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Multialkylation of Aqueous Ammonia with Alcohols Catalyzed by Water-Soluble Cp*Ir−Ammine Complexes

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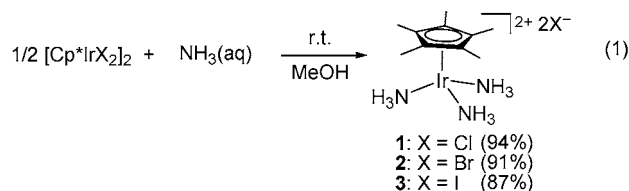
Abstract: Novel water-soluble Cp*Ir−ammine complexes have been synthesized, and a new and highly atom-economical system for the synthesis of organic amines using aqueous ammonia as a nitrogen source has been developed. With a water-soluble and air-stable Cp*Ir−ammine catalyst, $[Cp*Ir(NH_3)_3][I]_2$, a variety of tertiary and secondary amines were synthesized by the multi-alkylation of aqueous ammonia with theoretical equivalents of primary and secondary alcohols. The catalyst could be recycled by a facile procedure maintaining high activity. A one-flask synthesis of quinolizidine starting with 1,5,9-nonanetriol was also demonstrated. This new catalytic system would provide a practical and environmentally benign methodology for the synthesis of various organic amines.

Recently, much attention has been focused on the use of ammonia as a nitrogen source for organic synthesis because of its abundance and low price.[1] To date, there have been many reports on homogeneous transition-metal-catalyzed systems for the synthesis of organic amines using gaseous (or liquid) ammonia[2] and its solution in an organic solvent.[2e,3] Aqueous ammonia must be even more attractive as a substrate considering its advantages in terms of safety and handling. Some systems utilizing aqueous ammonia as a substrate for the synthesis of organic amines, such as Rh-catalyzed reductive amination of aldehydes,[4] Rh- and Ir-catalyzed hydroaminomethylation of olefins,[5] Pd-catalyzed allylic amination,[6] Pd-catalyzed telomerization with butadiene,[7] Cu-catalyzed coupling with aryl halides,[8] and Cu-catalyzed coupling with aryl boronic acids,[9] have been reported. However, most such systems require the employment of harmful organic halides as a reagent and/or the use of ammonia in excess amounts. Thus, an environmentally benign catalytic system that enables atom-economical synthesis of organic amines using aqueous ammonia has not been developed so far.

Meanwhile, we have revealed the high catalytic performance of Cp*Ir complexes in hydrogen transfer reactions and developed catalytic systems for the N-alkylation of amines and ammonium salts with alcohols.[10−12] However, utilization of aqueous ammonia as a nitrogen source in the N-alkylation with alcohols catalyzed by $[Cp*IrCl_2]_2$ has been most unsatisfactory (vide infra), probably because the catalyst is insoluble in aqueous conditions.[13] Here, we report a synthesis of novel water-soluble Cp*Ir complexes having ammine ligands and their high catalytic performance in the multialkylation of aqueous ammonia with alcohols.[14]

First, we focused on preparing a new catalyst that is soluble and stable in water. Treatment of a suspension of $[Cp*IrCl_2]_2$ in methanol with aqueous ammonia (28%) gave a new dicationic complex having ammine ligands, $[Cp*Ir(NH_3)_3][Cl]_2$ (**1**) in 94% yield (eq 1). A similar procedure starting with $[Cp*IrBr_2]_2$ and $[Cp*IrI_2]_2$ also gave $[Cp*Ir(NH_3)_3][X]_2$ (**2**: X = Br, **3**: X = I) in 91 and 87% yield, respectively (eq 1).[15] The structures of **1**−**3** were elucidated by their spectroscopic data (see the Supporting Information). The complexes **1**−**3** were highly soluble in water and stable in air for months without decomposition. Single-crystal X-ray analysis of **3** demonstrates that three ammine ligands are attached to the iridium center, and its geometry could be described

$$1/2\ [Cp*IrX_2]_2\ +\ NH_3(aq) \xrightarrow[MeOH]{r.t.} \left[\begin{array}{c} \\ H_3N{-}\overset{|}{Ir}{-}NH_3 \\ NH_3 \end{array} \right]^{2+} 2X^- \qquad (1)$$

1: X = Cl (94%)
2: X = Br (91%)
3: X = I (87%)

as a three-legged piano stool, which is common in Cp*Ir[III] complexes (see Figure S1 in the Supporting Information).

With a series of new water-soluble Cp*Ir complexes **1**−**3** in hand, we next examined their catalytic activity for the N-alkylation of aqueous ammonia (28%) with benzyl alcohol (**4a**) under various conditions. The results are shown in Table 1. The reaction of aqueous ammonia with **4a** never occurs in the absence of catalyst (entry 1). When the reaction of aqueous ammonia with 3 equiv of **4a** was carried out at 140 °C for 20 h in the presence of $[Cp*IrCl_2]_2$ (1.0 mol % Ir), tribenzylamine (**5a**) and dibenzylamine (**6a**) were obtained in low yields of 29% and 21%, respectively (entry 2). The reaction was considerably accelerated by using the water-soluble catalysts (entries 3−5). When the reaction was carried out in the presence of **1** (1.0 mol % Ir), **5a** (70%) and **6a** (18%) were

Table 1. N-Alkylation of Aqueous Ammonia with Benzyl Alcohol (**4a**) Catalyzed by Cp*Ir Complexes under Various Conditions[a]

$$NH_3(aq) + 3\ Ph{\diagup}OH \xrightarrow[\text{(1.0 mol% Ir)}]{cat.} \left(Ph{\diagup}\right)_3 N + \left(Ph{\diagup}\right)_2 NH$$

4a   **5a**   **6a**

				yield (%)[b]	
entry	catalyst	temp (°C)	time (h)	5a	6a
1	none	140	20	0	0
2	$[Cp*IrCl_2]_2$	140	20	29	21
3	**1**	140	20	70	18
4	**2**	140	20	49	23
5	**3**	140	20	82	7
6	**3**	120	20	79	6
7[c]	**3**	140	20	76	3
8	**3**	140	24	100	0

[a] The reaction was carried out with NH_3 (1.0 mmol, 28% aqueous solution), Cp*Ir catalyst (1.0 mol % Ir), and benzyl alcohol (**4a**, 3.0 mmol). [b] Determined by GC. [c] Catalyst **3** (0.50 mol % Ir) was used.

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obtained (entry 3). Among the water-soluble catalysts, **3** having iodide (I⁻) as a counteranion exhibited the highest catalytic activity with relatively good selectivity toward tertiary amine, giving **5a** (82%) along with **6a** (7%) (entry 5). The reaction also proceeded at a lower temperature (120 °C) or with lower amounts of the catalyst (0.50 mol % Ir), giving slightly lower total yields of **5a** and **6a** without affecting the selectivity (entries 6 and 7). The best result was achieved with a longer reaction time (24 h): **5a** was obtained quantitatively (entry 8). It should be noted that the present catalytic system quantitatively produces **5a** with complete selectivity without generating any waste by the employment of theoretical equivalents of starting materials (1.0 mmol of aqueous ammonia and 3.0 mmol of **4a**).[16]

The reactions of aqueous ammonia with various primary alcohols were conducted under the optimized reaction conditions. The results are summarized in Table 2. The reactions with benzylic alcohols bearing electron-donating and electron-withdrawing substituents at the aromatic ring proceeded smoothly to give the corresponding tertiary amines in good to excellent yields (entries 1−10). Methoxy, chloro, bromo, trifluoromethyl, and methoxycarbonyl substituents were tolerant in this catalytic reaction (entries 3−9). The reaction with sterically demanding 2-bromobenzyl alcohol gave the corresponding product in good yield (entry 7). The reactions with a variety of aliphatic primary alcohols also proceeded smoothly to give the corresponding tertiary amines in good to excellent yields by using 1.0 mol % Ir of the catalyst **3** (entries 11−16). 2-Ethoxyethanol having an ether substituent could be also used as an alkylating agent (entry 17). A large scale synthesis using 20 mmol of aqueous ammonia and 60 mmol of **4a** was achieved in high yield, giving 5.11 g of **5a** (entry 18).

We next investigated the reaction of aqueous ammonia with secondary alcohols. The results are summarized in Table 3. In these

Table 2. N-Alkylation of Aqueous Ammonia with a Variety of Primary Alcohols Catalyzed by **3** Affording Tertiary Amines[a]

entry	primary alcohol	catalyst 3 (mol% Ir)	product	yield (%)[b]
	R'—⟨⟩—OH			
1	R' = H (**4a**)	1.0	**5a**	94
2	R' = 4-Me (**4b**)	1.0	**5b**	92
3	R' = 4-OMe (**4c**)	1.0	**5c**	95
4	R' = 4-Cl (**4d**)	2.0	**5d**	86
5	R' = 4-Br (**4e**)	2.0	**5e**	81
6	R' = 3-Br (**4f**)	2.0	**5f**	85
7	R' = 2-Br (**4g**)	3.0	**5g**	81
8	R' = 4-CF₃ (**4h**)	3.0	**5h**	84
9	R' = 4-CO₂Me (**4i**)	2.0	**5i**	89
10	R' = 4-Ph (**4j**)	1.0	**5j**	94
11	n-C₅H₁₁⌒OH (**4k**)	1.0	**5k**	96
12	n-C₇H₁₅⌒OH (**4l**)	1.0	**5l**	86
13	i-Pr⌒OH (**4m**)	1.0	**5m**	86
14	t-Bu⌒OH (**4n**)	1.0	**5n**	87
15	Ph⌒OH (**4o**)	1.0	**5o**	85
16	Ph⌒OH (**4p**)	1.0	**5p**	86
17	EtO⌒OH (**4q**)	3.0	**5q**	65[c]
18[d]	Ph⌒OH (**4a**)	1.0	**5a**	89

[a] The reaction was carried out with NH₃ (1.0 mmol, 28% aqueous solution), catalyst **3** (1.0−3.0 mol % Ir), and primary alcohol (3.0 mmol) at 140 °C for 24 h. [b] Isolated yield. [c] Determined by ¹H NMR. [d] The reaction was carried out using 20 mmol of aqueous ammonia and 60 mmol of **4a**.
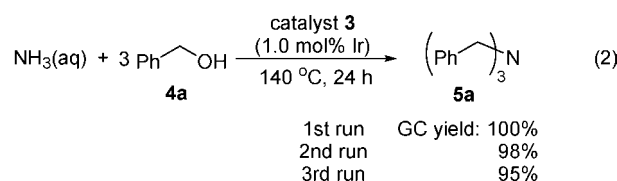
Table 3. N-Alkylation of Aqueous Ammonia with a Variety of Secondary Alcohols Catalyzed by **3** Affording Secondary Amines[a]

entry	secondary alcohol	catalyst 3 (mol% Ir)	product	yield (%)[b]
1	⬠—OH (**7a**)	1.0	**8a**	84
2	⬡—OH (**7b**)	1.0	**8b**	85
3	⬭—OH (**7c**)	1.0	**8c**	86
4	n-C₆H₁₃ (**7d**) OH	1.0	**8d**	83[c]
5	Ph (**7e**) OH	3.0	**8e**	89[d]
6	Ph (**7f**) OH	3.0	**8f**	81[c]
7	Ph (**7g**) OH	3.0	**8g**	63[c]

[a] The reaction was carried out with NH₃ (1.0 mmol, 28% aqueous solution), catalyst **3** (1.0−3.0 mol % Ir), and secondary alcohol (2.0 mmol) at 140 °C for 24 h. [b] Isolated yield. [c] Isolated as a mixture of diastereomers (50:50 by ¹H NMR). [d] Isolated as a mixture of diastereomers (meso/dl = 63:37 by ¹H NMR).
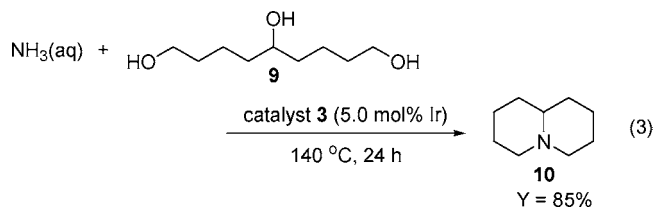
reactions, complete selectivity for the formation of secondary amines was observed probably due to steric hindrance.[17] The reactions with cyclic secondary alcohols gave dicycloalkylamines in high yields (entries 1−3). The reactions with aliphatic secondary alcohols gave mixtures of diastereomeric isomers of secondary amines in moderate to high yields (entries 4−7).

Interestingly, the catalyst could be recycled by a facile procedure to maintain high activity (eq 2). After the reaction of aqueous ammonia with **4a** catalyzed by **3** was conducted, aqueous ammonia and dichloromethane were added to the system, and the organic and aqueous phases were separated. By this simple procedure, the product **5a** could be extracted into the organic phase, and the catalyst **3** could be recovered into the aqueous phase. Then, the recovered catalyst was subjected to the second run (98% yield of **5a**) and third run (95% yield of **5a**), respectively, maintaining a high catalytic activity.

$$NH_3(aq) + 3 Ph\diagdown OH \xrightarrow[140\,°C,\,24\,h]{\text{catalyst 3}\,(1.0\,mol\%\,Ir)} (Ph\diagdown)_3 N \quad (2)$$

|	
1st run	GC yield: 100%
2nd run	98%
3rd run	95%

Furthermore, the multialkylation catalyzed by **3** was extended to the synthesis of quinolizidine by the reaction of aqueous ammonia with a water-soluble triol. When the reaction of aqueous ammonia with 1,5,9-nonanetriol (**9**) was carried out at 140 °C for 24 h in the presence of **3** (5.0 mol % Ir), quinolizidine (**10**) was obtained in 85% yield (eq 3). Thus, the present catalytic system provides a new and rapid approach to quinolizidine in a one-flask operation.[18]

The present catalytic reactions would proceed through multiple N-alkylations in which three elementary steps (dehydrogenation, imine or iminium ion formation, and hydrogenation) are involved.
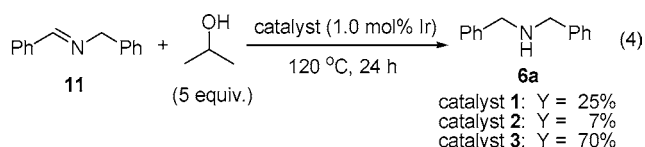
$$\text{NH}_3(aq) \; + \quad \text{scheme for 9} \quad \xrightarrow[\text{140 °C, 24 h}]{\text{catalyst 3 (5.0 mol% Ir)}} \quad \text{10} \qquad (3)$$

Y = 85%

Based on the mechanisms proposed for the Cp*Ir-catalyzed N-alkylation of amines,[10] a plausible mechanism for the first monoalkylation cycle transiently affording primary amine is depicted in Scheme 1.[19] The second and third N-alkylations to produce secondary and tertiary amines, respectively, would proceed through similar sequential processes.

Scheme 1. A Plausible Mechanism for the N-Alkylation of Aqueous Ammonia with an Alcohol
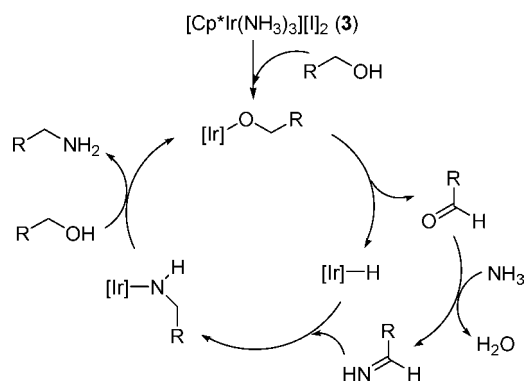
The superiority of catalyst **3** having iodide (I$^-$) as a counteranion among the water-soluble catalysts **1**−**3** could be attributed to the differences of activities for the hydrogenation of the iminic intermediate. When the transfer hydrogenations of *N*-benzylidenebenzylamine (**11**) were carried out in the presence of **1**−**3** as catalysts, the highest yield of the dibenzylamine (**6a**) was obtained in the reaction using **3** (eq 4). There have been many examples that iodide often exhibits a positive effect in the transition-metal-catalyzed hydrogenation of imines.[20]

$$\text{11} \;+\; \text{(5 equiv.)} \xrightarrow[\text{120 °C, 24 h}]{\text{catalyst (1.0 mol% Ir)}} \text{6a} \qquad (4)$$

catalyst 1: Y = 25%
catalyst 2: Y = 7%
catalyst 3: Y = 70%

In summary, novel water-soluble Cp*Ir−ammine complexes have been synthesized and a new and highly atom-economical system for the synthesis of organic amines using aqueous ammonia as a nitrogen source has been developed. With a water-soluble and air-stable Cp*Ir−ammine catalyst, [Cp*Ir(NH$_3$)$_3$][I]$_2$ (**3**), a variety of tertiary and secondary amines were synthesized by the multialkylation of aqueous ammonia with theoretical equivalents of primary and secondary alcohols. A one-flask synthesis of quinolizidine starting with triol was also demonstrated. This new catalytic system would provide a practical and environmentally benign methodology for the synthesis of various organic amines.

Supporting Information Available: Experimental procedures, characterization data of the products, and X-ray data for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) There are several examples of the transition-metal-catalyzed multialkylation of ammonia equivalent (aqueous ammonia, ammonium salt, and urea) with alcohols (refs 10f, 11d, 14a, and 14b and this work). A summary and comparison of these catalytic systems are shown in Table S1 in the Supporting Information. See also ruthenium-catalyzed monoalkylation of ammonia with alcohol (ref 2d).

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(19) Stoichiometric reaction of **3** with **4a** in D_2O at 140 °C for 0.5 h resulted in the formation of benzaldehyde (18%) along with a hydrido iridium complex (δ −15.49 in ^1H NMR). Although the structure of the hydrido complex has not been confirmed so far, the above result supports the proposed mechanism shown in Scheme 1.

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JA107274W