Ruthenium Complex-Controlled Catalytic *N*-Mono- or *N,N*-Dialkylation of Heteroaromatic Amines with Alcohols

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Heteroaromatic amines were *N*-alkylated with primary alcohols at 150−200 °C in the presence of a catalytic amount of various ruthenium complexes to give the corresponding monoalkylated and dialkylated amines in good to high yields. For example, 2-aminopyridine reacted with an excess of ethanol at 180 °C for 20 h in the presence of dichlorotris(triphenylphosphine)ruthenium [$RuCl_2(PPh_3)_3$] to give 2-(ethylamino)pyridine (**1**) and 2-(diethylamino)pyridine (**2**) in 9% and 70% yields, respectively. On the other hand, when (η^4-1,5-cyclooctadiene)(η^6-1,3,5-cyclooctatriene)ruthenium [Ru(cod)(cot)] was used as a catalyst, even in the presence of excess ethanol, **1** was obtained in 85% yield with high selectivity. The addition of tertiary phosphines and phosphites to Ru(cod)(cot) increased the yield of the dialkylated amine.

Introduction

The development of novel and versatile methods for the selective transformation of primary amines to secondary or tertiary amines has stimulated the reexamination of many amino compounds. Several methods for the *N*-alkylation of primary amines using alkyl halides, aldehydes, ketones, and alcohols have been explored,[1−8] including the ruthenium complex-catalyzed *N*-alkylation[6,9−11] and *N*-heterocyclization[6,12−16] of amines using alcohols.

This paper deals with the first ruthenium complex-catalyzed *N*-alkylation of heteroaromatic amines using alcohols. In the presence of ruthenium complexes, primary heteroaromatic amines readily react with alcohols to selectively give the corresponding *N*-monoalkylated and *N,N*-dialkylated heteroaromatic amines. The ratio of *N*-monoalkylated to *N,N*-dialkylated products depends on the molar ratio of amine to alcohol used.[10] We now report that the selectivity for the products can be controlled by the type of ruthenium complex used.

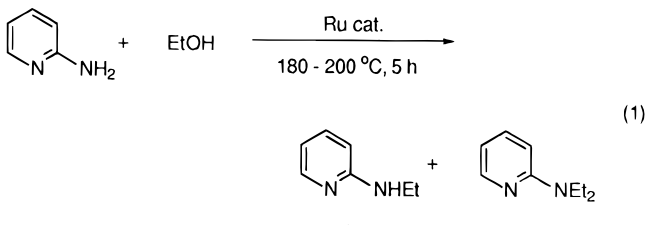
Table 1. Ruthenium-Catalyzed *N*-Ethylation of 2-Aminopyridine with Various Ruthenium Complexes[a]

			yield[b] (%)	
run	catalyst	conv[b] (%)	**1**	**2**
1	Ru(cod)(cot)	93	79	3
2	$Ru_3(CO)_{12}$	100	66	27
3	$RuCl_2(PPh_3)_3$	100	28	49
4	$RuH_2(CO)(PPh_3)_3$	100	40	37
5[c]	$RuHCl(CO)(PPh_3)_3$	100	73	15
6[c,d]	$[Cp^*RuCl_2]_2$	51	31	0
7	$RuCl_3 \cdot nH_2O$	100	26	21
8	none	0	0	0

[a] 2-Aminopyridine (4.0 mmol), ethanol (5.0 mL, 85 mmol), and catalyst (0.20 mmol) at 200 °C for 5 h under an argon atmosphere. [b] Determined by GLC. [c] 180 °C. [d] Cp* = C_5Me_5.

Results and Discussion

***N*-Ethylation of Heteroaromatic Amines with Ethanol.** 2-Aminopyridine was first used as a substrate. The reactions were carried out at 180−200 °C in the presence of catalytic amounts of various ruthenium complexes with an excess of ethanol (eq 1). The results are summarized in Table 1.



(1)

1 **2**

The reactions proceeded smoothly to give mixtures of the corresponding 2-(ethylamino)pyridine (**1**) and 2-(diethylamino)pyridine (**2**) in reasonable yields (runs 1−5). Dichlorotris(triphenylphosphine)ruthenium [$RuCl_2(PPh_3)_3$] showed catalytic activity to give *N,N*-disubstituted amine **2** as a major product (yield 49%, run 3). On the other hand, when (η^4-1,5-cyclooctadiene)(η^6-1,3,5-cyclooctatriene)-ruthenium [Ru(cod)(cot)] was used as a catalyst, *N*-monosubstituted amine **1** was obtained in high yield with high selectivity even in the presence of an excess of ethanol (run 1). The reaction did not proceed in the absence of catalyst.

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Table 2. $RuCl_2(PPh_3)_3$-Catalyzed *N*-Ethylation of Heteroaromatic Amines with Ethanol[a]

run	amine	conv[b] (%)	products (% yield[b])	
1	2-aminopyridine	100	2-(ethylamino)pyridine (**1**) (57)	2-(diethylamino)pyridine (**2**) (11)
2	3-aminopyridine	100	3-(ethylamino)pyridine (**3**) (42)	3-(diethylamino)pyridine (**4**) (53)
3	4-aminopyridine	86	4-(ethylamino)pyridine (**5**) (81)	−
4	2-aminopyrimidine	95	2-(ethylamino)pyridine (**6**) (55)	2-(diethylamino)pyrimidine (**7**) (7)
5[c]	aniline	100	*N*-ethylaniline (**8**) (13)	*N*,*N*-diethylaniline (**9**) (74)

[a] Amine (4.0 mmol), ethanol (5.0 mL), and $RuCl_2(PPh_3)_3$ (0.20 mmol) at 180 °C for 5 h under an argon atmosphere. [b] Determined by GLC. [c] *J. Org. Chem.* **1984**, *49*, 3359.

Table 3. Ru(cod)(cot)-Catalyzed *N*-Ethylation of Heteroaromatic Amines with Ethanol[a]

run	amine	conv[b] (%)	products (% yield[b])	
1	2-aminopyridine	93	2-(ethylamino)pyridine (**1**) (85)	2-(diethylamino)pyridine (**2**) (1)
2	3-aminopyridine	95	3-(ethylamino)pyridine (**3**) (92)	3-(diethylamino)pyridine (**4**) (1)
3	4-aminopyridine	86	4-(ethylamino)pyridine (**5**) (81)	−
4	2-aminopyrimidine	92	2-(ethylamino)pyrimidine (**6**) (40)	−
5	aniline	25	*N*-ethylaniline (**8**) (13)	−
6[c]	aniline	49	**8** (35)	**9** (6)
7[d]	aniline	63	**8** (43)	**9** (8)

[a] Amine (4.0 mmol), ethanol (5.0 mL), and Ru(cod)(cot) (0.20 mmol) at 180 °C for 5 h under an argon atmosphere. [b] Determined by GLC. [c] (Dimethylamino)pyridine (0.5 mmol) was added. [d] Pyridine (0.5 mmol) was added.

Table 4. Ru(cod)(cot)-Catalyzed *N*-Alkylation of 2-Aminopyridine with Primary Alcohols[a]

run	alcohol	temp (°C)	time (h)	conv[b] (%)	products (% yield[b])	
1	methanol	150	3	84	2-(methylamino)pyridine (**10**) (80)	−
2	ethanol	180	5	93	**1** (85)	**2** (1)
3	1-propanol	180	5	97	2-(propylamino)pyridine (**11**) (85)	2-(dipropylamino)pyridine (**12**) (4)
4	1-butanol	150	3	76	2-(butylamino)pyridine (**13**) (72)	2-(dibutylamino)pyridine (**14**) (3)
5	1-hexanol	150	3	83	2-(hexylamino)pyridine (**15**) (77)	−
6	benzyl alcohol	180	5	81	2-(benzylamino)pyridine (**16**) (58[c])	−

[a] 2-Aminopyridine (2.0 mmol), alcohol (3.0 mL), and Ru(cod)(cot) (0.10 mmol) under an argon atmosphere. [b] Determined by GLC. [c] Determined by NMR.

Various heteroaromatic amines reacted with ethanol at 180 °C in the presence of a catalytic amount of $RuCl_2(PPh_3)_3$ to give mixtures of *N*-monosubstituted and *N*,*N*-disubstituted heteroaromatic amines in high yields. The results are summarized in Table 2. Aniline readily reacted with ethanol to give *N*,*N*-diethylaniline as a major product (yield 74%, run 5). In contrast, the reaction of 4-aminopyridine selectively gave the corresponding *N*-monosubstituted amine in 81% yield (run 3).

Ru(cod)(cot) showed high catalytic activity for the *N*-monoalkylation of 2-, 3-, and 4-aminopyridine (Table 3). 2-Aminopyrimidine also reacted with ethanol to give the corresponding 2-(ethylamino)pyrimidine in moderate yield (run 4). In contrast with $RuCl_2(PPh_3)_3$, Ru(cod)(cot) was ineffective as a catalyst with aniline, as indicated in run 5. This suggests that coordination of a nitrogen atom on the pyridine ring is essential for Ru(cod)(cot)-catalyzed *N*-alkylation. In the case of 2-aminopyridine, it may act as a bidentate ligand. In the reaction of 3- or 4-aminopyridine, a second substrate may participate as a ligand. The addition of 2-(dimethylamino)pyridine or pyridine to the Ru(cod)(cot)-catalyzed *N*-alkylation of aniline improved the yield of the products (Table 3, runs 5−7).

Ru(cod)(cot)-Catalyzed *N*-Alkylation of 2-Aminopyridine with Several Primary Alcohols. Several primary alcohols were used in the *N*-alkylation of 2-aminopyridine in the presence of Ru(cod)(cot) as a catalyst (Table 4). These reactions proceeded smoothly to give *N*-monosubstituted 2-aminopyridine in high yield with high selectivity. Only a small amount of *N*,*N*-disubstituted 2-aminopyridine was obtained. In the reactions of 1-butanol, 1-hexanol, and benzyl alcohol, the corresponding Tischenko-type esters were obtained as a byproduct. Murahashi and co-workers reported that dihydridotetrakis(triphenylphosphine)ruthenium $[RuH_2(PPh_3)_4]$ is active for the oxidative transformation of alcohols and aldehydes into esters and lactones.[17] The Ru(cod)(cot)/2-aminopyridine catalyst system also showed catalytic activity for ester formation.

Interestingly, methanol reacted with 2-aminopyridine to give the corresponding 2-(methylamino)pyridine in high yield. *N*-Methylation of aminoarenes using methanol with a $RuCl_2(PPh_3)_3$ catalyst is usually unsuccessful. We previously reported that only the $RuCl_3 \cdot nH_2O-P(OBu)_3$ catalyst system is highly active for the *N*,*N*-dimethylation of aminoarenes with methanol.[11] The present results show that Ru(cod)(cot) is very active for monomethylation of 2-aminopyridine using methanol.

Effect of Reaction Temperature on the *N*-Ethylation of 2-Aminopyridine. Figure 1 shows the effect of reaction temperature on the $RuCl_2(PPh_3)_3$-catalyzed *N*-ethylation of 2-aminopyridine. In the case of $RuCl_2(PPh_3)_3$, the maximum yield of **1** (57%) was found at 180 °C. At higher temperatures, the yield of **1** decreased and that of **2** increased. At 200 °C, **2** was formed in 49% yield.

In contrast, in the presence of a catalytic amount of Ru(cod)(cot), the yield of **2** was very low, even at 200 °C (yield 3%). At 180 °C, the yields of 2-(ethylamino)-pyridine (**1**) and 2-(diethylamino)pyridine (**2**) were 85% and 1%, respectively; i.e., the *N*-monosubstituted amine was obtained with high selectivity.

Effects of Reaction Time on the *N*-Ethylation of 2-Aminopyridine. The effects of reaction time on the $RuCl_2(PPh_3)_3$- and Ru(cod)(cot)-catalyzed *N*-ethylation of 2-aminopyridine with ethanol were investigated, and the results are shown in Figures 2 and 3, respectively. In

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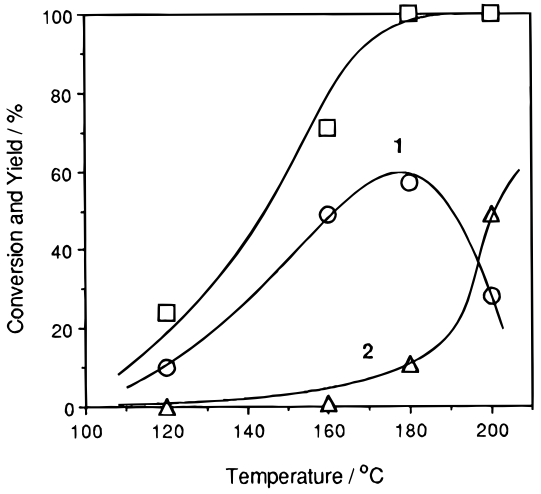


Figure 1. Effects of reaction temperature on $RuCl_2(PPh_3)_3$-catalyzed *N*-ethylation of 2-aminopyridine with ethanol. Conversion of 2-aminopyridine (□), yield of **1** (○), and yield of **2** (△). 2-Aminopyridine (4.0 mmol), ethanol (5.0 mL), and $RuCl_2(PPh_3)_3$ (0.20 mmol) for 5 h.

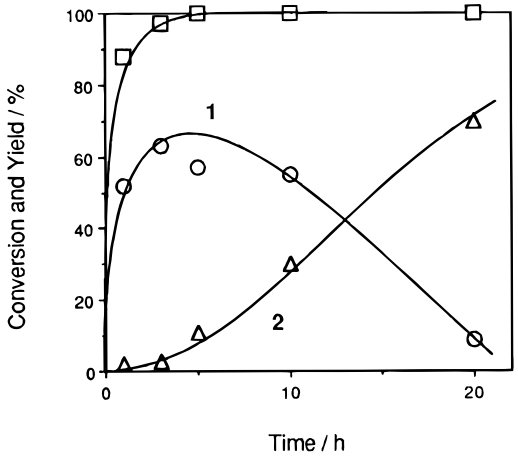


Figure 2. Effects of reaction time on $RuCl_2(PPh_3)_3$-catalyzed *N*-ethylation of 2-aminopyridine with ethanol. Conversion of 2-aminopyridine (□), yield of **1** (○), and yield of **2** (△). 2-Aminopyridine (4.0 mmol), ethanol (5.0 mL), and $RuCl_2(PPh_3)_3$ (0.20 mmol) at 180 °C.

the reaction with $RuCl_2(PPh_3)_3$ catalyst, **2** was isolated as a sole product (yield 70%) in 20 h.

These results show that the Ru(cod)(cot)-catalyzed *N*-alkylation of the resulting secondary amine proceeds more slowly than the corresponding $RuCl_2(PPh_3)_3$-catalyzed reaction.

Mechanism of the *N*-Alkylation of 2-Aminopyridine and the Effects of the Addition of Phosphines. 2-Aminopyridine coordinates to a ruthenium complex to form a chelated complex.[18,19] With 3- and 4-aminopyridine, the nitrogen atom on the pyridine ring coordinates to ruthenium.[20] The nucleophilicity of the amino group of 3-aminopyridine does not decrease for meta substitution. In the case of the 4-aminopyridine, the nucleophilicity of the exocyclic nitrogen is weakened because the delocalization of the lone-pair electrons on the aromatic

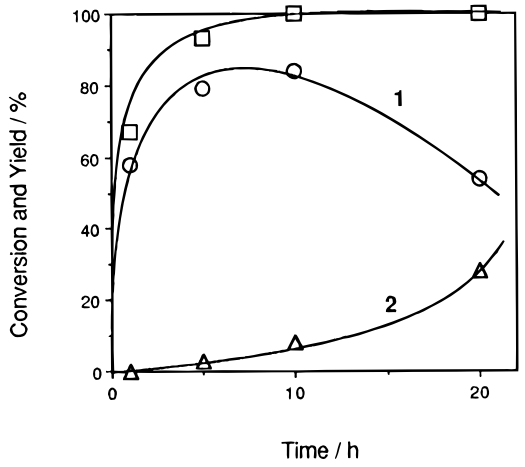
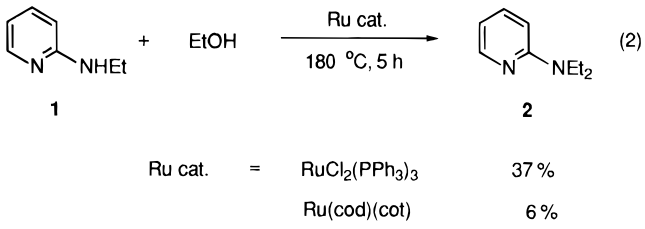


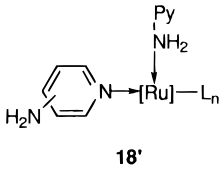
Figure 3. Effects of reaction time on Ru(cod)(cot)-catalyzed *N*-ethylation of 2-aminopyridine with ethanol. Conversion of 2-aminopyridine (□), yield of **1** (○), and yield of **2** (△). 2-Aminopyridine (4.0 mmol), ethanol (5.0 mL), and Ru(cod)(cot) (0.20 mmol) at 180 °C.

ring is enhanced by coordination of the pyridine ring to a metal. We suggest that the amino group in the coordinated 4-(ethylamino)pyridine does not have enough nucleophilicity to overcome steric hindrance, and the reaction stops predominantly at the monoalkylation stage. Consequently, only the monoethylated 4-aminopyridine is obtained even with a $RuCl_2(PPh_3)_3$ catalyst.

When 2-(ethylamino)pyridine (**1**) was reacted with a large excess of ethanol at 180 °C for 5 h in the presence of $RuCl_2(PPh_3)_3$ or Ru(cod)(cot) as a catalyst, 2-(diethylamino)pyridine (**2**) was formed in 37% and 6% yield, respectively (eq 2). Apparently, the present reactions proceed stepwise.



On the basis of the mechanism proposed for the ruthenium-catalyzed *N*-alkylation of aminoarenes,[10] the *N*-alkylation of 2-aminopyridine can be explained as follows (Scheme 1). 2-Aminopyridine coordinates to the active ruthenium species **17** to generate **18**. In the case of 3- or 4-aminopyridine, a nitrogen atom of another pyridine ligand coordinates to the ruthenium to give **18′**.



18'

The alcohol oxidatively adds to **18** to give alkoxide intermediate **19**, and subsequent β-hydrogen elimination gives an aldehyde-coordinated complex **20**. A similar oxidation pathway has been proposed by several authors.[21–26] The nucleophilic attack of the coordinated

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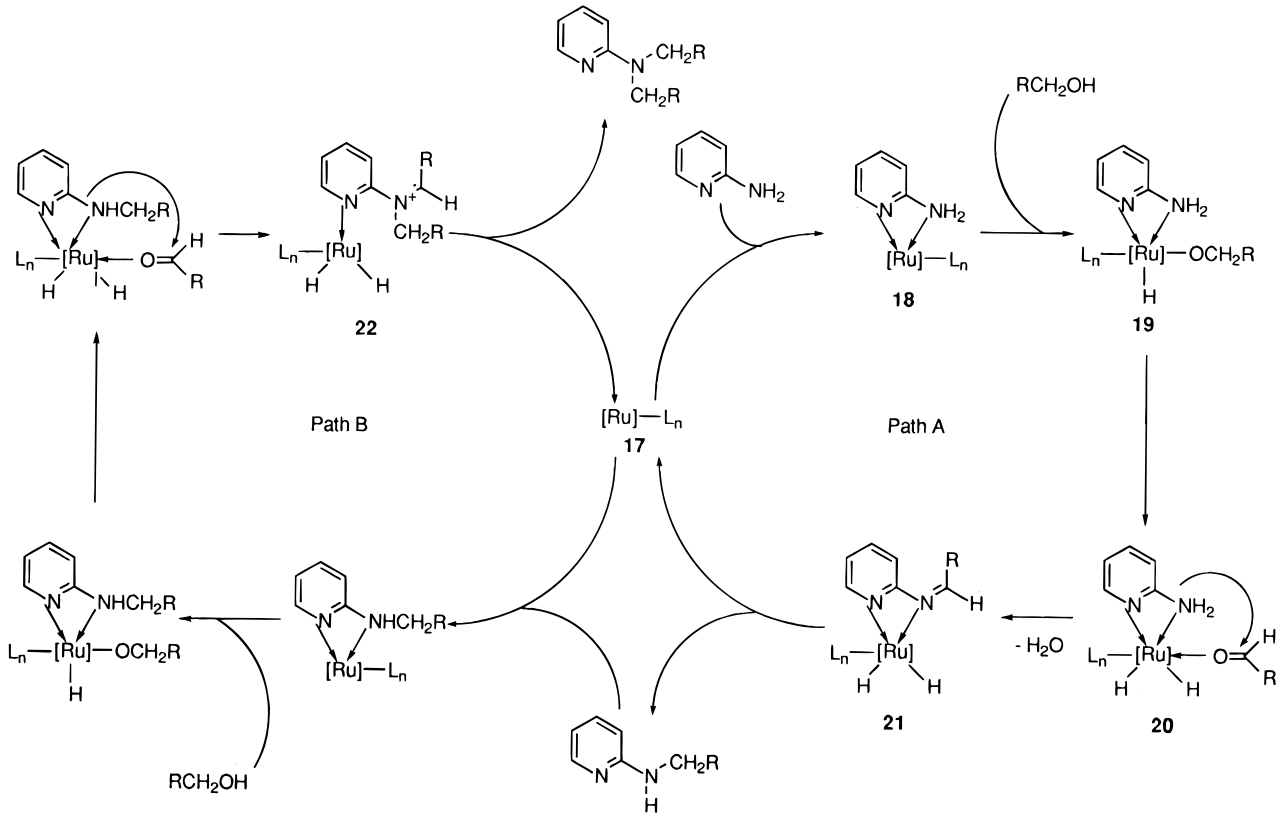
Scheme 1



amine to the carbonyl carbon of the coordinated aldehyde takes place to give a Schiff base complex **21**. We previously reported that this is the rate-determining step for the *N*-alkylation of aminoarenes.[10] Thus, path A produces the corresponding *N*-monoalkylated 2-aminopyridine and regenerates the active catalyst species **17**. *N*,*N*-Dialkylation can be similarly illustrated in path B. In path B, the catalytic cycle proceeds via an iminium intermediate **22** to give the *N*,*N*-(dialkylamino)pyridine.

The present results suggest that in $RuCl_2(PPh_3)_3$-catalyzed *N*-alkylation, the nucleophilic attack of *N*-monoalkylated heteroaromatic amines to the coordinated aldehyde on the ruthenium takes place with relative ease, while in Ru(cod)(cot)-catalyzed *N*-alkylation, this nucleophilic attack is hindered. Both steric and electronic effects should be considered. To investigate these effects, 2-aminopyridine was treated with ethanol in the presence of a catalytic amount of Ru(cod)(cot) with various phosphines (P/Ru = 2). The results are summarized in Table 5. In the presence of phosphines, the yield of 2-(diethylamino)pyridine (**2**) increased (runs 1−10). With the addition of PPh_2Cl, **2** was formed in 71% yield with high selectivity (run 9). However, the nature of the active ligand is not entirely clear because PPh_2Cl reacts with ethanol and aromatic amines to give $PPh_2(OEt)$ or PPh_2-NHAr and a chloride ion.

The effect of the addition of phosphine ligands is not yet clear. A quantitative comparison of the ligand effects of amines and phosphines is required to explain these results. Our results indicate that *N*,*N*-disubstituted compounds are obtained by the addition of phosphine to the Ru(cod)(cot) catalyst. In conclusion, *N*-monoalkylation and *N*,*N*-dialkylation of aminopyridines can be controlled by the catalysts $RuCl_2(PPh_3)_3$ and Ru(cod)(cot).

Table 5. Effects of Phosphine Ligands on Ru(cod)(cot)-Catalyzed *N*-Ethylation of 2-Aminopyridine with Ethanol[a]

			yield[b] (%)	
run	phosphine ligand	conv[b] (%)	**1**	**2**
1	PCy_3	100	82	15
2	$P(i\text{-}Pr)_3$	100	64	35
3	PBu_3	100	84	11
4	$P(o\text{-tolyl})_3$	99	79	9
5	PPh_2Et	96	77	8
6	PPh_3	100	59	34
7	$P(p\text{-}C_6H_4F)_3$	100	43	47
8	$P(OBu)_3$	98	71	24
9	PPh_2Cl	100	7	71
10	$P(OPh)_3$	100	36	49
11	none	93	85	1

[a] 2-Aminopyridine (4.0 mmol), ethanol (5.0 mL), Ru(cod)(cot) (0.20 mmol), and phosphine (0.40 mmol) at 180 °C for 5 h under an argon atmosphere. [b] Determined by GLC. [c] Cy = cyclohexyl.

Experimental Section

Materials. $Ru_3(CO)_{12}$ and $RuCl_3 \cdot nH_2O$ were purchased from Strem Chemicals and Wako Pure Chemical Industries, respectively, and used without further purification. Ru(cod)(cot),[27] $RuCl_2(PPh_3)_3$,[28] $RuH_2(CO)(PPh_3)_3$,[29] $RuHCl(CO)(PPh_3)_3$,[30] and $[Cp^*RuCl_2]_2$[31] were prepared as described in the

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literature. 2-, 3-, and 4-Aminopyridine were purchased from Wako Pure Chemical Industries and recrystallized from $CHCl_3$/petroleum ether, benzene, and benzene/ethanol, respectively. 2-Aminopyrimidine was purchased from Nacalai Tesque and used after recrystallization from ethanol.

General Procedures. A mixture of 2-aminopyridine (4.0 mmol), $RuCl_2(PPh_3)_3$ (0.20 mmol), and ethanol (5.0 mL) was placed in a 50 mL stainless steel autoclave equipped with a glass liner and a magnetic stirring bar. The mixture was magnetically stirred at 180 °C for 5 h under an argon atmosphere. Products were isolated by Kugelrohr distillation.

Analytical Procedures. The products were identified by ^{1}H-NMR, ^{13}C-NMR, IR, GC-MS, and elemental analysis. The yields of the products were determined by GLC. 2-(Ethylamino)pyridine (**1**),[32] 2-(diethylamino)pyridine (**2**),[33] 3-(ethylamino)pyridine (**3**),[34] 3-(diethylamino)pyridine (**4**),[35] 4-(ethylamino)-pyridine (**5**),[36] 2-(ethylamino)pyrimidine (**6**),[37] 2-(diethylamino)-pyrimidine (**7**),[38] 2-(propylamino)pyridine (**11**),[39] 2-(dipropylamino)pyridine (**12**),[40] 2-(butylamino)pyridine (**13**),[41] and 2-(dibutylamino)pyridine (**14**),[42] are known compounds. ^{1}H- and ^{13}C-NMR data for **1**−**15** and an elemental analysis for **15** are cited below.

2-(Ethylamino)pyridine (1). ^{1}H NMR (400 MHz) δ 1.20 (t, J = 7.2 Hz, 3 H), 3.20 (q, J = 6.8 Hz, 2 H), 5.32 (br s, 1 H), 6.33 (d, J = 8.4 Hz, 1 H), 6.50 (t, J = 8.8 Hz, 1 H), 7.38 (t, J = 1.6 Hz, 1 H), 7.93 (d, J = 5.2 Hz, 1 H); ^{13}C{^{1}H} NMR (100 MHz) δ 14.7, 36.8, 106, 113, 137, 148, 159. MS m/z 122 (M^+).

2-(Diethylamino)pyridine (2). ^{1}H NMR (400 MHz) δ 1.16 (t, J = 4.0 Hz, 6 H), 3.50 (q, J = 7.2 Hz, 4 H), 6.45 (m, 2 H), 7.38 (m, 1 H), 8.14 (d, J = 4.8 Hz); ^{13}C{^{1}H} NMR (100 MHz) δ 12.8, 42.3, 105, 110, 137, 148, 157. MS m/z 150 (M^+).

3-(Ethylamino)pyridine (3). ^{1}H NMR (400 MHz) δ 1.24 (t, J = 8.4 Hz, 3 H), 3.15 (q, J = 7.2 Hz, 2 H), 3.83 (br s, 1 H), 6.84 (d, J = 8.0 Hz, 1 H), 7.06 (m, 1 H), 7.93 (d, J = 4.8 Hz, 1 H), 8.01 (d, J = 4.8 Hz, 1 H); ^{13}C{^{1}H} NMR (100 MHz) δ 14.5, 37.9, 118, 124, 136, 138, 144. MS m/z 122 (M^+).

3-(Diethylamino)pyridine (4). ^{1}H NMR (400 MHz) δ 1.16 (t, J = 7.2 Hz, 6 H), 3.34 (q, J = 6.8 Hz, 4 H), 6.92 (m, 1 H), 7.06 (m, 1 H), 7.88 (d, J = 4.4 Hz, 1 H), 8.09 (d, J = 5.6 Hz, 1 H); ^{13}C{^{1}H} NMR (100 MHz) δ 12.2, 43.9, 118, 123, 134, 136, 143. MS m/z 150 (M^+).

4-(Ethylamino)pyridine (5). ^{1}H NMR (400 MHz) δ 1.25 (t, J = 7.2 Hz, 3 H), 3.17 (q, J = 5.2 Hz, 2 H), 4.28 (br s, 1 H), 6.44 (m, 2 H), 8.17 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz) δ 14.3, 37.1, 107, 109, 150. MS m/z 122 (M^+).

2-(Ethylamino)pyrimidine (6). ^{1}H NMR (400 MHz) δ 1.39 (t, J = 7.2 Hz, 3 H), 3.60 (m, 2 H), 5.18 (br s, 1 H), 6.51 (t, J = 4.8 Hz, 1 H), 8.42 (d, J = 4.8 Hz, 2 H); ^{13}C{^{1}H} NMR (100 MHz) δ 14.9, 36.2, 110, 158, 162. MS m/z 123 (M^+).

2-(Diethylamino)pyrimidine (7). ^{1}H NMR (400 MHz) δ 1.19 (t, J = 7.2 Hz, 6 H), 3.61 (q, J = 6.8 Hz, 4 H), 6.40 (t, J = 4.8 Hz, 1 H), 8.28 (d, J = 4.4 Hz, 2 H); ^{13}C{^{1}H} NMR (100 MHz) δ 13.0, 41.8, 109, 158, 161. MS m/z 151 (M^+).

2-(Propylamino)pyridine (11). ^{1}H NMR (400 MHz) δ 0.995 (t, J = 7.2 Hz, 3 H), 1.64 (m, 2 H), 3.21 (q, J = 6.0 Hz, 2 H), 4.60 (br s, 1 H), 6.37 (d, J = 8.4 Hz, 1 H), 6.54 (m, 1 H), 7.41 (m, 1 H), 8.07 (d, J = 4.8 Hz, 1 H); ^{13}C{^{1}H} NMR (100 MHz) δ 11.4, 22.6, 44.0, 106, 112, 137, 148, 159. MS m/z 136 (M^+).

2-(Dipropylamino)pyridine (12). ^{1}H NMR (400 MHz) δ 0.850 (t, J = 7.6 Hz, 6 H), 1.54 (m, 4 H), 3.32 (t, J = 8.0 Hz, 4 H), 6.36 (m, 2 H), 7.29 (m, 1 H), 8.04 (d, J = 5.2 Hz, 1 H); ^{13}C{^{1}H} NMR (100 MHz) δ 12.0, 21.3, 51.0, 106, 111, 137, 149, 159. MS m/z 178 (M^+).

2-(Butylamino)pyridine (13). ^{1}H NMR (400 MHz) δ 0.953 (t, J = 7.6 Hz, 3 H), 1.42 (m, 2 H), 1.61 (m, 2 H), 3.24 (q, J = 6.4 Hz, 2 H), 4.55 (br s, 1 H), 6.36 (d, J = 8.0 Hz, 1 H), 6.54 (m, 1 H), 7.4 (t, J = 7.2 Hz, 1 H), 8.07 (d, J = 4.8 Hz, 1 H); ^{13}C{^{1}H} NMR (100 MHz) δ 13.8, 20.2, 31.6, 42.0, 106, 113, 137, 148, 159. MS m/z 150 (M^+).

2-(Dibutylamino)pyridine (14). ^{1}H NMR (400 MHz) δ 0.926 (t, J = 7.2 Hz, 6 H), 1.33 (m, 4 H), 1.55 (m, 4 H), 3.40 (t, J = 7.6 Hz, 4 H), 6.42 (m, 2 H), 7.34 (m, 1 H), 8.10 (d, J = 2.8 Hz, 1 H); ^{13}C{^{1}H} NMR (100 MHz) δ 14.0, 20.3, 29.8, 48.3, 105, 111, 137, 148, 158. MS m/z 202 (M^+).

2-(Hexylamino)pyridine (15). Pale yellow oil: bp 130−135 °C (2 mmHg, Kugelrohr); IR (neat) 3422 (N−H) cm^{-1}; ^{1}H NMR (400 MHz) δ 0.892 (t, J = 7.2 Hz, 3 H), 1.31 (m, 4 H), 1.40 (m, 2 H), 1.62 (m, 2 H), 3.23 (q, J = 5.2 Hz, 2 H), 4.51 (br s, 1 H), 6.36 (d, J = 8.4 Hz, 1 H), 6.54 (m, 1 H), 7.41 (m, 1 H), 8.06 (d, J = 4.0 Hz, 1 H); ^{13}C{^{1}H} NMR (100 MHz) 14.0, 22.6, 26.7, 29.5, 31.6, 42.3, 106, 113, 138, 148, 159. MS m/z 178 (M^+). Anal. Calcd for $C_{11}H_{18}N_2$: C, 74.11; H, 10.18; N, 15.71. Found: C, 73.83; H, 10.34; N, 15.62.

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