A Novel Reductive Dimerization/Oxidative Dehydrogenation of Aldimines Mediated by Lanthanoid Metals

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Received September 5, 2000

A lanthanoid metal-mediated novel reductive dimerization/oxidative dehydrogenation of a variety of aldimines has been achieved. Aromatic aldimines (**1**) were dimerized in the presence of 0.5 mol of ytterbium metal (Yb) and 1-naphthaldehyde (1-NpCHO) to give the corresponding vicinal diimines (**2**) in good to high yields. Samarium metal (Sm) or samarium(II) diiodide (SmI_2) gives unsatisfied yields under the same reaction conditions. As an oxidant, 1-NpCHO gives the best result. In addition, HMPA plays an important role as a cosolvent in this reaction. Reaction of various aldimines with Yb metal is disscussed in detail. Moreover, it has been found that the electron-donating substitutents on the benzene ring promote the reaction and that the electron-withdrawing substitutents retard the reaction. The reaction of deuterated *N*-benzylideneaniline with Yb metal confirmed that transformation of the hydride occurred from aldimines to the oxidant aldehyde. The mechanism of the reaction was discussed.

Introduction

Carbon−carbon bond formation via coupling reaction is one of the most important methods in synthetic organic chemistry. Recently, lanthanoid reagents have been developed for organic synthetic reactions.[1] Among lanthanoid reagents, lanthanoid metals themselves have been also utilized for various transformations of organic functional groups or carbon−carbon bond formations via coupling reactions.[2] In our studies of lanthanoid chemistry, we have succeeded in using the zerovalent lanthanoid metals as reagents for organic reactions. For instance, we have demonstrated that diaryl ketones are “umpoled” by ytterbium metal and react with various electrophiles[3] and that imine compounds undergo a similar reaction to give 1,2-diamines[4] or α-amino acids.[5] Recently, a triphenylimine dianion complex [Yb(η^2-Ph_2-CNPh)-$(HMPA)_3$] has been successfully isolated from the direct reaction of ytterbium metal with triphenylimine and characterized by X-ray analysis.[6] It is interesting that the ytterbium−imine complexes have unique chemical properties such as strong basicity and little nucleophilicity, which are different from those of lanthanoid−diaryl ketone complexes.[7] We report here a lanthanoid metal mediated novel reductive dimerization/oxidative dehydrogenation of aldimines to give vicinal diimines.

The vicinal diimine compounds are useful substrates in organic reactions. Diimines such as 1,4-diazabutadiene (*t*-BuDAB) and their derivatives have been applied in coordination chemistry and asymmetric synthesis as excellent ligands (or co-ligands).[8] Despite the importance of those functional units, few general methods for the synthesis of diimines are reported. So far, most of the vicinal diimines are still preparaed from the reactions of α-dicarbonyl compounds with amines.[9] Recently, Ito et al. reported that vicinal diimines could be obtained

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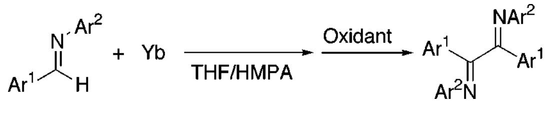
10.1021/jo001328d CCC: $20.00

Table 1. Effect of Various Oxidants on the Dehydrogenative Coupling Reaction of Aldimine 1a[a]

entry	oxidant	yield (%) of **2a**[b]
1	1-NpCHO[c]	60
2	1-NpCHO	81[d]
3	1-NpCHO	39[e]
4	p-MeC_6H_4CHO	31
5	o-$MeOC_6H_4CHO$	49
6	i-PrCHO	7
7	$CuCl_2$	
8	m-$ClC_6H_4CO_3H$	6
9	$K_2S_2O_8$	
10	t-BuONO	1
11	O_2	17[f]
12	CO	17[f]

[a] Reaction conditions: **1a** (1.0 mmol), Yb (0.5 mmol), THF (2 mL), HMPA (0.5 mL), MeI (2 μL), oxidant (2.0 mmol), rt, 2 h. [b] GC yield based on the aldimine **1a**. [c] 1-Naphthaldehyde. [d] 1-NpCHO (1.0 mmol) was used. [e] Yb (0.25 mmol) and 1-NpCHO (1.0 mmol) were used. [f] One atm, 24 h.

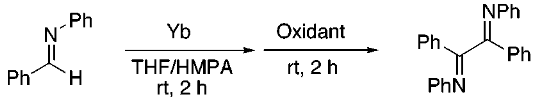
by SmI_2-mediated double insertion of isocyanides into organic halides.[10] However, no reports on the direct synthesis of vicinal diimines via dehydrogenative coupling of aldimines are available to date. Previously, we have reported that the reaction of ytterbium metal with aldimines followed by hydrolysis of reaction mixture gives diamines.[11] Imamoto and Nishimura and others reported that divalent samarium compounds are also capable of the coupling imines to give 1,2-diamines.[12] In our continuing studies on application of lanthanoid metals to organic reactions, we have found that vicinal diimines can be prepared from the reaction of aryl aldimines with Yb metal followed by the treatment with an appropriate oxidant (eq 1). Now we report these results.[13]



(1)

Results and Discussion

It have been found that aldimines react smoothly with Yb metal at room temperature in THF solvent to give a dark-red suspension solution, which affords reductive dimerization products, 1,2-diamines followed by treatment of water.[11] On the contrary, treatment with a proper oxidant gives vicinal diimines. To investigate the suitable oxidant for the reaction, we performed model reactions using various oxidants and *N*-benzylideneaniline (**1a**) in the presence of Yb metal (eq 2).[13] The results are summarized in Table 1. From the data of Table 1, one can see that aromatic aldehydes are the best compared with others (entries 1−5). Among various aromatic aldehydes, the best results were obtained when 1-naphthaldehyde (1-NpCHO) was used (entries 1−3), which implied that the structure of aromatic aldehydes is important for the dehydrogenative coupling of aldimines. In addition, the fact that bulky 1-NpCHO is appropriate as an oxdant indicates that reaction is restricted by steric factors to a greater or lesser extent. Moreover, the high yield of **2a** was obtained by using an equimolar amount of 1-NpCHO and **1a** in the reaction (entry 2). On the other hand, the yield of the product is only 7% when an aliphatic aldehyde is used (entry 6). In addition, it is apparent that copper(II) chloride ($CuCl_2$), peroxides (m-$ClC_6H_4CO_3H$; $K_2S_2O_3$), and *tert*-butyl nitrite (*t*-BuONO) give inferior results (entries 7−10) and that only 17% yield is obtained in the case of oxygen (entry 11). It is interesting that the desired reaction can also proceed with carbon monoxide as an oxidant to give diimine **2a** in 17% yield (entry 12), and no insertion product was observed.[14]



(2)

1a **2a**

It is worthy to note that the reaction of 0.5 mol of Yb metal with *N*-benzylideneaniline (**1a**) gives the corresponding coupling product, *N,N′*-diphenyl-1,2-diphenylethane-1,2-diimine (**2a**) in high yield (81%, entry 2, Table 1). When a small amount of the Yb metal (0.25 mmol) was used in the present reaction, the dehydrogenative coupling product **2a** was obtained only in 39% yield, and some starting material **1a** remained unreacted (entry 3). To find optimum reaction conditions, we studied the effects of the solvents and reaction temperature on the model reaction of *N*-benzylideneaniline (**1a**) with Yb metal. The presence of cosolvent is necessary in this reaction since the reaction of **1a** and Yb metal cannot proceed in THF alone as a solvent. Several polar compounds are chosen as cosolvents to study dehydrogenative coupling of **1a**, and hexamethylphosphoramide (HMPA) was found to give the highest yield of **2a** (CAUTION: see the Experimental Section). Coordination of HMPA to Yb would enhance the stability of a ytterbium−aldimine complex.[15] Although the *N,N′*-dimethyl-*N,N′*-propyleneurea can be also used, the product yield is low. Other cosolvents such as *N,N,N′N′*-tetramethylurea, *N,N,N′,N′*-tetramethylethylenediamine, and pyridine did not work. The dehydrogenative coupling of **1a** can also occur in the absolute toluene to give diimine **2a** in 62% yield. However, the reaction proceeded slowly and longer reaction times were necessary. In the case of *N*-(*p*-dimethylamino)benzylideneaniline (**1d**), no reaction was observed with Yb metal in toluene/HMPA even if the reaction time was extended from 2 to 24 h at room temperature, while the reaction of **1d** with Yb metal proceeded smoothly in THF/HMPA (vide infra). This result indicates that the polar solvent is the more suitable in this reaction.

The effect of the reaction temperature was then studied. The reaction was carried out as follows: first, aldimine **1a** was allowed to react with Yb metal at room temperature for 2 h, and then the reaction temperature was changed and 1-NpCHO was added with stirring during a period of 2 h. The results are listed in Table 2.

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Table 2. Effect of Temperature on the Dehydrogenative Coupling Reaction of 1a[a]

entry	T (°C)	yield (%) of **2a**[b]
1	rt	81
2	−35	34
3	0	51
4	40	67
5	66	66

[a] Reaction conditions: **1a** (1.0 mmol), Yb (0.5 mmol), THF (2 mL), HMPA (0.5 mL), MeI (2 μL), 1-NpCHO (1.0 mmol), rt, 2 h. [b] GC yield based on the aldimine **1a**.

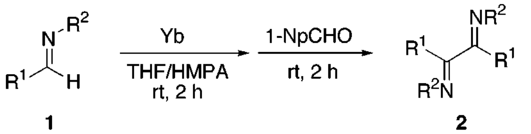
Table 3. Dehydrogenative Coupling Reaction of Various Aldimines Mediated by Ytterbium Metal[a]

entry	substrate	R^1	R^2	product	yield[b] (%)
1	**1a**	Ph	Ph	**2a**	81
2	**1b**	p-MeC$_6$H$_4$	Ph	**2b**	90
3	**1c**	p-MeOC$_6$H$_4$	Ph	**2c**	86
4	**1d**	p-Me$_2$NC$_6$H$_4$	Ph	**2d**	34[c]
5	**1e**	p-ClC$_6$H$_4$	Ph	**2e**	45
6	**1f**	p-CNC$_6$H$_4$	Ph	**2f**	5[c]
7	**1g**	p-NO$_2$C$_6$H$_4$	Ph	**2g**	*d*
8	**1h**	Ph	p-MeC$_6$H$_4$	**2h**	74
9	**1i**	Ph	p-MeOC$_6$H$_4$	**2i**	73
10	**1j**	Ph	p-ClC$_6$H$_4$	**2j**	55
11	**1k**	Ph	t-Bu	**2k**	*e*
12	**1l**	p-MeC$_6$H$_4$	p-MeC$_6$H$_4$	**2l**	78
13	**1m**	p-MeOC$_6$H$_4$	p-MeC$_6$H$_4$	**2m**	58[c]
14	**1n**	p-MeOC$_6$H$_4$	p-ClC$_6$H$_4$	**2n**	16[c]
15	**1o**	m-MeC$_6$H$_4$	Ph	**2o**	61
16	**1p**	m-MeOC$_6$H$_4$	Ph	**2p**	72
17	**1q**	o-MeC$_6$H$_4$	Ph	**2q**	50[f]
18	**1r**	o-MeOC$_6$H$_4$	Ph	**2r**	*d*
19	**1s**	Ph	m-MeC$_6$H$_4$	**2s**	67
20	**1t**	Ph	m-MeOC$_6$H$_4$	**2t**	34
21	**1u**	Ph	o-MeC$_6$H$_4$	**2u**	65[f]

[a] Reaction conditions: **1** (1.0 mmol), Yb (0.5 mmol), THF (2 mL), HMPA (0.5 mL), MeI (2 μL), 1-NpCHO (1.0 mmol), rt, 2 h. [b] GC yield based on the aldimine **1**. [c] Isolated yield. [d] Complex mixtures were formed. [e] No reaction. [f] At reflux temperature.

The data in Table 2 show that room temperature is the best to obtain the highest yield of diimine **2a** in this reaction (entry 1). Both lower and higher temperatures result in the decrease of the yield of diimines (entries 2−5). The low temperature would decrease the reactivity of the ytterbium−aldimine intermediate, while the high-temperature accelerates the decomposition of the intermediate.

Optimized reaction conditions are employed for the dehydrogenative coupling of various aldimine derivatives mediated by Yb metal (eq 3). The representative results of the dehydrogenative coupling reactions are given in Table 3.



(3)

1 **2**

When the substrates are nonsubstituted, or p-methyl- and p-methoxy-substituted aromatic aldimines (**1a**−**c**,**h**,**i**,**l**,**m**) (entries 1−3, 8, 9, 12, and 13), the reactions proceed smoothly to give dark-brown or dark-red suspension in several minutes, and addition of 1-NpCHO affords the corresponding diimines (**2a**−**c**,**h**,**i**,**l**,**m**) in good to high yields. On the contrary, the yields of **2** are low in the reactions of p-cyano- and p-chloro-substituted aldimines (**1e**,**f**,**j**,**n**) (entries 5, 6, 10, and 14), and reaction proceeded slowly. For example, the color of the reaction mixture did not change to blue-black until the mixture of **1f** and Yb metal was stirred for about 1 h under the present conditions. These results suggest that the electron-donating substituent on the benzene ring promotes the reaction. In the case of **1g**, a complex mixture was formed. It might be due to the nitro group on the benzene ring, which also reacts with Yb metal to make the reaction complicated.[16] It is noteworthy that aliphatic aldimines are unsuitable to the reaction. For instance, in the case of **1k** (entry 11), the reaction proceeded slowly and most of Yb metal remained unreacted in the reaction mixture. The lower reactivity of aliphatic aldimines was also observed in the reaction of aldimines with SmI$_2$.[12a] To investigate possible steric effects of substitutents on the dehydrogenative coupling reaction, o- and m-substituted aldimines were examined (entries 15−21). As for m-substituted aldimines (**1o**,**p**,**s**,**t**) (entries 15, 16, 19, and 20), the reaction proceeded smoothly to give good yields of diimines (**2o**,**p**,**s**) except **1t**. In the case of **1t**, only 34% yield of **2t** was obtained due to coordination of methoxy group on the benzene ring to the Yb, which would lower the reactivity of a Yb−aldimine complex to 1-NpCHO. However, all yields of diimines (**1o**,**p**,**s**,**t**) (entries 15, 16, 19, and 20) are lower than those corresponding to p-substituted aldimines (**1b**,**c**,**h**,**i**) (entries 2, 3, and 8, 9). This may be due to the less steric hindrance of p-substituted aldimines (**1b**,**c**,**h**,**i**). On the other hand, as for o-substituted aldimines (**1q**,**r**,**u**), a great steric hindrance is observed. From the reactions of the o-methyl-substituted aldimines **1q** and **1u** at room temperature no diimines **2q** and **2u** were formed, but from the hydrogenation product, diamines were formed as the main products. In the cases of **1q** and **1u**, reflux temperature was needed to cause the reactions (entries 17 and 21). In the case of o-methoxy-substituted aldimine **1r** (entry 18), the complex mixture was obtained even at reflux temperature.

The cross-coupling diimine could be obtained by the reaction of two different aldimines with Yb metal. For example, after Yb metal (0.5 mmol) had been allowed to react with the mixture of aldimines **1b** (0.5 mmol) and **1c** (0.5 mmol) at room temperature for 2 h, 1-NpCHO (1 mmol) was added and the mixture continuously stirred for 2 h, there was obtained the cross-coupling product, N,N'-diphenyl-1-(p-methoxy)-2-(p-methyl)-ethane-1,2-diimine **2bc**, in 23% yield together with homocoupling products **2b** (43%) and **2c** (29%) (eq 4). This result indicates that the unsymmetrical dimeric intermediate would be formed in the reaction.

We also investigated dehydrogenative coupling of various aldimines mediated by Sm metal. The reaction was carried out under conditions similar to those in the case of Yb metal (Table 4). It is of interest to note that Yb and Sm metals exhibit different reactivities in this reaction. The yields of diimines by Sm in Table 4, compared with those in the case of Yb metal (Table 3), are low (entries 1−7 in Table 4). The different reactivities of Yb and Sm metals have been observed in the reduction of nitroarenes.[16]

In addition, when the samarium diiodide (SmI$_2$) was used in the reaction of **1c**, the yield of diimine (**2c**) was

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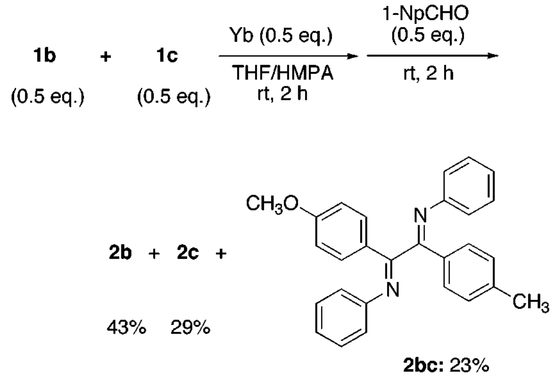
Table 4. Dehydrogenative Coupling Reaction of Various Aldimines Mediated by Samarium Metal[a]

entry	aldimine	R^1	R^2	product	yield[b] (%)
1	**1a**	Ph	Ph	**2a**	38[c]
2	**1b**	p-MeC_6H_4	Ph	**2b**	68
3	**1b**	p-MeC_6H_4	Ph	**2b**	38[c]
4	**1c**	p-$MeOC_6H_4$	Ph	**2c**	37
5	**1h**	Ph	p-MeC_6H_4	**2h**	56
6	**1i**	Ph	p-$MeOC_6H_4$	**2i**	23
7	**1j**	Ph	p-ClC_6H_4	**2j**	40
8	**1q**	o-MeC_6H_4	Ph	**2q**	36[d]

[a] Reaction conditions: **1** (1.0 mmol), Sm (0.5 mmol), THF (2 mL), HMPA (0.5 mL), MeI (2 μL), 1-NpCHO (1.0 mmol), rt, 2 h. [b] GC yield based on aldimine **1**. [c] Sm (1.0 mmol) was used. [d] At reflux temperature.



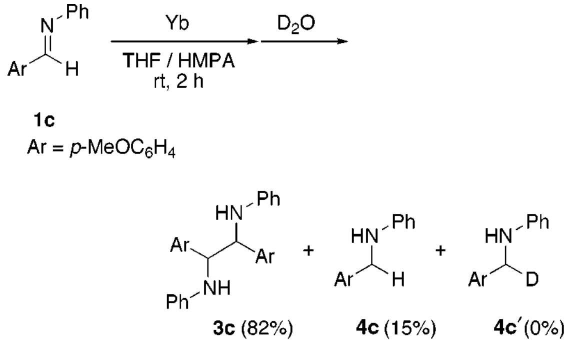
(4)

very low, only 13% yield (eq 5). Metallic Yb or Sm plays as a two-electron reductant in this reaction, while the SmI_2 generally plays as a one-electron reductant;[1a,e,f,g] thus, SmI_2 seems to be a poor regent for the dehydrogenative coupling reaction.

$$\underset{(1\text{ eq.})}{\mathbf{1c}} + \underset{(1\text{ eq.})}{SmI_2} \xrightarrow[\text{THF/HMPA, rt, 2 h}]{} \xrightarrow[\text{rt, 2 h}]{\text{1-NpCHO (1 eq.)}} \underset{13\%}{\mathbf{2c}} \qquad (5)$$

As mentioned above, the present reaction seems to consists of two steps: (1) formation of a Yb−aldimine complex by the reaction of aldimines with Yb metal in the first step and (2) coordination and reduction of 1-NpCHO to the Yb−aldimine complex to give the diimine product in the second step. We believe that the reaction proceeds according to a pinacol-type mechanism in a manner similar to that of carbonyl compounds in the first step.[3b,17] Deuterium oxide (D_2O) treatment of the reaction mixture of **1c** and Yb metal was carried out under the same reaction conditions. The reaction gave diamine **3c** (82%) and amine **4c** (15%), but no *C*-deuterated product **4c′** was formed (eq 6). This result suggests that a metallacycle aldimine dianion intermediate[3b] is not the precursor of amine **4c**. Thus, **4c** would be formed by hydrogen abstraction from solvent (THF or HMPA).[12c]

In this reaction, hydrogen transfer from the aldimine to 1-NpCHO must take place to give the diimine product and 1-$NpCH_2OH$ (1-naphthalenemethanol). To comfirm this point, a *C*-deuterated aldimine [*N*-benzylideneaniline-*d* (**1a′**)] was allowed to react with Yb metal under the same conditions. The reaction of **1a′** with Yb metal followed by treatment with 1-NpCHO gave **2a** and the corresponding deuterated 1-naphthalenemethanol **5′** (eq 7).



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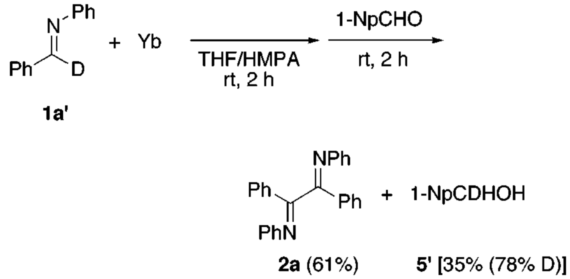

(7)

This result clearly indicates that transformation of hydride from aldimine **1a′** to 1-NpCHO takes place. In addition, D_2O treatment of the final reaction mixture did not afford *C*-deuterated alcohol **5′** (1-NpCHDOH), indicating that the deuterium atom of 1-NpCHDOH is not derived from water.

On the basis of the above several control experiments, we propose a plausible mechanism of dehydrogenative coupling reaction of aldimines mediated by Yb metal as depicted in Scheme 1.

First, Yb metal reacts with one molecule of aldimine **1** via single-electron transfer (SET) mechanism in a manner similar to pinacol coupling of carbonyl compounds,[17] to give univalent species **A**. The highly reactive species **A** would immediately react with another molecule of aldimine **1** to produce azametallacyclopentane **C**[18] via formation of a diradical intermediate **B**, which rapidly forms **C** via intramolecular homocoupling. Then two molecules of the aldehyde coordinate to the Yb of intermediate **C** to give complex **D**, in which double-hydride transfer to the carbon atom of the carbonyl group of the coordinated aldehyde takes place as in a manner similar to that of the Meerwin−Pondorf−Varley reduction/Oppenauer oxidation,[19] to give vicinal diimine **2** and ytterbium alkoxides **E**. The later species **E** gives an alcohol R^3CH_2OH (**5**) and trivalent ytterbium(III) salts **F** when quenched with water. In addition, if the reaction intermediate **C** is treated with water, reductive dimerization product, diamine **3** can be obtained.[11] Thus, the present reaction proceeds via a reductive dimerization/oxidative dehydrogenation mechanism. As mentioned above, the diimine yields of the reaction of Yb metal with aldimines are higher than those of the reaction of Sm metal. It is

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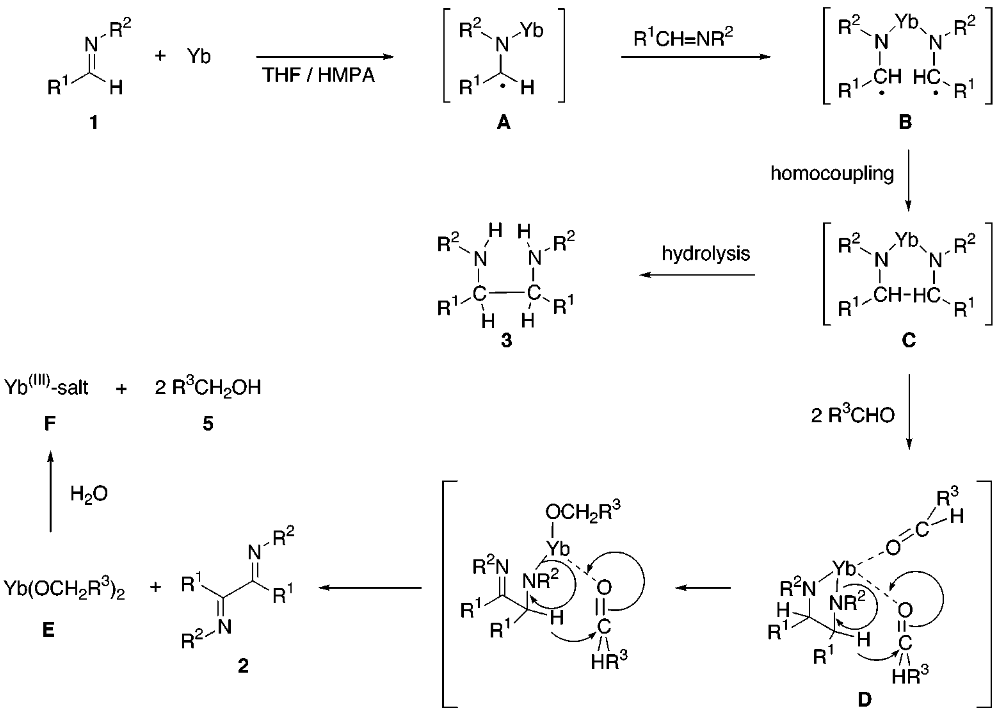
(17) Wirth, T. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 61.

(18) We attempted to prepare and isolate the intermediate **C** (Ar = Ar′ = Ph) and obtained dark-red needles. Since the complex is very air- and moisture-sensitive the X-ray analysis was not successful. However, this complex gave the diimine upon treatment with 1-NpCHO in THF.

(19) (a) Ponndorf, W. *Angew. Chem.* **1926**, *39*, 138. (b) Djerassi, C. *Org. React.* **1951**, *6*, p 208.

Scheme 1



noted that the tendency to hydride transfer toward aldehyde is strongly dependent on the Lewis acidity of the center metal ion in this reaction. The carbonyl group of the aldehyde in **D** is more easily polarized and more easily accepts hydride in complex **D** having metal atom which has the stronger Lewis acidity. Thus Yb metal which has the higher stronger Lewis acidity than Sm,[20] would give higher yield of diimines (**2**).

Conclusions

We have demonstrated a novel reductive dimerization/oxidative dehydrogenation reaction of aldimines mediated by lanthanoid metals, to give ethane-1,2-diimines **2** in good to high yields. The reaction proceeds in the presence of aromatic aldehydes under midle conditions such as room temperature in THF. Although there are many reports on the reductive dimerization of aldimines by low-velant metal reagents,[21] this kind of two-step one-pot dehydrogenative coupling of aldimines is not reported to date. To the best of our knowledge, this is the first example of metal mediated dehydrogenative coupling of aldimines. It has been made clear that the reaction of aldimines with lanthanoid metals followed by treating with an aromatic aldehyde proceeds via a reductive dimerization/oxidative dehydrogenation mechanism. This is a quite new type reaction mediated by lanthanoid metals. The finding of this reaction should contribute to the developments of synthetic chemistry as well as chemistry of lanthanoids.

Experimental Section

General Methods. Melting points were recorded on a YANACO micro melting appratus and are uncorrected. IR spectra were recorded with a HORIBA FT-200 spectrophotometer. ^1H NMR spectra were recorded on a JEOL JNM-AL 300 FT-NMR (300 MHz) spectrometer in $CDCl_3$ solution and are reported in parts per million (δ) downfield from internal tetramethylsilane (TMS). ^{13}C NMR spectra were recorded on a JEOL JNM-AL 300 FT-NMR (75.5 MHz) spectrometer in $CDCl_3$ solution. The center peak of $CDCl_3$ (77.0 ppm) was used as the internal reference. GC analysis of the reaction mixture was done on a Shimadzu GC-6A system. Elemental analyses were performed by the Chemical Analysis Center of Kyushu University. Ytterbium (40 mesh) and samarium (20 mesh) metals were obtained from Shiga Rare Metallic Co. Ytterbium metal was washed with anhydrous hexane under argon and dried in vacuo. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under argon prior to use. Hexamethylphosphoramide (HMPA) was dried over calcium hydride, distilled, and then stored under argon. *Caution: care must be taken in the handing of HMPA because of toxicity.* Toluene was distilled from sodium metal under argon. All reactions were carried out under argon atmosphere. The aldimines were prepared from aldehydes and the corresponding aniline derivatives by published procedures.[22] All other starting organic compounds were commercially available and were used without further purification.

General Procedures for the Synthesis of *N,N′*-Diaryl-1,2-diarylethane-1,2-diimines (2) from the Dehydrogenative Coupling Reaction of Aldimines Mediated by Lanthanoid Reagents. THF (2.0 mL), HMPA (0.5 mL), and methyl iodide (2 μL) were successively added to a mixture of aldimines **1** (1.0 mmol) and lanthanoid metals (0.5 mmol; in the case of SmI_2 (0.1 mol/l), 1.0 mmol (10 mL) was used) under argon atmosphere, and when the solution turned to brown-black or blue-black, it was stirred for 2 h at room temperature. Then, 1-naphthaldehyde (1.0 mmol, 156 mg) was added to the mixture. The resulting mixture was stirred for an additional 2 h at room temperature. The reaction mixture was quenched with water (0.1 mL) and diluted with ether (20 mL). After usual workup followed by a silica gel column chromatography (*n*-hexanes−ethyl acetate), the desired compounds **2** were

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[20] The Lewis acidity is affected by the charge density (Z/r; Z = nuclear charge, r = cation radius) of metal cations. Because of lanthanoid contraction, the atomic and the ionic radii decrease monotonically with increasing atomic number. See also ref 8a.

[21] (a) Talukdar, S.; Banerji, A. *J. Org. Chem.* **1998**, *63*, 3468. (b) Rieke, R. D.; Kim, S.-H. *J. Org. Chem.* **1998**, *63*, 5235 and references quoted therein.

[22] (a) Layer, R. W. *Chem. Rev.* **1963**, *63*, 489 and references therein. (b) Colebourne, N.; Foster, R. G.; Robson, E. *J. Chem. Soc. C* **1967**, 685. (c) Padawa, A.; Bergmark, W.; Pashayan, D. *J. Am. Chem. Soc.* **1969**, *91*, 2653.

obtained. GC yields of the diimines were obtained by using triphenylphosphine oxide as an internal standard based on aldimine.

***N,N′*-Diphenyl-1,2-diphenylethane-1,2-diimine (2a):** mp 141−143 °C (methanol); ^{1}H NMR (CDCl$_3$) δ 6.50−6.53 (m, 4H), 6.96−7.09 (m, 6H), 7.35−7.44 (m, 6H), 7.88−7.90 (m, 4H); ^{13}C NMR (CDCl$_3$) δ 120.0, 124.9, 128.3, 128.4, 128.7, 131.1, 137.6, 149.3, 163.9; IR (KBr) 1622 cm^{-1}. Anal. Calcd for $C_{26}H_{20}N_2$: C, 86.67; H, 5.56; N, 7.78. Found: C, 86.69; H, 5.64; N, 7.84.

***N,N′*-Diphenyl-1,2-di(*p*-methylphenyl)ethane-1,2-diimine (2b):** mp 147−149 °C (methanol); ^{1}H NMR (CDCl$_3$) δ 2.38 (s, 6H), 6.47−6.50 (m, 4H), 6.97−7.07 (m, 6H), 7.19 (d, J = 8.7 Hz, 4H), 7.78 (d, J = 8.7 Hz, 4H); ^{13}C NMR (CDCl$_3$) δ 21.5, 120.1, 124.6, 128.3, 128.3, 129.4, 135.2, 141.5, 149.5, 163.9; IR (KBr) 1622 cm^{-1}. Anal. Calcd for $C_{28}H_{24}N_2$: C, 86.60; H, 6.19; N, 7.22. Found: C, 86.32; H, 6.37; N, 7.20.

***N,N′*-Diphenyl-1,2-di(*p*-methoxyphenyl)ethane-1,2-diimine (2c):** mp 151−153 °C (methanol); ^{1}H NMR (CDCl$_3$) δ 3.83 (s, 6H), 6.47−6.50 (m, 4H), 6.88−7.08 (m, 10H), 7.83−7.86 (m, 4H); ^{13}C NMR (CDCl$_3$) δ 55.3, 114.0, 120.2, 124.5, 128.3, 130.1, 130.7, 149.6, 161.8, 163.3; IR (KBr) 1622 cm^{-1}. Anal. Calcd for $C_{28}H_{24}N_2O_2$: C, 80.00; H, 5.71; N, 6.67. Found: C, 79.89; H, 5.80; N, 6.72.

***N,N′*-Diphenyl-1,2-di(*p*-dimethylaminophenyl)ethane-1,2-diimine (2d):** mp 245−247 °C (methanol); ^{1}H NMR (CDCl$_3$) δ 3.02 (s, 12H), 6.47 (d, J = 7.5 Hz, 4H), 6.65 (d, J = 9.0 Hz, 4H), 6.93−7.06 (m, 6H), 7.80 (d, J = 9.0 Hz, 4H); ^{13}C NMR (CDCl$_3$) δ 40.1, 111.3, 120.5, 123.8, 126.2, 128.1, 130.0, 150.2, 151.9, 164.0; IR (KBr) 1618 cm^{-1}. Anal. Cacd for $C_{30}H_{30}N_4$: C, 80.72; H, 6.73; N, 12.56. Found: C, 80.63; H, 6.82; N, 12.56.

***N,N′*-Diphenyl-1,2-di(*p*-chlorophenyl)ethane-1,2-diimine (2e):** mp 145−147 °C (methanol); ^{1}H NMR (CDCl$_3$) δ 6.49−6.52 (m, 4H), 7.02−7.12 (m, 6H), 7.36−7.40 (m, 4H), 7.77−7.81 (m, 4H); ^{13}C NMR (CDCl$_3$) δ 120.0, 125.3, 128.5, 129.1, 129.5, 135.7, 137.5, 148.9, 162.3; IR (KBr) 1610 cm^{-1}. Anal. Calcd for $C_{26}H_{18}N_2Cl_2$: C, 72.74; H, 4.20; N, 6.53. Found: C, 72.91; H, 4.34; N, 6.43.

***N,N′*-Diphenyl-1,2-di(*p*-cyanophenyl)ethane-1,2-diimine (2f):** mp 222−224 °C (methanol); ^{1}H NMR (CDCl$_3$) δ 6.59−6.63 (m, 4H), 7.06−7.15 (m, 6H), 7.66−7.69 (m, 4H), 7.89−7.92 (m, 4H); ^{13}C NMR (CDCl$_3$) δ 114.8, 118.1, 120.1, 126.3, 128.5, 128.8, 132.7, 140.4, 148.3, 161.4; IR (KBr) 2229,-1614 cm^{-1}. Anal. Calcd for $C_{28}H_{18}N_4$: C, 81.95; H, 4.39; N, 13.66. Found: C, 81.66; H, 4.47; N, 13.57.

***N,N′*-Di(*p*-methylphenyl)-1,2-diphenylethane-1,2-diimine (2h):** mp 160−162 °C (methanol); ^{1}H NMR (CDCl$_3$) δ 2.24 (s, 6H), 6.50−6.53 (m, 4H), 6.88 (d, J = 7.8 Hz, 4H), 7.34−7.42 (m, 6H), 7.85−7.88 (m, 4H); ^{13}C NMR (CDCl$_3$) δ 20.9, 120.3, 128.2, 128.7, 129.0, 130.9, 134.6, 137.6, 146.8, 163.8; IR (KBr) 1622 cm^{-1}. Anal. Calcd for $C_{28}H_{24}N_2$: C, 86.60; H, 6.19; N, 7.22. Found: C, 86.37; H, 6.30; N, 7.12.

***N,N′*-Di(*p*-methoxyphenyl)-1,2-diphenylethane-1,2-diimine (2i):** mp 171−172 °C (methanol); ^{1}H NMR (CDCl$_3$) δ 3.72 (s, 6H), 6.65−6.66 (m, 8H), 7.36−7.41 (m, 6H), 7.84−7.87 (m, 4H); ^{13}C NMR (CDCl$_3$) δ 55.4, 113.7, 122.1, 128.1, 128.7, 130.8, 137.4, 142.5, 157.3, 163.3; IR (KBr) 1622 cm^{-1}. Anal. Calcd for $C_{28}H_{24}N_2O_2$: C, 80.00; H, 5.71; N, 6.67. Found: C, 80.08; H, 5.76; N, 6.74.

***N,N′*-Di(*p*-chlorophenyl)-1,2-diphenylethane-1,2-diimine (2j):** mp 168−170 °C (methanol); ^{1}H NMR (CDCl$_3$) δ 6.42−6.47 (m, 4H), 7.04−7.07 (m, 4H), 7.38−7.48 (m, 6H), 7.84−7.88 (m, 4H); ^{13}C NMR (CDCl$_3$) δ 121.4, 128.3, 128.5, 128.9, 130.4, 131.6, 137.2, 147.7, 164.3; IR (KBr) 1622 cm^{-1}. Anal. Calcd for $C_{26}H_{18}N_2Cl_2$: C, 72.74; H, 4.20; N, 6.53. Found: C, 73.00; H, 4.22; N, 6.59.

***N,N′*-Di(*p*-methylphenyl)-1,2-di(*p*-methylphenyl)ethane-1,2-diimine (2l):** mp 164−166 °C (methanol); ^{1}H NMR (CDCl$_3$) δ 2.23 (s, 6H), 2.37 (s, 6H), 6.47 (d, J = 8.4 Hz, 4H), 6.86 (d, J = 8.4 Hz, 4H), 7.17 (d, J = 7.8 Hz, 4H), 7.76 (d, J = 7.8 Hz, 4H); ^{13}C NMR (CDCl$_3$) δ 20.9, 21.5, 120.3, 128.2, 128.9, 129.4, 134.2, 135.1, 141.2, 146.9, 163.8; IR (KBr) 1618 cm^{-1}. Anal. Calcd for $C_{30}H_{28}N_2$: C, 86.54; H, 6.73; N, 6.73. Found: C, 86.33; H, 6.86; N, 6.77.

***N,N′*-Di(*p*-methylphenyl)-1,2-di(*p*-methoxyphenyl)ethane-1,2-diimine (2m):** mp 126−128 °C (methanol); ^{1}H NMR (CDCl$_3$) δ 2.23 (s, 6H), 3.82 (s, 6H), 6.47−6.49 (m, 4H), 6.86−6.89 (m, 8H), 7.80−7.83 (m, 4H); ^{13}C NMR (CDCl$_3$) δ 20.9, 55.4, 114.0, 120.5, 128.9, 130.0, 130.6, 134.1, 147.0, 161.7, 163.2; IR (KBr) 1618 cm^{-1}. Anal. Calcd for $C_{30}H_{28}N_2O_2$: C, 80.36; H, 6.25; N, 6.25. Found: C, 80.25; H, 6.43; N, 6.18.

***N,N′*-Di(*p*-chlorophenyl)-1,2-di(*p*-methoxyphenyl)ethane-1,2-diimine (2n):** mp 150−152 °C (methanol); ^{1}H NMR (CDCl$_3$) δ 3.85 (s, 6H), 6.42 (d, J = 8.4 Hz, 4H), 6.91 (d, J = 8.7 Hz, 4H), 7.04 (d, J = 8.4 Hz, 4H), 7.82 (d, J = 8.7 Hz, 4H); ^{13}C NMR (CDCl$_3$) δ 55.4, 114.2, 121.6, 128.4, 130.0, 130.1, 130.2, 147.8, 162.2, 163.8; IR (KBr) 1601 cm^{-1}. Anal. Calcd for $C_{28}H_{22}Cl_2N_2O_2$: C, 68.73; H, 4.50; N, 5.73. Found: C, 69.12; H, 4.62; N, 5.70.

***N,N′*-Diphenyl-1,2-di(*m*-methylphenyl)ethane-1,2-diimine (2o):** mp 168−170 °C (methanol); ^{1}H NMR (CDCl$_3$) δ 2.37 (s, 6H), 6.49−6.53 (m, 2H), 6.96−7.09 (m, 6H), 7.25−7.27 (m, 6H), 7.57−7.60 (m, 2H), 7.79 (s, 2H); ^{13}C NMR (CDCl$_3$) δ 21.5, 120.1, 124.8, 126.1, 128.2, 128.3, 128.5, 131.9, 137.7, 138.5, 149.4, 164.2; IR (KBr) 1622 cm^{-1}. Anal. Calcd for $C_{28}H_{24}N_2$: C, 86.60; H, 6.19; N, 7.22. Found: C, 86.61; H, 6.29; N, 7.23.

***N,N′*-Diphenyl-1,2-di(*m*-methoxyphenyl)ethane-1,2-diimine (2p):** mp 144−146 °C (methanol); ^{1}H NMR (CDCl$_3$) δ 3.82 (s, 6H), 6.51 (d, J = 7.2 Hz, 4H), 6.99−7.10 (m, 8H), 7.26−7.38 (m, 4H), 7.54 (s, 2H); ^{13}C NMR (CDCl$_3$) δ 55.4, 112.1, 117.6, 120.1, 121.6, 124.9, 128.4, 129.6, 139.1, 149.2, 159.8, 163.6; IR (KBr) 1622 cm^{-1}. Anal. Calcd for $C_{28}H_{24}N_2O_2$: C, 80.00; H, 5.71; N, 6.67. Found: C, 80.00; H, 5.77; N, 6.71.

***N,N′*-Di(*m*-methylphenyl)-1,2-diphenylethane-1,2-diimine (2s):** mp 105−106 °C (methanol); ^{1}H NMR (CDCl$_3$) δ 2.13 (d, 6H), 6.25 (d, 2H), 6.38 (d, J = 7.8 Hz, 2H), 6.81 (d, J = 7.8 Hz, 2H), 6.96 (t, J = 7.8 Hz, 2H), 7.36−7.47 (m, 6H), 7.86 (d, J = 7.8 Hz, 4H); ^{13}C NMR (CDCl$_3$) δ 21.3, 116.3, 121.3, 125.4, 128.1, 128.3, 128.7, 131.0, 137.8, 138.0, 149.4, 163.9; IR (KBr) 1626 cm^{-1}. Anal. Calcd for $C_{28}H_{24}N_2$: C, 86.60; H, 6.19; N, 7.22. Found: C, 86.45; H, 6.23; N, 7.25.

***N,N′*-Di(*m*-methoxyphenyl)-1,2-diphenyl-1,2-diimine (2t):** mp 140−141 °C (methanol); ^{1}H NMR (CDCl$_3$) δ 3.50 (s, 6H), 6.00 (s, 2H), 6.18 (d, J = 7.8 Hz, 2H), 6.57 (dd, J = 2.1 Hz, 2H), 7.98 (t, J = 7.8 Hz, J = 8.4 Hz, 2H), 7.38−7.46 (m, 6H), 7.89 (d, J = 8.4 Hz, 4H); ^{13}C NMR (CDCl$_3$) δ 54.8, 105.2, 111.6, 111.7, 128.4, 128.8, 129.1, 131.2, 137.7, 150.7, 159.6, 164.1; IR (KBr) 1610 cm^{-1}. Anal. Calcd for $C_{28}H_{24}N_2O_2$: C, 80.00; H, 5.71; N, 6.67. Found: C, 80.01; H, 5.79; N, 6.69.

Dehydrogenative Coupling of *o*-Substituted Aldimines (1q,u) Mediated by Ytterbium Metal. THF (2.0 mL), HMPA (0.5 mL), and methyl iodide (2 μL) were successively added to a mixture of aldimines **1q** (or **1u**) (1.0 mmol, 195 mg) and ytterbium metal (0.5 mmol, 87 mg) under argon atmosphere, and when the solution turned brown-black, it was stirred for 2 h at room temperature. Then, the reaction mixture was heated to refluxing temperature, and 1-NpCHO (1.0 mmol, 156 mg) was added to the mixture. The resulting mixture was stirred for an additional 2 h at reflux temperature. The reaction mixture was quenched with water (0.1 mL) and diluted with ether (20 mL). After usual workup followed by a silica gel column chromatography (*n*-hexanes−ethyl acetate) the desired compound **2q** (or **2u**) was obtained.

***N,N′*-Diphenyl-1,2-di(*o*-methylphenyl)ethane-1,2-diimine (2q):** mp 181−182 °C (methanol); ^{1}H NMR (CDCl$_3$) δ 2.31 (s, 6H), 6.60−6.61 (m, 4H), 6.63−6.64 (m, 2H), 6.86−7.19 (m, 12H); ^{13}C NMR (CDCl$_3$) δ 20.49, 119.0, 120.1, 124.2, 125.0, 128.1, 128.2, 128.7, 129.7, 135.8, 149.9, 169.8; IR (KBr) 1612 cm^{-1}. Anal. Calcd for $C_{28}H_{24}N_2$: C, 86.60; H, 6.19; N, 7.22. Found: C, 86.26; H, 6.26; N, 7.21.

***N,N′*-Di(*o*-methylphenyl)-1,2-diphenyl-1,2-diimine (2u):** mp 145−147 °C (methanol); ^{1}H NMR (CDCl$_3$) δ 1.31 (s, 6H), 6.52 (d, J = 7.8 Hz, 2H), 6.77−6.95 (m, 6H), 7.40−7.47 (m, 6H), 7.95−7.99 (m, 4H); ^{13}C NMR (CDCl$_3$) δ 16.6, 116.7, 125.0, 125.5, 128.4, 128.8, 129.9, 130.9, 132.3, 138.3, 147.9, 162.5; IR (KBr) 1614 cm^{-1}. Anal. Calcd for $C_{28}H_{24}N_2$: C, 86.60; H, 6.19; N, 7.22. Found: C, 86.33; H, 6.27; N, 7.25.

Cross-Coupling Reaction of Aldimines 1b and 1c Mediated by Ytterbium Metal. THF (2.0 mL), HMPA (0.5 mL), and methyl iodide (2 μL) were successively added to a mixture of aldimines **1b** (0.5 mmol, 98 mg) and **1c** (0.5 mmol, 106 mg) and ytterbium metal (0.5 mmol, 87 mg) under argon atmosphere, and when the color of the mixture turned brown-black, it was stirred for 2 h at room temperature. Then, 1-naphthaldehyde (1.0 mmol, 156 mg) was added to the mixture. The resulting mixture was stirred for an additional 2 h at room temperature. The reaction mixture was quenched with water (0.1 mL) and diluted with ether (20 mL). Usual workup followed by a silica gel column chromatography (*n*-hexanes−ethyl acetate) gave the cross-coupling product **2bc**.

***N*,*N*′-Diphenyl-1-*p*-methoxyphenyl-2-*p*-methylphenylethane-1,2-diimine (2bc):** mp 154−156 °C (methanol); ^{1}H NMR (CDCl$_3$) δ 2.39 (s, 3H), 3.84 (s, 3H), 6.47 (d, J = 7.8 Hz, 4H), 6.89 (d, J = 8.7 Hz, 2H), 6.97−7.08 (m, 6H), 7.20 (d, J = 8.4 Hz, 2H), 7.80 (dd, J = 8.4 Hz, J = 8.7 Hz, 4H); ^{13}C NMR (CDCl$_3$) δ 21.5, 55.4, 114.0, 120.1, 120.2, 124.5, 124.6, 128.3, 128.3, 129.5, 130.1, 130.6, 135.2, 141.5, 149.5, 149.5, 161.8, 163.2, 163.9; IR (KBr) 1620 cm^{-1}. Anal. Calcd for $C_{28}H_{24}N_2O$: C, 83.17; H, 5.94; N, 6.93. Found: C, 83.09; H, 6.06; N, 6.88.

Acknowledgment. The present work was supported in part by a Grant-in-Aid for Scientific Research on Priority Areas No. 283, “Innovative Synthetic Reactions”. from Monbusho. Y.M. gratefully acknowledges the financial support of this research by the Japan Society for the Promotion of Science in the form of Research Fellowships for Young Scientists.

JO001328D