively. Moreover, the mechanism of this aminoalkylation reaction was investigated based on isolation and characterization of some key intermediates as well as kinetic study.

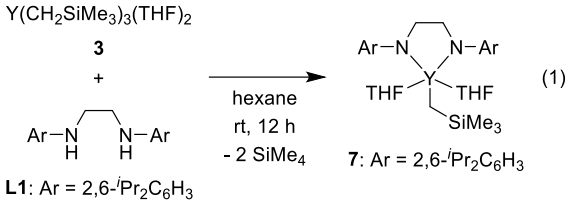
Scheme 1. Different regioselectivity in metal-catalyzed C—H bond aminoalkylation of 2-phenylpyridine with imines**.**



Results and Discussion

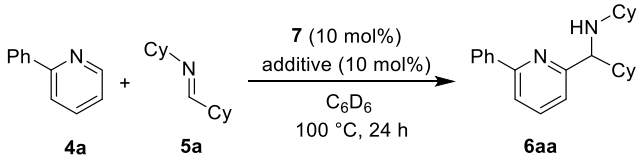
We previously reported that a homoleptic tris(amido)yttrium complex, $Y[N(SiMe_3)_2]_3$ (**1**), and a mixed-ligated yttrium complex, $Y[N(SiMe_3)_2]_2(NBn_2)(THF)$ (**2**), can serve as first catalysts for *ortho* C—H bond aminoalkylation of 2-substituted pyridines with imines to give *ortho*-aminoalkylated compounds, in which the mixed-ligated complex **2** has higher activity than homoleptic complex **1**.[14] Hence, to further screen for mixed-ligated tris(amido)yttrium complexes, we evaluated the catalytic activity of a chelating system derived by treating $Y(CH_2SiMe_3)_3(THF)_2$ (**3**) with 1 equiv of various chelating bidentate diamines and tridentate-triamines, and found that *N,N'*-bis(2,6-diisopropylphenyl)ethylenediamine (**L1**) was the best chelating ligand to support the yttrium center among the other bidentate and tridentate ligands we examined (see Supporting Information). In fact, an *in situ* mixture of **3** and **L1** exhibited catalytic activity for the aminoalkylation of 2-phenylpyridine (**4a**) with *N*,1-dicyclohexylmethanimine (**5a**) at 100 °C for 24 h to give the aminoalkylated product **6aa** in 79% yield. Catalytic performance of this *in situ* mixture prompted us to isolate alkylyttrium complex **7** according to the procedure reported in the literature (eq. 1),[17] and the catalytic activity of **7** was found to be the same as that observed for the *in situ* mixture of **3** and **L1**.





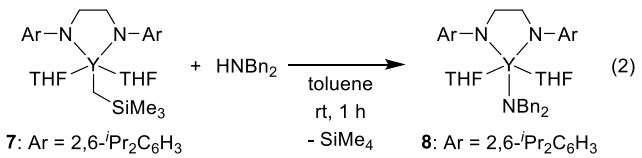
We further checked the additive effects of secondary amines on alkylyttrium complex **7**, and the results are shown in Table 1. The yield of the aminoalkylated product **6aa** was improved to 92% yield when combined with $HNBn_2$, whereas the addition of $HN(SiMe_3)_2$ to **7** suppressed the yield of **6aa** to 66% (entries 1—3), consistent with the experimental results that the *in situ* mixture of **1** and **L1**, liberating $HN(SiMe_3)_2$, was inferior to that of **3** and **L1**, releasing $SiMe_4$. Bulkiness of the $SiMe_3$ group on the nitrogen atom on the yttrium species retarded the catalytic reaction. Other secondary dialkylamines, such as $HNCy_2$, $HN(^iPr)(^tBu)$, and HN^nBu_2, gave **6aa** in good yields (83—85%, entries 4—6). Consequently, we selected the combination of **7** and $HNBn_2$, whose mixture quantitatively yielded the corresponding five-coordinated complex **8** (eq. 2), as the best catalyst system for the aminoalkylation reaction. In fact, isolated complex **8** without the addition of $HNBn_2$ exhibited almost the same catalytic activity (94% yield) as that of the *in situ* mixture of **7** and $HNBn_2$ (entries 2 and 7).

Table 1. Monodentate amine screening for *ortho*-C—H aminoalkylation reaction of 2-phenylpyridine.



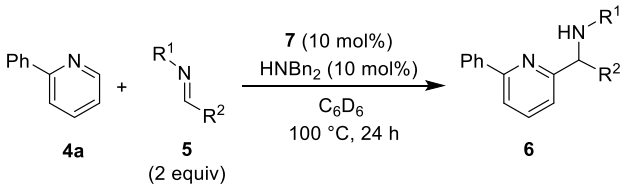
Entry	Additive	Yield (%)[a]
1	-	80
2	$HNBn_2$	92
3	$HN(SiMe_3)_2$	66
4	$HNCy_2$	83
5	$HN(^tBu)(^iPr)$	85
6	HN^nBu_2	83
7[b]	-	94

[a] Determined by ^1H NMR with 1,1,2,2-tetrachloroethane as an internal standard. [b] Isolated complex **8** was used.



The substrate scope of imines was examined for the aminoalkylation of **4a** with various imines **5**, and the results are summarized in Table 2. Steric effects of substituents at the carbon atom of *N*-cyclohexylimines were highly sensitive: *N*-cyclohexyl-2,2-dimethylpropan-1-imine (**5b**) bearing a tertiary butyl group at the imine carbon gave aminoalkylated product **6ab** in 63% yield (entry 1). When secondary alkyl substituents such as $CHEt_2$ and isopropyl were introduced at the imine carbon, the corresponding aminoalkylated compounds **6ac** and **6ad** were obtained in moderate yields (57% yield for **6ac**; 69% yield for **6ad**; entries 2 and 3), suggesting that no significant effect of the bulkiness at the imine carbon substituent was observed for the aminoalkylation reaction. In sharp contrast, reaction of **4a** with less hindered *N*-cyclohexylhexan-1-imine (**5e**) resulted in a much lower yield of the aminoalkylated product **6ae** (entry 4), presumably due to the decomposition of the catalyst by preferentially reacting the yttrium complex with **5e**. In fact, complex **7** rapidly reacted with **5e** to afford complicated mixture, from which we could not characterize any yttrium species. The aminoalkylation reaction using *N*-cyclohexylbenzylideneimine (**5f**) afforded **6af** in 34% yield, even when using 20 mol% of **7** and $HNBn_2$ at 130 °C for a prolonged reaction time (72 h, entry 5). It was likely assumed that the low reactivity of **5f** was ascribed to the low coordination ability of the imine nitrogen atom of **5f** to the yttrium center, while electron-rich imines **5a-d** preferentially coordinated to the metal center to promote the aminoalkylation reaction. The steric bulkiness of the nitrogen substituents also affected the product yield. In fact, no product was observed for aminoalkylation using *N*-*tert*-butyl-2,2-dimethylpropan-1-imine (**5g**) (entry 6), whereas *N*-*tert*-butylimines with cyclohexyl and isopropyl groups at the imine carbons, i.e., *N*-*tert*-butyl-1-cyclohexylmethanimine (**5h**) and *N*-(*tert*-butyl)-2-methylpropan-1-imine (**5i**), were applicable to reach 70% and 80% yields, respectively (entries 7 and 8). Aminoalkylations with *N*-isopropylimine, 1-cyclohexyl-*N*-isopropylmethanimine (**5j**), occurred effectively to give **6aj** in 76% yield (entry 9). When a primary alkyl substituent bound to the imine nitrogen atom, such as *N*-(*n*-hexyl)-1-cyclohexylmethanimine (**5k**), aminoalkylated product **6ak** was obtained in only a trace amount (entry 10), probably due to the low reactivity of the Y—N(primary alkyl) bond.

Table 2. Scope and limitations of imine substrates.



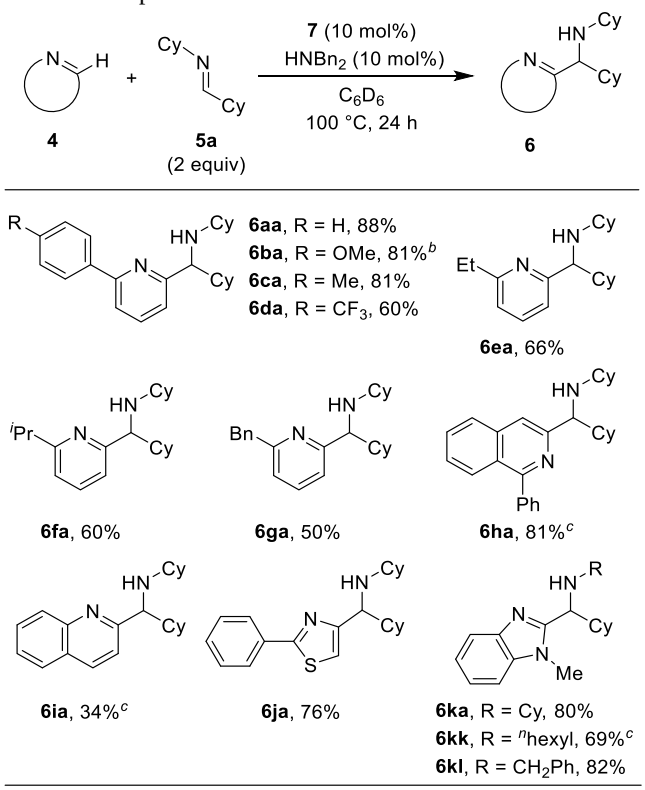
4a **5** (2 equiv) **6**

Entry	Imine	R^1	R^2	Product	Yield (%)[a]
1	**5b**	Cy	^{t}Bu	**6ab**	63
2	**5c**	Cy	$CHEt_2$	**6ac**	57[b]
3	**5d**	Cy	^{i}Pr	**6ad**	69
4	**5e**	Cy	^{n}pentyl	**6ae**	<5
5	**5f**	Cy	Ph	**6af**	34[c]
6	**5g**	^{t}Bu	^{t}Bu	**6ag**	n.d.
7	**5h**	^{t}Bu	Cy	**6ah**	70
8	**5i**	^{t}Bu	^{i}Pr	**6ai**	80
9	**5j**	^{i}Pr	Cy	**6aj**	76
10	**5k**	^{n}hexyl	Cy	**6ak**	trace

[a] Isolated yield. [b] $HNCy_2$ was used for 48 h. [c] 20 mol% catalyst and $HNCy_2$ was used at 130 °C for 72 h.

We further evaluated the substrate scope for the aminoalkylation reaction of *N*-heteroaromatic compounds with *N*,1-dicyclohexylmethanimine (**5a**), and the results are shown in Table 3. 2-Arylpyridines with electron-donating methoxy and methyl substituents at the *para*-position of the phenyl ring afforded aminoalkylated products **6ba** and **6ca** in 81% yield. In contrast, aminoalkylated product **6da** bearing a trifluoromethyl group at the *para*-position of the phenyl ring was obtained in lower yield (60%) compared with **6ba** and **6ca**. Under the same conditions, 3- and 4-phenylpyridines did not afford any corresponding products, suggesting that the substituent at the 2-position was indispensable for the aminoalkylation reaction. Pyridines with 2-ethyl, (**4e**), 2-isopropyl (**4f**), and 2-benzyl (**4g**) substituents were converted to the corresponding aminoalkylated pyridines **6ea—ga** in 66%, 60%, and 50% yield, respectively. 1-Phenylisoquinoline (**4h**) reacted with **5a** at the 3-position to produce **6ha** in 81% yield, and the yield and regioselectivity were comparable to the aminoalkylation of 2-phenylpyridine. In contrast, aminoalkylation of quinoline (**4i**) did not proceed smoothly and product **6ia** was obtained in only 34% yield; however, no other regioisomers, such as aminoalkylation at the 8-position, were detected. Aminoalkylation of 2-phenylthiazole (**4j**) occurred exclusively at the 5-position to afford **6ja** in 76% yield. As *N*-methylbenzimidazole (**4k**) was one of the most suitable substrates for C—H activation, treatment with **5a** produced **6ka** in 80% yield, and *N*-alkyl substituted imines such as **5k** and **5l** having *n*-hexyl and benzyl substituents on the imine nitrogen atom were also applicable to produce the corresponding aminoalkylated products **6kk** and **6kl** in 69% and 82% yield. When pyridine or 3- and 4-substituted pyridines were used as the substrates, no aminoalkylated products were obtained as consistent with the our previous observation of the dimerization of the pyridine derivatives *via ortho*-C—H bond activation and C=N insertion of the pyridine ring.[10a,b,18]

Table 3. Scope and limitations of *N*-heteroaromatics.[a]



[a] Isolated yield. [b] $HNCy_2$ was used for 24 h. [c] $HNCy_2$ was used for 48 h.

Kinetic study of 7 in the absence of $HNBn_2$

We measured the rate concentration dependences of **7**, 2-phenylpyridine (**4a**), and *N*,1-dicyclohexylmethanimine (**5a**) to catalytically producing **6aa** *in the absence of* $HNBn_2$. We observed a first–order rate dependence on the catalyst concentration of **7** over a 4-fold range, and the initial rate of the reaction was independent of the concentration of **5a** in the range of 0.30 M to 0.60 M. On the other hand, the reaction showed a second–order rate dependence on the concentration of **4a**. Overall, the rate law obeyed $[\mathbf{4a}]^2[\mathbf{5a}]^0[\mathbf{7}]$, the same as in our previous kinetic study of $Y[N(SiMe_3)_2]_2(NBn_2)(THF)$ (**2**). Monitoring the reaction progress allowed us to determine k_{obs} using ^1H NMR spectroscopy in the temperature range of 101 to 120 °C, and Eyring analysis provided the following activation parameters: $\Delta H^{\ddagger}$ = 50.0 ± 3.1 kJmol^{-1}, $\Delta S^{\ddagger}$ = -144.2 ± 8.0 JK^{-1}mol^{-1}, and $\Delta G^{\ddagger}$(298 K) = 93.0 ± 5.5 kJmol^{-1} (Figures 2 and 3). The large negative $\Delta S^{\ddagger}$ value suggested that an ordered five-coordinated intermediate involving two molecules of **4a** might play a key role in the C—H activation process.

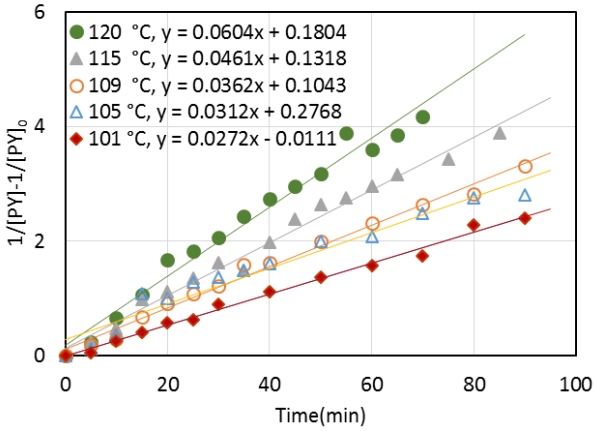


Figure 2. Second-order plot on 2-phenylpyridine at five different temperatures in the absence of $HNBn_2$.

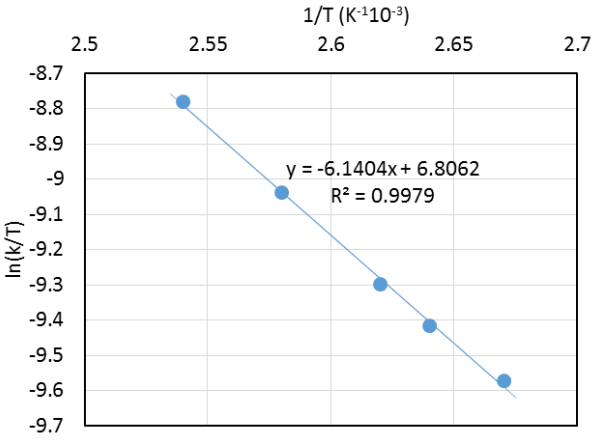


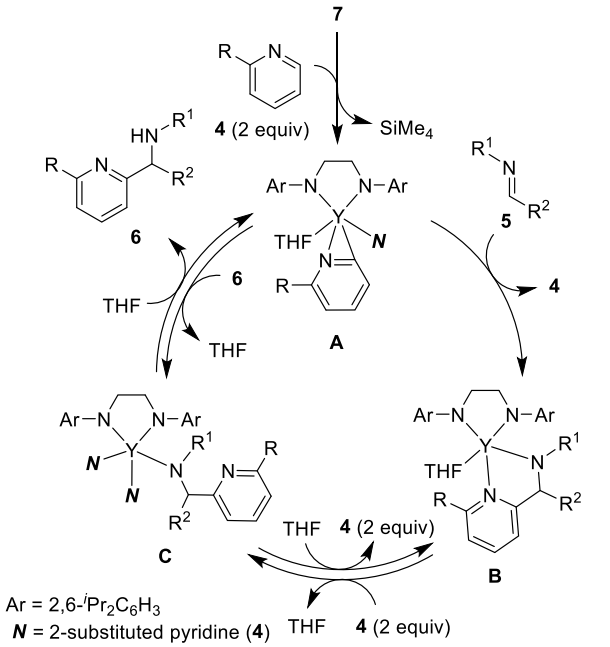
Figure 3. Eyring plot for the aminolakylation reaction in the absence of $HNBn_2$.

Catalytic cycle for 7 in the absence of $HNBn_2$

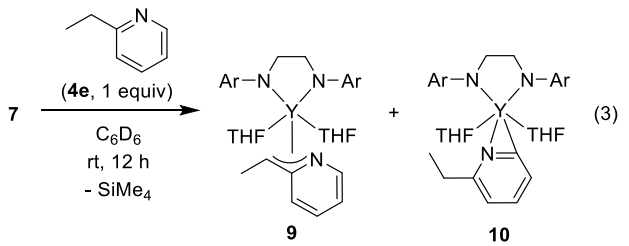
Scheme 2 shows a plausible mechanism for the aminoalkylation reaction of 2-substituted pyridines **4** with imines **5** catalyzed by complex **7** *in the absence of* $HNBn_2$. The initial step is a σ-bond metathesis of **7** with **4** to produce a five-coordinated η^2-pyridyl species **A**, which was confirmed by the controlled experiment of **7** and 2-ethylpyridine (*vide infra*). Further reaction of the Y—C(sp^2) bond in **A** with **5** generates species **B** containing five-membered 2,5-diazametallacyclopentane with coordination of THF, which was observed during the catalytic reaction and isolated in a stoichiometric reaction (*vide infra*). Ligand exchange of the THF to **4** as well as dissociation of the chelating pyridine ring with coordination of second molecule of **4** produce five-coordinated amidoyttrium species **C**. Subsequent C—H bond activation by the Y—N bond is expected to be the rate-determining step. Aminoalkylated product **6** is finally eliminated along with regeneration of the catalytically active species **A** with coordination of THF. Coordination of two molecules of **4** to the metal center in the rate-determining step is supported by the second-order rate dependence of **4** in the catalytic reaction. Observation of species **B** during the catalytic reaction is likely ascribed to the equilibrium between species **A** and **B**, in which species **A** with a five-membered chelation is assumed to be a major species in the equilibrium. In addition,

at a later stage of the catalytic reaction, a reverse reaction of the protonation of (η^2-pyridyl)yttrium **A** by **6** was in equilibrium.

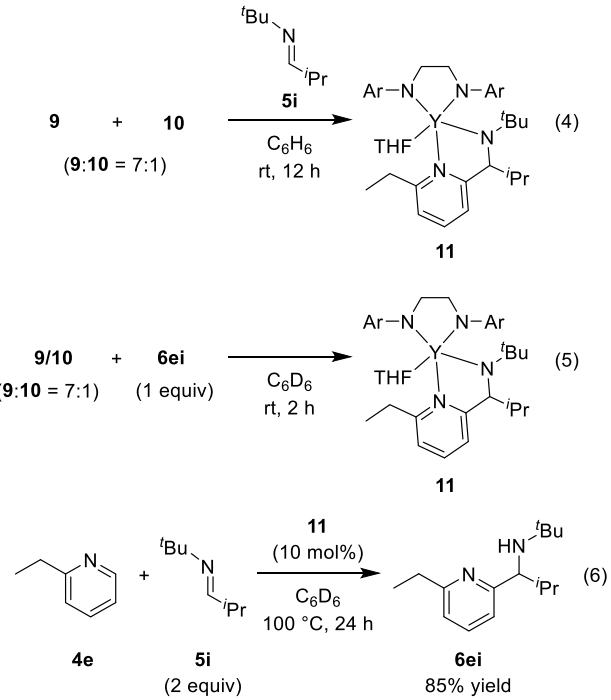
Scheme 2. A reaction mechanism for the aminoalkylation reaction in the absence of $HNBn_2$.



Aiming to elucidate the mechanism, we performed some control experiments. We conducted the reaction of complex **7** with 2-ethylpyridine (**4e**) to give a mixture of (η^3-pyridylmethyl)yttrium complex **9** and (η^2-pyridyl)yttrium complex **10** in a 7:1 ratio (eq. 3). We previously reported the C—H bond activation of 2-arylpyridines by **7**, producing dianionic 2,2'-bipyridyl-bridged dinuclear yttrium complexes.[19] In the ^{1}H NMR spectrum of the major product **9**, we observed a doublet signal assignable to the methyl group at δ 1.44 ($^3J_{HH}$ = 5.2 Hz). In addition, four signals were detected due to the pyridine ring at δ 6.15 (3-py), 6.63 (4-py), 5.63 (5-py), and 7.67 (6-py), indicating that C(sp^3)—H bond activation at the α-position of the ethyl group occurred in complex **9**. The ^{13}C NMR spectrum displayed one doublet signal for the methylene carbon bound to yttrium at δ 62.8 ($^1J_{YC}$ = 2.1 Hz). The coupling constant with yttrium was smaller than that observed for normal carbons attached to yttrium with a sp^3-configuration, such as $Cp^*_2YCH(SiMe_3)_2$ ($^1J_{YC}$ = 36.6 Hz) and **7** ($^1J_{YC}$ = 45.3 Hz), whereas it was comparable to the terminal carbons of the η^3-allyl moiety observed for $Cp^*_2Y(\eta^3\text{-}C_3H_5)$ ($^1J_{YC}$ = 3.8 Hz), indicating that the C(sp^3)—H activated 2-ethylpyridine moiety in complex **9** coordinated to the metal center as a η^3-aza-allyl structure.[20]



Treatment of the *in situ*-generated mixture of **9** and **10** with imine **5i** in benzene at room temperature for 12 h afforded five-membered chelate complex **11** as a single product in 85% yield (eq. 4). In the ^{1}H NMR spectrum of **11**, signals assignable to the methylene protons of the ethyl group bound to the pyridine ring were separately observed as broad multiplets at δ 2.03 and 1.88, and one broad triplet signal with 3H intensity assignable to the methyl group of the ethyl moiety was detected at δ 0.63 ($^3J_{HH}$ = 8.0 Hz), in accordance with the selective insertion of **5i** into the Y—C(sp^2) bond in complex **10**, even though a mixture of **9** and **10** was generated. Overall, the structure of **11** was revealed by X-ray analysis as shown in Figure 4. The selective formation of **11** indicated that major complex **9** was isomerized into the more reactive complex **10** in the presence of **5i**, though the details of the isomerization mechanism between **9** and **10** are not clear; similar isomerization of cyclometallated yttrium complexes into the corresponding (η^2-pyridyl)yttrium complexes was reported by Jordon[21a] and Diaconescu.[21b] A notable observation was that complex **11** was detected upon ^{1}H NMR spectroscopy monitoring of the catalytic reaction mixture of **4e** and **5i** in the presence of 10 mol% of **7** at 100 °C after 30 min, clearly revealing that complex **11** was a key reaction intermediate corresponding to **B** in Scheme 2 (*vide supra*). Inversely, quantitative formation of complex **11** was also achieved upon reacting the mixture of **9** and **10** with the isolated aminoalkylated product **6ei** *via* protonation of the yttrium—carbon bonds of **9** and **10** (eq. 5). Finally, we confirmed that the five-membered chelate complex **11**, corresponding to **B** in the catalytic cycle, served as an effective catalyst for the aminoalkylation reaction of **4e** and **5i** to give the corresponding product **6ei** in 85% yield after 24 h under optimized reaction conditions (eq. 6).



A single crystal of complex **11** suitable for X-ray crystallographic analysis was obtained from a saturated hexane solution of complex **11** at -40 °C. The molecular structure of **11** is shown in Figure 4. The yttrium atom is surrounded by the N1 and N2 atoms of **L1**, the N3 atom of the amido group, the N4

atom of the pyridyl group, and one THF molecule to adopt a distorted five-coordinated square pyramidal geometry where N1—N4 occupies the square plane and O1 occupies the axial position. The bond lengths of Y1—N1 (2.216(3) Å), Y1—N2 (2.279(3) Å), and Y1—N4 (2.239(4) Å) are similar to the Y—N bonds in four-coordinated Y(**L1**)[N(SiMe$_3$)$_2$](THF) (2.191(10), 2.213(11), and 2.261(13) Å, respectively)[22] and related five-coordinated yttrium complexes containing amido ligands (2.25—2.35 Å).[22] The bond length of Y1—N3 (2.586(11) Å) is within the range of other Y—N(pyridine) bonds (2.48—2.62 Å).[20a,23]

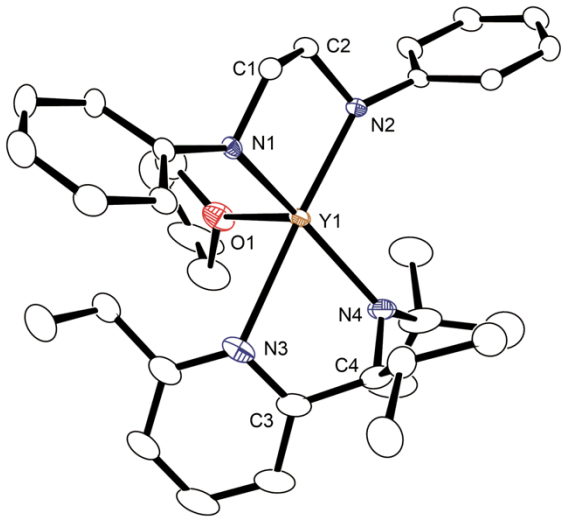


Figure 4. Molecular structure of **11** with 30% thermal ellipsoids. Isopropyl groups on **L1** and all hydrogens are omitted for clarity. Selected distances (Å) and angles (deg): Y1—N1 = 2.216(3), Y1—N2 = 2.279(3), Y1—N3 = 2.586(11), Y1—N4 = 2.239(4), Y1—O1 = 2.384(3), N1—Y1—N2 = 80.74(11), N3—Y1—N4 = 69.32(13), N4—Y1—O1 = 107.20(14), N3—Y1—O1 = 83.98(12), N2—Y1—O1 = 102.78(12), N1—Y1—O1 = 102.01(11).

Kinetic study of 7 in the presence of HNBn$_2$

We checked for additive effects of HNBn$_2$ on the reaction rate using the same amounts of **7** and HNBn$_2$. HNBn$_2$ increased the overall reaction rate. The reaction rate had a first–order rate dependence on **7**/HNBn$_2$ concentration, was independent of the imine concentration, and had a second–order rate dependence on the **4a** concentration, which was similar to the catalytic reaction *in the absence of HNBn*$_2$. Eyring analysis of the catalytic reaction provided the following activation parameters, $\Delta H^{\ddagger}$ = 36.5 ± 1.2 kJmol^{-1}, $\Delta S^{\ddagger}$ = -166.9 ± 3.1 JK^{-1}mol^{-1}, and $\Delta G^{\ddagger}$(298 K) = 86.3 ± 2.1 kJmol^{-1}. Furthermore, a deuterium-labeling experiment using 2-phenylpyridine-d_9 afforded a kinetic isotope effect value of 2.65, indicating that C—H bond activation was the rate-determining step, similar to the catalytic system of **2**. Thus, the large negative $\Delta S^{\ddagger}$ value suggested a highly ordered transition state for the C—H bond activation step *via* σ-bond metathesis between a Y—N bond in five-coordinated amido yttrium species **8'** where two of the THF molecules in **8** were replaced by substrates or solvent, as shown in Scheme 3 (*vide infra*), and a C—H bond of pyridines **4**.[14]

The additive effects of HNBn$_2$ on the initial reaction rate were further investigated over the range of 0—2.5 equiv to the alkylyttrium complex **7**. The overall reaction was accelerated by increasing the amounts of HNBn$_2$ up to 1.5 equiv added to the catalyst compared with the reaction *in the absence of HNBn*$_2$, and in the range of 1.5—2.5 equiv, the reaction rate was almost the same.

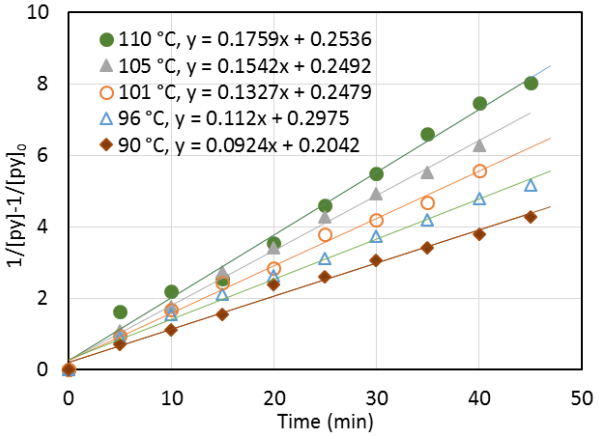


Figure 5. Second-order plot on 2-phenylpyridine at five different temperatures in the presence of HNBn$_2$.

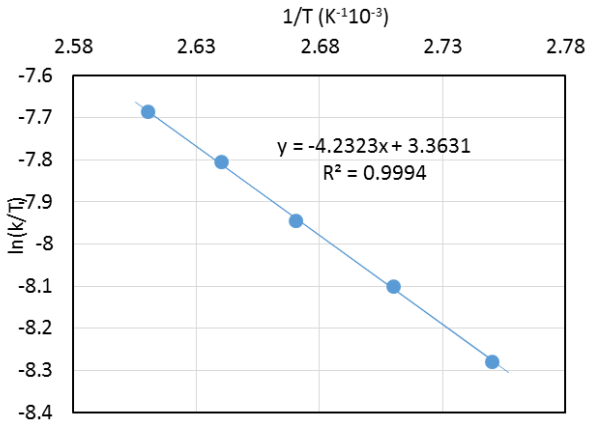


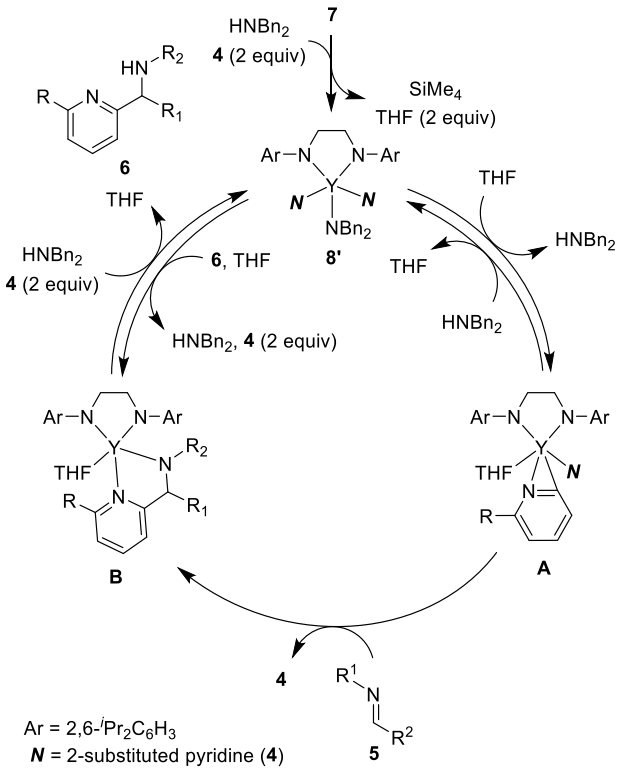
Figure 6. Eyring plot for the aminoalkylation reaction in the presence of HNBn$_2$.

Catalytic cycle of 7 in the presence of HNBn$_2$

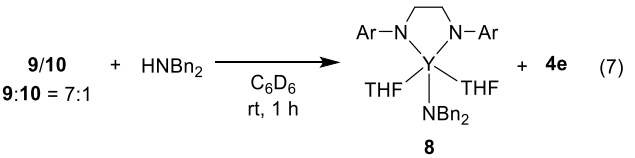
Scheme 3 shows a plausible reaction mechanism for the aminoalkylation reaction of pyridine derivatives **4** with imines **5** catalyzed by complex **7** *in the presence of HNBn*$_2$, giving the coupling products **6**. The initial step is the spontaneous reaction of **7** with HNBn$_2$ to give (dibenzylamido)yttrium complex **8'** with coordination of two molecules of **4**, similar to the bis(THF) adduct **8** in eq 2. In fact, the decreased effectiveness of HN(SiMe$_3$)$_2$ as the additive in the catalytic reaction, as shown in Table 1, was consistent with the formation of isolable four-coordinated amidoyttrium complex Y(**L1**)[N(SiMe$_3$)$_2$](THF), in which the coordination sphere around the yttrium is very crowded.[22] A σ-bond metathesis reaction between Y—N bond in **8'** and *ortho* C—H bond of **4** occurs to afford η^2-pyridyl species **A**. Second-order rate dependence on the concentration of **4** and KIE value suggest that this C—H bond activation is the rate-determining step during the catalytic cycle. Insertion of imine **5** into to the Y—C(sp^2) bond of **A** is a C—C bond forming step to generate imine-inserted species **B**, which is a similar step to the catalytic reaction without HNBn$_2$, as shown in Scheme 2. Product **6** was eliminated by protonation of **B** by HNBn$_2$ to preferentially generate **8'**, which is interconvertible

to **B** by protonation by product **6** (*vide infra*). Kinetic analysis of the aminoalkylation reaction in the presence/absence of $HNBn_2$ revealed that the reaction rate (k_{obs}) in the presence of $HNBn_2$ was four times faster than that without $HNBn_2$. The observed additive effects of $HNBn_2$ in the range of 1.0 to 1.5 equiv indicated that $HNBn_2$ worked as a free secondary amine to increase the reaction rate by protonation of species **B** in Scheme 3 to regenerate the amidoyttrium **8'** and the product. In addition, facile formation of **8'** from species **B** is an additional factor for enhancing the catalytic activity due to the no necessity for dissociating the chelating pyridine ring in species **B**.

Scheme 3. A reaction mechanism for the aminoalkylation reaction in the presence of $HNBn_2$.

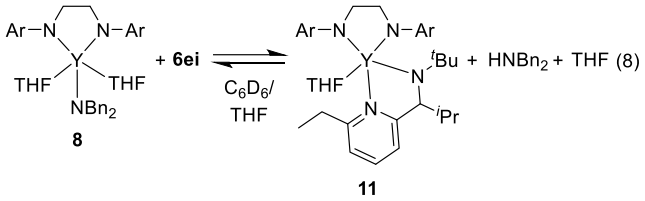


When a mixture of **7**, $HNBn_2$, **4e**, and **5i** in C_6D_6 was monitored by ^1H NMR spectroscopy, we observed signals due to **11** corresponding to species **B**, but no signals were detected assignable to the C—H bond activated complexes **9** and **10** corresponding to species **A**, probably due to the rapid insertion of imine **5i** to **A** to form diazametallacycle **B** as well as rapid protonation of the Y—C bond of species **A** by *in situ* generated $HNBn_2$. In fact, the mixture of complexes **9** and **10**, *in situ* generated from **7** and **4e**, was immediately protonated by $HNBn_2$ to give complex **8** with the release of **4e** (eq. 7).



(7)

We further examined the reaction of **8** and aminoalkylated product **6ei** in C_6D_6/THF at room temperature and monitored the reaction by NMR spectroscopy, where THF was used as the coordinating molecule to simplify the characterization of the yttrium species. In the reaction mixture, we found signals due to both of complexes **8** and **11** in a 5:1 ratio in the reaction mixture at room temperature (eq. 8), suggesting that complexes **8** and **11** were in equilibrium and complex **8** preferably formed in the catalytic reaction, even in the presence of **6ei**. A van't Hoff analysis on the 1:1 mixture of complex **8** and **6ei** gave a linear slope between 304-346 K with the values of $\Delta H^{\ominus} = 36.8 \pm 2.7$ kJmol^{-1}, $\Delta S^{\ominus} = 93.4 \pm 8.3$ JK^{-1}mol^{-1}, $\Delta G^{\ominus}$ (298 K) $= 9.02 \pm 0.21$ kJmol^{-1}. The positive standard Gibbs free energy also consistent with the favored formation of complex **8** in the presence of **6ei**. This amido exchange reaction to release the reaction product was similar to the product elimination step in the lanthanide-catalyzed hydroamination.[24]



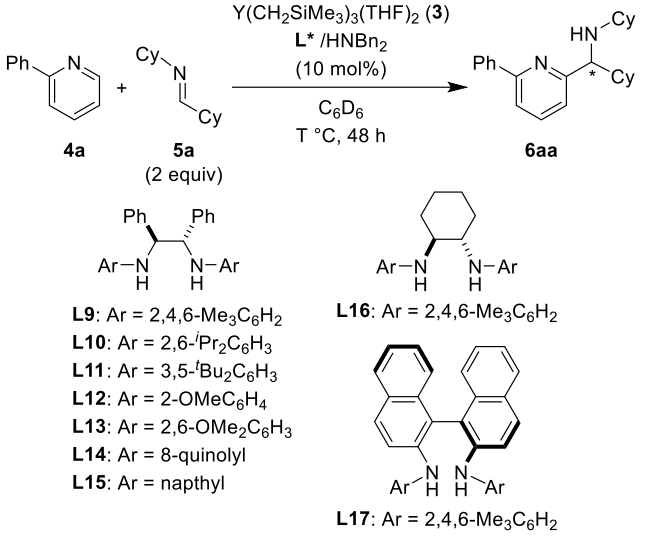
Asymmetric C—H aminoalkylation

It is a challenging task to accomplish the asymmetric aminoalkylation reaction *via* C—H bond activation of pyridine derivatives.[16] We thus focused our attention on the usage of chiral diamines with an ethylene skeleton and a binaphthyl-based skeleton[25] for $Y(CH_2SiMe_3)_3(THF)_2$ (**3**), and the results are shown in Table 5. The enantioselective aminoalkylation reaction of **4a** with **5a** using a catalyst system of **3** (10 mol%), (1*S*,2*S*)-*N*,*N*'-dimesityl-1,2-diphenylethane-1,2-diamine (**L9**) (10 mol%), and $HNBn_2$ (10 mol%) under optimized conditions (100 °C, 48 h) gave **6aa** in 57% yield with 65% ee (entry 1). When 2,6-diisopropylphenyl group was introduced on the nitrogen atom, the catalytic activity was decreased to 14% yield and no chiral induction was observed (entry 2), though the *N*-aryl substituent was similar to the best ligand to the non-chiral system. Removal of substituents at the 2,6-positions resulted in a significantly lower yield (entry 3). The use of (1*S*,2*S*)-*N*,*N*'-bis(2-methoxyphenyl)-1,2-diphenylethane-1,2-diamine (**L12**) improved enantioselectivity up to 97%, although the catalytic activity was much lower (20% yield, entry 4), while introducing two methoxy groups at the *ortho* positions of the aryl rings in **L13** did not afford the product in good yield (entry 5). Ligands **L14** and **L15** with less bulky substituents than **L9** produced the aminoalkylated product with low yield and low enantioselectivity (entries 6 and 7). The cyclohexane backbone in **L16** decreased not only the catalytic activity but also the enantioselectivity of the product compared with the **L9** system, while binaphthyldiamine-based ligand **L17** exhibited no catalytic activity (entries 8 and 9). Enantioselectivity increased as the reaction temperature decreased for the **L9** system, 75% ee at 80 °C and 82% ee at 60 °C (entries 10 and 11). Accordingly, we selected **L9** as the best chiral diamine ligand.

We checked the effect of the metal center for the enantioselective aminoalkylation reaction. When $Sc(CH_2SiMe_3)_3(THF)_2$ was used instead of **3** under the same reaction conditions using **L9**, **6aa** was obtained in 14% yield and 65% ee (entry 12). In

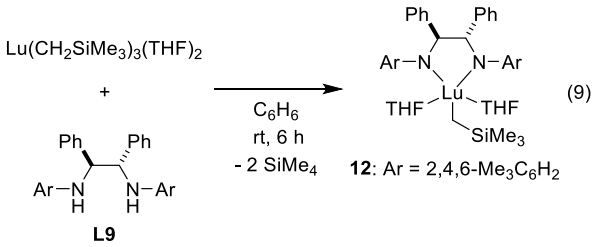
contrast, an *in situ* catalyst system of $Lu(CH_2SiMe_3)_3(THF)_2$ and **L9** showed good catalytic behavior to give the product in 57% yield with 78% ee (entry 13). The superiority of the lutetium complex was attributed to the low solubility of the lutetium complex **12** for removing the impurity; in fact, we isolated **12** in 42% yield by treating $Lu(CH_2SiMe_3)_3(THF)_2$ with an equimolar amount of **L9** in C_6H_6 at room temperature for 6 h (eq. 9) and subsequent recrystallization gave the light yellow microcrystalline solid, whereas the same reactions of trialkyl complexes of scandium and yttrium with **L9** resulted in the formation of semi-solids that contained unidentified byproducts.[26]

Table 4. Enantioselective aminoalkylation of **4a**.



Entry	Ligand	M	Temp. (°C)	Yield (%)[a]	ee (%)[b]
1	**L9**	Y	100	57	65
2	**L10**	Y	100	14	*racemic*
3	**L11**	Y	100	9	n.d.
4	**L12**	Y	100	20	97
5	**L13**	Y	100	<5	n.d.
6	**L14**	Y	100	16	27
7	**L15**	Y	100	21	5
8	**L16**	Y	100	32	29
9	**L17**	Y	100	<1	n.d.
10	**L9**	Y	80	55	75
11	**L9**	Y	60	41	82
12[c]	**L9**	Sc	80	14	65
13[d]	**L9**	Lu	80	57	78

[a] Determined by ^{1}H NMR with 1,1,2,2-tetrachloroethane as an internal standard. [b] Determined by HPLC analysis. [c] $Sc(CH_2SiMe_3)_3(THF)_2$ was used instead of **3**. [d] $Lu(CH_2SiMe_3)_3(THF)_2$ was used instead of **3**.



(9)

Complex **12** was characterized by ^{1}H and ^{13}C NMR spectroscopy together with X-ray crystallographic analysis. The ^{1}H NMR of **12** in C_6D_6 displayed two sets of broad doublet signals at δ 0.09 and -0.36 ($^2J_{HH}$ = 11.2 Hz) assignable to diastereotopic methylene protons of LuCH_2SiMe$_3$ along with aromatic protons (δ 7.27—6.69) and methine protons (δ 5.69). The integral ratio in the ^{1}H NMR confirmed coordination of the two THF molecules to the lutetium center. In addition, a single crystal of complex **12** suitable for X-ray crystallographic analysis was obtained from a saturated hexane solution of complex **12** at -40 °C, and the molecular structure of **12** is shown in Figure 7. The lutetium atom is surrounded by the N1 and N2 atoms of the (1*S*,2*S*)-*N,N'*-dimesityl-1,2-diphenylethane-1,2-diamido ligand, O1 and O2 atom of THF molecules, and C5 atom of the neosilyl group, to adopt a distorted square pyramidal geometry where N1, N2, O1, and O2 occupies the basal plane and C5 occupies the axial position. The bond lengths of Lu1—N1 (2.193(3) Å), Lu1—N2 (2.176(3) Å) are similar to the Lu—N bonds in related five-coordinated lutetium alkyl complex with a ferrocenyldiamido ligand (range 2.18—2.24 Å).[17] The Lu—O bonds are in the range of 2.33—2.35 Å observed in related penta-coordinated Lu alkyl complexes.[17,27] The angles of Lu1—N1—C1 and Lu1—N2—C4 (127.5(2)° and (125.4(2)°) are smaller than those observed in group 3 metal alkyl complexes bearing ethylenediamine ligands.[17]

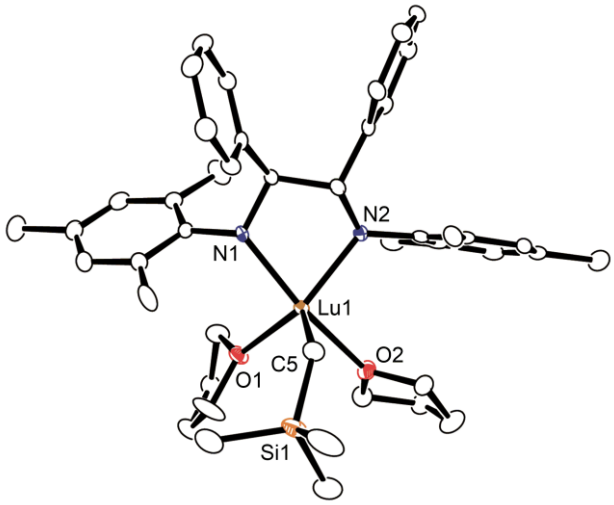
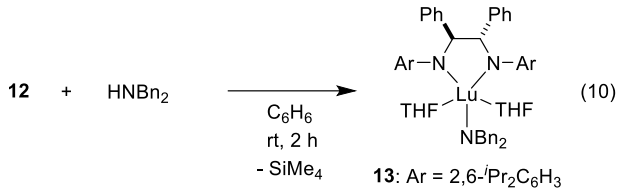


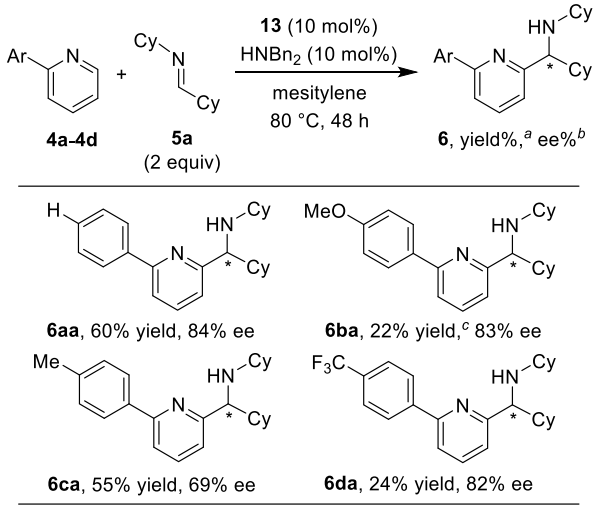
Figure 7. Molecular structure of **12** with 30% thermal ellipsoids. All hydrogens are omitted for clarity. Selected distances (Å) and angles (deg): Lu1—N1 = 2.193(3), Lu1—N2 = 2.176(3), Lu1—O1 = 2.336(3), Lu1—O2 = 2.302(3), Lu1—N1—C1 = 127.5(2), Lu1—N2—C4 = 125.4(2), N1—Lu1—N2 = 77.56(11).

Similar to the formation of amidoyttrium complex **8**, an alkyllutetium moiety reacted with $HNBn_2$ at room temperature to afford the corresponding amide complex **13** (eq. 10). The ^{1}H NMR of **13** displayed two doublet signals at δ 4.57 and 4.47 ($^2J_{HH}$ = 13.6 Hz) due to diastereotopic benzylic protons of NCH_2Ph. The integral ratio in the ^{1}H NMR confirmed coordination of the two THF molecules to the lutetium center, forming the five-coordinated amidolutetium complex.



The isolated chiral lutetium complex **13** was used as a catalyst for the aminoalkylation reaction of 2-arylpyridines **4a—d** having different substituents at the *para*-position of the aryl ring, and the results are summarized in Table 5. Chiral aminoalkylated product **6aa** was obtained in 60% yield with 84% ee at 80 °C for 48 h. Methoxy-substituted substrate **4b** was less effective for the catalytic reaction, whereas the enantioselectivity was almost the same. When electron-donating methyl group was introduced at the *para*-position of the phenyl group, the yield of **6ca** was similar, whereas the enantioselectivity decreased to 69%. By introducing an electron-withdrawing substituent, the yield of **6da** decreased to 24%, while the enantioselectivity was the same as that of **6aa**.

Table 5. Enantioselective aminoalkylation reaction of 2-arylpyridine **4a—d**.



[a] Isolated yield. [b] Determined by HPCL analysis. [c] $HNCy_2$ was used.

Conclusion

We demonstrated that a mixed ligated amidoyttrium complex **8** supported by a *N,N'*-diarylethylenediamido ligand and a dibenzylamido ligand exhibited sufficient catalytic activity for aminoalkylation reaction of 2-substituted pyridine derivatives through insertion of a non-activated C=N bond of imines into an *ortho*-C(sp^2)—H bond. Control experiments to isolate some intermediate species and measure the kinetics revealed plausible reaction mechanisms, leading us to propose a five-coordinated species as a key intermediate before the C—H bond breaks through a highly ordered σ-bond metathesis transition state, and additive amine $HNBn_2$ worked to accelerate the formation of product **6** and the regeneration of **8** as shown in Scheme 3. Because **8** involved a five-membered chelating ligand, we introduced (1*S*,2*S*)-*N*,*N*'-dimesityl-1,2-diphenylethane-1,2-diamine (**L9**) as a chiral diamine to a trialkyllutetium complex $Lu(CH_2SiMe_3)_3(THF)_2$ for a chiral C—H aminoalkylation reaction of 2-arylpyridine derivatives to gain the corresponding chiral products with moderate to good enantiomeric excess.

Experimental section

General

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out under argon using the standard Schlenk technique or argon-filled glovebox. Organometallic reagents, $LiCH_2SiMe_3$ and $M(CH_2SiMe_3)_3(THF)_2$ (M = Y, Sc, Lu), and achiral chelating diamines ligands **L1**—**L8** were prepared according to the literatures.[22,28,29] The chiral diamine ligands **L9**—**L17** were prepared according to the literatures using Buchwald-Hartwig C—N cross coupling recation.[30] Alkylyttrium complex **7** was synthesized in similar manner to the literature.[17] Amines and aldehydes for synthesizing imines and chiral diamines for synthesizing **L9**—**L17** were purchased and used as received. *N*-heteroaromatics and secondary amines were purchased and purified by distillation over CaH_2. Hexane, pentane, toluene, and benzene-d_6 were distilled over CaH_2 and thoroughly degassed by trap-to-trap distillation before use. NMR spectra were recorded on a Bruker AV 400M spectrometer in 5 mm NMR tube. Chemical shifts were reported in parts per million and referenced to residual proton signal of the solvent (^{1}H benzene-d_6, δ = 7.15; chloroform, δ = 7.26) or the solvent itself (^{13}C{^{1}H} benzene-d_6, δ = 128.06; chloroform, δ = 77.16). HPLC spectra were recorded on a JASCO UV-2075 and PU-2089. Optical rotation values were recorded on a JASCO DIP-370 polarimeter at 589 nm (sodium lamp) and given in 10^{-1} deg cm^2 g^{-1}. Melting points were recorded by a BUCHI Melting Point M-565. The elemental analyses were recorded by using Perkin Elmer 2400 at the Faculty of Engineering Science, Osaka University. Flash column chromatography was performed using silica gel 60 (0.040–0.063 mm, 230–400 mesh ASTM).

Preparation of (L1)YNBn$_2$(THF)$_2$ (8)

Complex **7** (80.0 mg, 0.114 mmol) dissolved in 2 mL of toluene was dropwise added to a solution of dibenzylamine (22.5 mg, 0.114 mmol) in 2 mL toluene at room temperature. The reaction solution was stirred for 2 h at room temperature and changes color from yellow to orange, and then all volatiles were evaporated. The resulting oily compound was washed with pentane. After drying the solid under reduced pressure, **8** was isolated as light orange powder in 54% yield (50.0 mg, 61.8 μmol), mp 130-132 °C (dec). ^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 7.41(d, $^3J_{HH}$ = 5.6 Hz, 4H, *o*-Ph), 7.32-7.17 (m, 7H, Ar + Ph), 7.17-7.04 (m, 5H, Ar + Ph), 4.37 (s, 4H, NCH_2), 4.25 (sept, $^3J_{HH}$ = 6.4 Hz, 4H, C*H*(CH_3)$_2$), 4.11 (s, 4H, NC*H*$_2$Ph), 3.34 (br s, 8H, α-CH_2 of THF), 1.38 (d, $^3J_{HH}$ = 6.4 Hz, 24H, CH(C*H*$_3$)$_2$)1.01 (br s, 8H, β-CH_2 of THF). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 30 °C): δ 156.0, 145.7, 144.5, 128.6, 128.5, 126.3, 123.5, 122.0 (Ar and Ph), 70.3 (α-CH_2 of THF), 60.2 (NCH_2), 54.9 (N*C*H$_2$Ph), 28.3 (*C*H(CH_3)$_2$), 26.0 (β-CH_2 of THF), 25.0 (CH(*C*H$_3$)$_2$). Anal. Calcd for $C_{48}H_{68}N_3O_2Y$: C, 71.35; H, 8.48; N, 5.20. Found: C, 71.07; H, 8.76; N, 5.71. Small deviation of the E.A. values is due to high sensitivity of **8** to air.

Reaction of 7 with 2-ethylpyridine

To a solution of **7** (132.0 mg, 0.188 mmol) in benzene was added a solution of 2-ethylpyridine (**4e**, 20.0 mg, 0.188 mmol) in benzene at room temperature. The reaction mixture was stirred for 12 h at room temperature and the reaction mixture color changed from orange to brown, then it was filtered and

volatiles were removed under vacuum to obtain a brown solid as a mixture of **9** and **10** in 1:7 ratio, mp 75-77 °C (dec). For **10**: ^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 7.67 (d, $^3J_{HH}$ = 7.2 Hz, 1H, H of C6 2-Etpy), 7.23 (d, $^3J_{HH}$ = 7.6 Hz, 4H, *m*-Ar), 7.11 (t, $^3J_{HH}$ = 7.6 Hz, 2H, *p*-Ar), 6.62 (t, $^3J_{HH}$ = 7.6 Hz, 1H, H of C4 2-Etpy), 6.16 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H of C3 2-Etpy), 5.63 (t, $^3J_{HH}$ = 6.0 Hz, 1H, H of C5 2-Etpy), 4.15 (sept, $^3J_{HH}$ = 6.4 Hz, 4H, C*H*(CH$_3$)$_2$), 4.04 (s, 4H, NCH$_2$), 3.37 (br s, 8H, α-CH$_2$ of THF), 2.58 (br s, 1H, YC*H*CH$_3$), 1.45 (d, $^3J_{HH}$ = 5.2 Hz, 3H, YCHC*H*$_3$), 1.40 (d, $^3J_{HH}$ = 6.4 Hz, 24H, CH(C*H*$_3$)$_2$), 1.05 (br s, 8H, β-CH$_2$ of THF). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 30 °C): δ 161.6 (C2 of 2-Etpy), 156.4 (*i*-Ar), 146.7 (C6 of 2-Etpy), 145.0 (*o*-Ar), 134.6 (C4 of 2-Etpy), 123.4 (*m*-Ar), 122.2 (*p*-Ar), 113.1 (C3 of 2-Etpy), 102.9 (C5 of 2-Etpy), 70.3 (α-CH$_2$ of THF), 62.8 (d, $^1J_{YC}$ = 2.1 Hz, Y*C*HCH$_3$), 61.0 (NCH$_2$), 28.3 (*C*H(CH$_3$)$_2$), 25.9 (β-CH$_2$ of THF), 25.1 (CH(*C*H$_3$)$_2$).

Preparation of (L1)[*N*-{2-methyl-1-(6-ethylpyridine-2-yl)propyl}*tert*-butylamido]Y(THF) (11)

To a solution of **7** (300 mg, 0.429 mmol) in benzene was added a solution of 2-ethylpyridine (**4e**, 46.0 mg, 0.429 mmol) in benzene at room temperature. The reaction mixture was stirred for 12 h at room temperature. *N*-(*t*-butyl)-2-methylpropan-1-imine (**5i**, 55.0 mg, 0.429 mmol) was added to the reaction mixture and stirred again at room temperature for 12 h. The reaction solution was filtered and volatiles were removed under vacuum to obtain a brown solid, which was washed with hexane (2 mL ×2). After drying the remaining solid *in vacuo*, **11** was isolated as brown powder in 85% yield (292 mg, 0.364 mmol), mp 73-75 °C (dec). ^{1}H NMR (400 MHz, C_6D_6 + 5 equiv of THF-d_8, 30 °C): δ 7.17 (m, 4H, *m*-Ar), 7.04 (br t, $^3J_{HH}$ = 7.2 Hz, 2H, *p*-Ar), 6.91 (br t, $^3J_{HH}$ = 6.8 Hz, 1H, H of C4 2-Etpy), 6.53 (br d, $^3J_{HH}$ = 6.8 Hz, 1H, H of C3 or C5 2-Etpy), 6.36 (br d, $^3J_{HH}$ = 6.8 Hz, 1H, H of C3 or C5 2-Etpy), 4.46 (br d, $^3J_{HH}$ = 6.8 Hz, 2H, NC*H*H), 4.13 (br s, 4H, C*H*(CH$_3$)$_2$ of Ar), 3.66 (br d, $^3J_{HH}$ = 6.8 Hz, 2H, NCH*H*), 3.53 (br s, 4H, α-CH$_2$ of THF), 3.21 (br s, 1H, NC*H*{CH(CH$_3$)(CH$_3$)}), 2.08-1.96 (br m, 1H, 6-C*H*HCH$_3$ of 2-Etpy), 1.96-1.81 (br m, 1H, 6-CH*H*CH$_3$ of 2-Etpy), 1.43-1.28 (br m, 42H, NCH{C*H*(CH$_3$)(CH$_3$)}, NCH{CH(C*H*$_3$)(CH$_3$)}, YNC(CH$_3$)$_3$, CH(C*H*$_3$)$_2$ of Ar, and β-CH$_2$ of THF), 0.63 (br t, $^3J_{HH}$ = 8.0 Hz, 3H, 6-CHHC*H*$_3$ of 2-Etpy), 0.44 (br s, 3H, NCH{CH(CH$_3$)(C*H*$_3$)}). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6 + 5 equiv of THF-d_8, 30 °C): δ 174.9, 163.9 (C2 and C6 of 2-Etpy), 157.4 (*i*-Ar), 144.7 (*o*-Ar), 137.8 (C4 of 2-Etpy), 123.7 (*m*-Ar), 121.1 (*p*-Ar), 119.6 (C3 or C5 of 2-Etpy), 118.6 (C5 or C3 of 2-Etpy), 70.0 (N*C*H{CH(CH$_3$)(CH$_3$)}), 68.2 (α-CH$_2$ of THF), 59.7 (N*C*HH), 56.1 (YN*C*(CH$_3$)$_3$), 40.6 (NCH{*C*H(CH$_3$)(CH$_3$)}), 32.1 (YNC(*C*H$_3$)$_3$), 31.1 (6-*C*HHCH$_3$ of 2-Etpy), 28.2 (*C*H(CH$_3$)$_2$ of Ar), 25.7 ((CH(*C*H$_3$)$_2$ of Ar) and β-CH$_2$ of THF), 22.5 (NCH{CH(*C*H$_3$)(CH$_3$)}), 21.7 (NCH{CH(CH$_3$)(*C*H$_3$)}), 12.6 (6-CHH*C*H$_3$ of 2-Etpy). Anal. Calcd for $C_{45}H_{71}N_4OY$: C, 69.92; H, 9.26; N, 7.25. Found: C, 69.24; H, 9.16; N, 7.10. Small deviation of the E.A values is due to high sensitivity of **11** to air.

Preparation of (L9)LuCH$_2$SiMe$_3$(THF)$_2$ (12)

Lu(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (150 mg, 0.258 mmol) dissolved in 10 mL of benzene was dropwise added to a solution of ArN-HCH(Ph)CH(Ph)NHAr, Ar = 2,4,6-Me$_3$C$_6$H$_2$ (116 mg, 0.258 mmol) in 10 mL benzene at room temperature. The reaction solution was stirred for 6 h at room temperature. The color of reaction mixture was changed from colorless to yellowish orange, and then all volatiles were evaporated. The resulting oily compound was washed with hexane (1 mL × 3). After drying the solid *in vacuo* for 3 h, **12** was isolated as light yellow powder in 42% yield (92.0 mg, 0.108 mmol), mp 128-130 °C (dec). ^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 7.25 (d, $^3J_{HH}$ = 5.6 Hz, 4H, *o*-Ph), 6.91 (t, $^3J_{HH}$ = 7.2 Hz, 4H, *m*-Ph), 6.77 (t, $^3J_{HH}$ = 6.8 Hz, 2H, *p*-Ph), 6.69 (s, 4H, *m*-Ar), 5.68 (s, 2H, NC*H*Ph), 3.34 (br s, 4H, α-CH$_2$ of THF), 3.15 (br s, 4H, α-CH$_2$ of THF), 2.69 (s, 12H, *o*-CH$_3$ of Ar), 2.08 (s, 6H, *p*-CH$_3$ of Ar), 0.91-1.14 (br m, 8H, β-CH$_2$ of THF), 0.37 (s, 9H, SiMe$_3$), 0.09 (d, $^2J_{HH}$ = 11.2 Hz, 1H, LuC*H*H), -0.36 (d, $^2J_{HH}$ = 11.2 Hz, 1H, LuCH*H*). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 30 °C): δ 152.4, 146.3, 132.7, 129.4 (*m*-Ar + *o*-Ph), 127.6, 126.9 (*m*-Ph), 125.7 (*p*-Ph), 77.9 (N*C*HPh), 69.8 (α-CH$_2$ of THF), 34.8 (LuCH$_2$), 24.9 (CH$_3$), 22.3 (CH$_3$), 20.8 (CH$_3$), 5.0 (SiMe$_3$). Anal. Calcd for $C_{44}H_{61}N_2O_2SiLu$: C, 61.95; H, 7.21; N, 3.28. Found: C, 60.05; H, 6.82; N, 3.86. Small deviation of the E.A. values is due to high sensitivity of **12** to air.

Preparation of (L9)LuNBn$_2$(THF)$_2$ (13)

Complex **9** (104 mg, 0.122 mmol) dissolved in 2 mL of benzene was dropwise added to a solution of dibenzylamine (24.1 mg, 0.122 mmol) in 2 mL benzene at room temperature. The reaction solution was stirred for 2 h at room temperature. The color of reaction mixture was changed from yellow to orange, and then all volatiles were evaporated. The resulting oily compound was washed with pentane. After drying the solid *in vacuo* for 3 h, **13** was isolated as light orange powder in 55% yield (65.0 mg, 67.0 μmol), mp 113-115 °C (dec). ^{1}H NMR (400 MHz, C_6D_6, 30 °C): δ 7.42-7.32 (br m, 3H, Ph), 7.31-7.18 (m, 6H, Ph), 7.13-7.06 (m, 2H, Ph), 6.97-6.84 (m, 4H, Ph), 6.84-6.61 (m, 8H, Ph + Ar), 5.70 (s, 2H, NC*H*Ph), 4.56 (d, $^2J_{HH}$ = 13.6 Hz , 2H, NC*H*HPh), 4.46 (d, $^2J_{HH}$ = 14.4 Hz , 2H, NCH*H*Ph), 3.37 (br s, 4H, α-CH$_2$ of THF), 3.29 (br s, 4H, α-CH$_2$ of THF), 2.70 (s, 12H, *o*-CH$_3$ of Ar), 2.10 (s, 6H, *p*-CH$_3$ of Ar), 1.03 (br m, 8H, β-CH$_2$ of THF). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 30 °C): δ 152.2, 146.2, 144.2, 132.8. 129.6, 129.3, 129.0, 128.7, 128.6, 126.9, 126.6, 125.7, 77.7 (N*C*HPh), 70.7 (α-CH$_2$ of THF), 55.9 (N*C*H$_2$Ph), 25.0 (, β-CH$_2$ of THF), 22.2 (CH$_3$), 20.8 (CH$_3$). Anal. Calcd for $C_{54}H_{64}N_3O_2Lu$: C, 67.41; H, 6.71; N, 4.37. Found: C, 66.79; H, 6.88; N, 4.71. Small deviation of the E.A values is due to high sensitivity of **13** to air.

Reaction profile for the catalytic aminoalkylation reaction.

In a glovebox under argon, catalyst **7** (6.9 mg, 10 μmol), HNBn$_2$ (1.9 μL, 10 μmol), 2-phenypyridine (**4a**, 15.5 mg, 0.100 mmol), imine **5a** (38.7 mg, 0.200 mmol), phenanthrene (8.9 mg, 50 μmol) and C_6D_6 (0.5 mL) were added to a J-young capped NMR tube. The NMR tube was heated in a 100 °C oil bath. The rates of the reactions were monitored by ^{1}H NMR spectroscopy. Yield of product **6aa** was determined by the integration of ^{1}H NMR signals of phenanthrene and CyNC*H*(Ar)Cy.

Kinetic analysis of the catalytic aminoalkylation reaction in the presence of HNBn$_2$.

In a glove box under argon, catalyst **7** (0.020—0.080 M), 2-phenylpyridine (**4a**, 15.5 mg, 0.100 mmol), imine **5a** (0.30—0.60 M), phenanthrene (8.9 mg, 50 μmol), and toluene-d_8 (0.5 mL) were added to a J-young capped NMR tube with/without HNBn$_2$. The NMR tube was heated at 90—110 °C using oil bath. The rates of the reactions were monitored by ^{1}H NMR spectroscopy. Yield of product **6aa** was determined by the integration of ^{1}H NMR signals of phenanthrene and CyNC*H*(Ar)Cy.

X-Ray crystallographic analysis.

All crystals were handled similarly. The crystals were mounted on the CryoLoop (Hampton Research Corp.) with a layer of

light mineral oil and placed in a nitrogen stream at 113(1) K. All measurements were made on a Rigaku XtaLAB P200 diffractometer using multi-layer mirror monochromated Mo-Kα (0.71075 Å) radiation. Crystal data and structure refinement parameters were listed in Table S5. The structures were solved by SIR-92[31] and refined on F^2 by full-matrix least-squares method, using SHELXL-2013.[32] Non-hydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\Sigma w(Fo^2 - Fc^2)^2]$ ($w = 1 / [\sigma^2 (Fo^2) + (aP)^2 + bP]$), where $P = (\mathrm{Max}(Fo^2,0) + 2Fc^2) / 3$ with $\sigma^2(Fo^2)$ from counting statistics. The function $R1$ and $wR2$ were $(\Sigma||Fo| - |Fc||) / \Sigma|Fo|$ and $[\Sigma w(Fo^2 - Fc^2)^2 / \Sigma(wFo^4)]^{1/2}$, respectively. The ORTEP-3 program was used to draw the molecule.[33]

ASSOCIATED CONTENT

Experimental details, kinetic study, NMR spectra of products, crystal data and data collection parameters, and CIF file giving data for complexes **11** and **12**. This material is available free of charge *via* the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors

* mashima@chem.es.osaka-u.ac.jp
* tsurugi@chem.es.osaka-u.ac.jp

Notes

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