



Preparation of ionic liquids bearing *o*-carborane anion via *N,N'*-dialkylimidazol-2-ylidene carbene

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ARTICLE INFO

Article history:

Received 16 September 2008

Received in revised form 30 October 2008

Accepted 31 October 2008

Available online 7 November 2008

Keywords:

Carborane

Ionic liquid

Carbene

Ionic conductivity

ABSTRACT

In the present study, a novel ionic liquid including *o*-carborane anion was prepared. After the carbene formation of 1-ethyl-3-methylimidazolium halide ([EMIm]⁺[X][−]) by reaction with *n*-BuLi, the subsequent reaction with *o*-carborane afforded the desired ionic liquid in moderate yields. The structure of the ionic liquid was supported by ¹H NMR and ¹¹B NMR spectra.

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1. Introduction

In recent years, numerous number of papers have been published on ionic liquids (ILs) because of their intriguing characteristics such as non volatility, non flammability and high ionic conductivity. Their potential utilities range from reaction media [1], solvents for biomaterials [2], electrolytes for electrochemical devices [3] and so forth. A versatile types of ILs have been developed so far, however, boron containing ILs are relatively limited except that BF₄[−] is widely employed as anion. These days, a variety of organoboron functional materials [4] has been developed especially in the field of light emitting materials, electron transporting materials, and bio-sensors. Because of diversity of organoboron chemistry, it is attractive approach to further expand the library of ILs.

To improve the selectivity of target cation transport, imidazolium type molten salts bearing organoboron anion receptor [5] were prepared via hydroboration of 1-allylimidazolium type molten salts. This strategy was extended to design of organoboron solid polymer electrolytes [6] and organoborate type zwitterionic molten salt [7]. The ILs bearing a perfluoroalkyltrifluoroborates [8] were also reported by Tatsumi et al. Watanabe et al. reported lithium cation containing organoborate ILs bearing oligoethers [9]. ILs including a boronium cation were also reported by Rogers and co-workers [10].

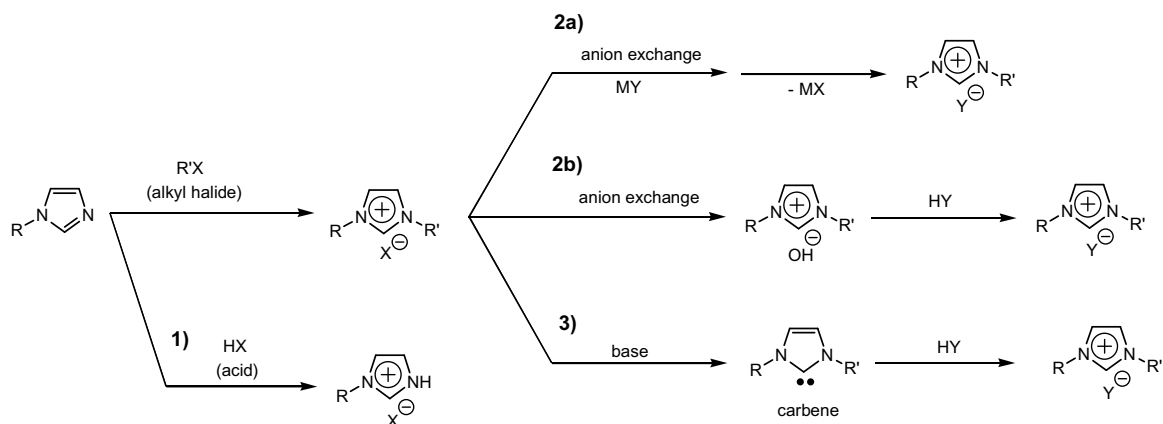
On the other hand, more boron-rich type molten salts including carborane were reported in 2000. Larsen and Reed et al. reported a

series of carborane anion based imidazolium salts via ion exchange reaction of silver or cesium salts of carborane anions [11]. By a similar method, alkylpyridinium carborane salts were also prepared by Zhu et al. [12]. It was found that alkylpyridinium type carborane salt showed a comparatively low melting point. An open-face carborane cluster anion was also recently incorporated into ILs [13]. These ionic carboranes are interesting as potential reaction media for nucleophilic substitution reactions, because carborane anions generally show low coordinating power. Such ILs are also considered important for further investigation of super acid chemistry. Moreover, ionic carborane derivatives have potential utility as tumor targeting reagent in boron–neutron–capture–therapy (BNCT) [14] or liquid neutron moderators in nuclear processing [15]. Very recently, ILs having trialkylammoniododecaborates were also reported by Gabel et al. [16].

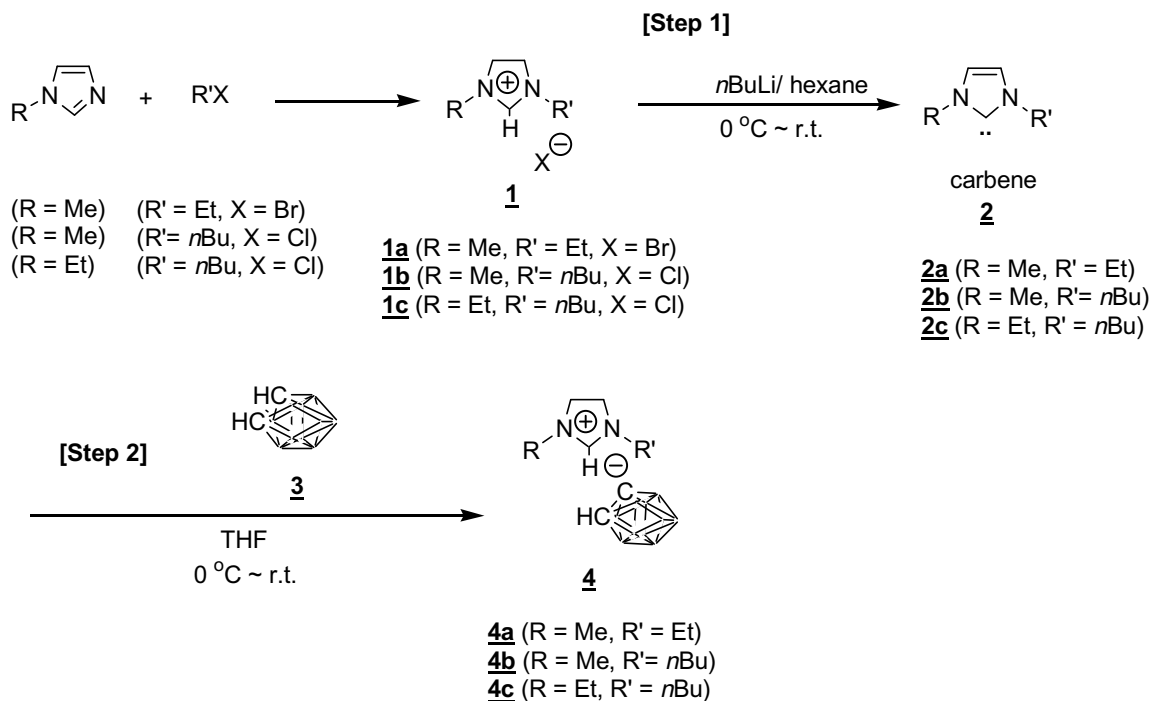
In the present study, we have undertaken to develop an alternative method for the preparation of carborane anion based ILs. As synthetic method for ILs, several different approaches such as (1) neutralization of amine with Brønsted acid [17], (2) ion exchange reaction of imidazolium salts [18] and (3) reaction of imidazolidene carbene [19] are known so far (Scheme 1). We have examined to utilize these methodologies for the preparation of carborane anion based ILs. Because of relatively low brønsted acidity of carboranes, neutralization of amines with *o*-carborane did not take place at all. A reaction of imidazolium hydroxide with *o*-carborane was also attempted under several reaction conditions, however, the mixture of starting materials was recovered. On the other hand, desired molten salts bearing carborane anion were successfully prepared via the reaction of imidazolyidene carbene with *o*-carborane (Scheme 2).

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Scheme 1. Synthetic method for ionic liquids. (1) Neutralization of amine with Brønsted acid, (2) ion exchange reaction of imidazolium salts and (3) reaction of imidazolylidene carbene.



Scheme 2. Synthesis of ionic liquids bearing *o*-carborane anion.

It is widely known that deprotonation of 1,3-dialkylimidazolium cation leads to formation of a carbene which is stabilized by adjacent nitrogen atoms [20]. It is reported that such imidazolylidene carbene undergoes a reaction with methyl carboxylate whose pK_a is 25 to form the corresponding IL. Since pK_a of *o*-carborane is 23.3 [21], *o*-carborane is expected to readily react with 1,3-dialkylimidazol-2-ylidene carbenes under a similar reaction condition.

In the present method, it is not necessary to prepare silver or cesium salts of carborane anions prior to the synthesis of ILs. Such a facile synthetic procedure should be industrially more accessible in comparison with the reported methods.

2. Results and discussion

The preparation of carborane anion based ILs was carried out as depicted in Scheme 2. To a THF solution of *N,N'*-dialkylimidazolium halide, an equimolar amount or slight excess amount of *n*-BuLi in

n-hexane was added at 0 °C, and the reaction mixture was stirred for 5–60 min. Then, THF solution of equimolar amount of *o*-carborane was added, and the resulting solution was further stirred for 12 h while the reaction mixture was gradually warmed up to room temperature. After the evaporation of the solvent, the residue was extracted with 2-propanol and then purified by reprecipitation into diethylether. The products were obtained as yellowish soft solid in moderate yields. The results of the reactions using various molten salts are listed in Table 1. With increasing the reaction time for carbene formation step, yields of the product were improved. When 1-butyl-3-methylimidazolium chloride (**1b**) or 1-ethyl-3-butylimidazolium chloride (**1c**) was employed as starting materials, the yields of the products were relatively lower compared with the case of 1-ethyl-3-methylimidazolium bromide (**1a**). This should be due to higher viscosity of the reaction mixture including **1b** or **1c**. Moreover, some of **1b** and **1c** frozen during the reaction with *n*-BuLi at 0 °C. When the reaction mixture was extracted with

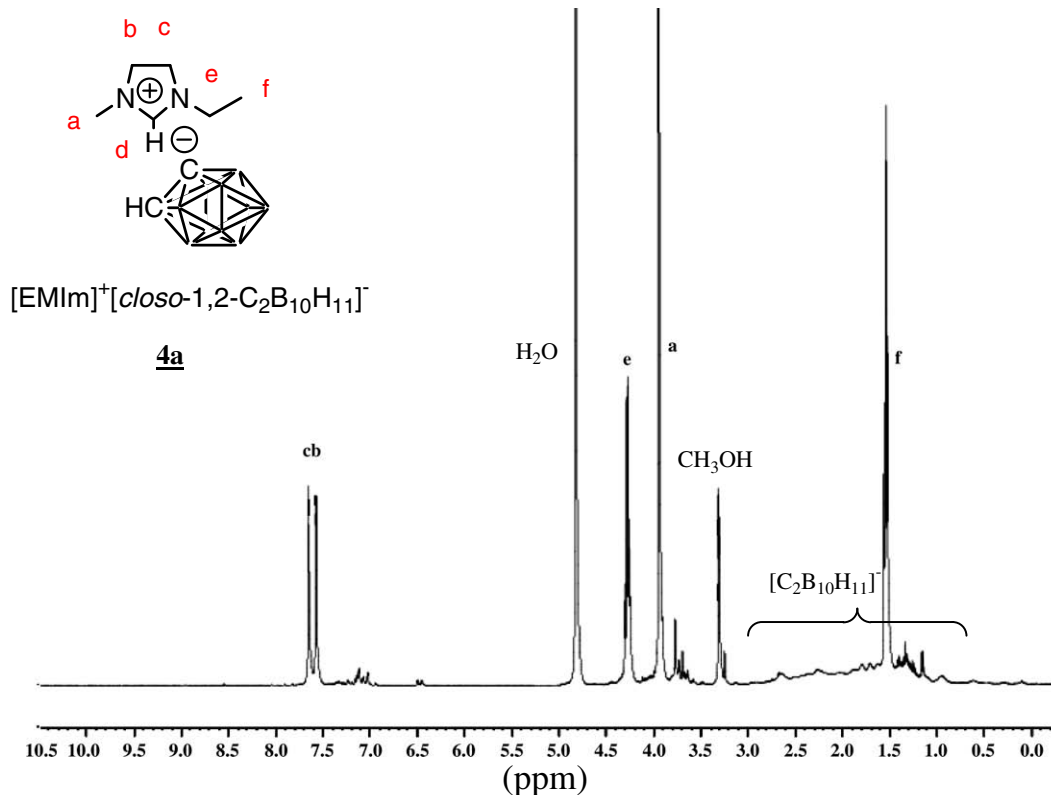
Table 1
Synthesis of **4** under various reaction conditions^a.

Entry	Ionic liquid, mg (mmol)	<i>n</i> BuLi ^b , mmol	Time ^c , min	3 ^d , mg (mmol)	Time ^e , h	Yield, mg (%)
1	1a 204 (1.07)	1.20	60	145 (1.01)	12	249 (91)
2	306 (1.60)	2.00	10	231 (1.60)	12	317 (78)
3	307 (1.61)	1.65	5	232 (1.61)	12	242 (59)
4	1b 269 (1.70)	1.80	10	245 (1.70)	12	232 (49)
5	320 (1.83)	2.12	10	247 (1.71)	12	192 (37)
6	1c 189 (1.00)	1.00	30	144 (1.00)	19	187 (69)

^a Under nitrogen atmosphere.^b *n*-butyllithium, in *n*-hexane, 1.63 mol/l.^c Reaction time for Step 1, 0 °C ~ r.t.^d In THF (entry 1; 0.42 ml, entry 2; 0.6 ml, entry 3; 0.8 ml, entry 4; 0.8 ml, entry 5; 0.8 ml, entry 6; 0.4 ml).^e Reaction time for Step 2; 0 °C ~ r.t.

2-propanol, some insoluble part whose structure was unclear remained. On the other hand, from the TLC analysis (ethyl acetate: methanol (v/v) = 10:1) of the 2-propanol soluble part using PdCl₃-HCl(aq.) [22], one main spot (R_f 0.36) was observed, while no other spot due to by-product or unreacted carborane was detected. The structures of the obtained organoboron ILs were characterized by ¹H (Fig. 1) and ¹¹B NMR spectra. The ¹H NMR spectrum of [EMIm]⁺[*closo*-1,2-C₂B₁₀H₁₁]⁻ (**4a**) is represented in Fig. 1. In the ¹H NMR spectra measured in CD₃OD, wavy peaks that are characteristic for carborane structure were observed for each system. The peak due to the proton at 2nd position of imidazolium ring did not appear in the ¹H NMR spectrum, similarly to the case of previously reported carborane based molten salts. This should be due to rapid proton–deuterium exchange in CD₃OD as reported in Ref. [23].

Instead of *o*-carborane, *m*-carborane was also examined as a starting material, however, the reaction did not take place at all possibly due to significantly larger pK_a of *m*-carborane (27.9) in comparison with that of *o*-carborane (23.3) [21].

**Fig. 1.** ¹H NMR spectrum of **4a** in CD₃OD.**Table 2**
Solubility test for **4a**.

Solvent	Dipole moment [D]	Solubility
Hexane	0.09	×
Toluene	0.31	×
CHCl ₃	1.15	×
Et ₂ O	1.15	×
<i>i</i> PrOH	1.66	○
EtOH	1.66	○
THF	1.75	×
H ₂ O	1.78	×
THF/H ₂ O ^a	–	○
Acetone	2.69	×
MeOH	2.87	○
CH ₃ CN	3.44	×
DMSO	3.90	○

^a THF/H₂O (v/v) = 1/1.

The obtained ILs were stable under air. After stored under air for 4 weeks, no significant spectroscopic change was observed in the ¹H NMR spectra.

The solubility of **4a** in various organic solvents was examined at room temperature. The results are listed in Table 2. The IL **4a** was well soluble in 2-propanol, ethanol, methanol and DMSO, while it was insoluble in *n*-hexane, toluene, chloroform, diethylether, THF, H₂O, acetone and acetonitrile. Although *o*-carborane was not soluble in THF/H₂O (v/v = 1/1), **4a** was readily soluble in THF/H₂O (v/v = 1/1), indicating improved hydrophilicity of **4a**.

The ionic conductivity of **4a** was evaluated by ac impedance method after the sample was dried thoroughly. The observed ionic conductivity was 2.9×10^{-5} S cm⁻¹ at 51 °C, which was comparatively low among ILs. However, the observed bulk ionic conductivity was one order of magnitude higher than those for carborane type ILs that were recently reported by Gabel et al. [16]. As represented in Fig. 2, **4a** showed relatively large temperature dependence of ionic conductivity possibly because of high viscosity.

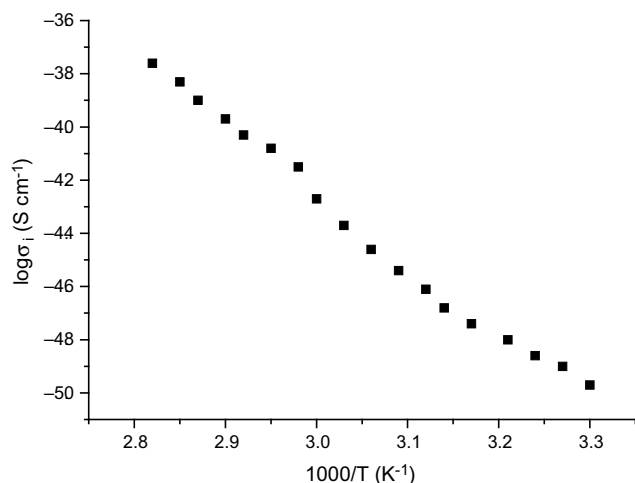


Fig. 2. Temperature dependence of ionic conductivity for **4a**.

From the DSC (differential scanning calorimetry) measurement, melting point of **4a** was observed at 30.4 °C. Although the melting point was slightly higher than that of $[N\text{-pentyl-C}_5\text{H}_5\text{N}]^+[\textit{closo-CB}_{11}\text{H}_{12}]^-$ (m.p. 19 °C) [12], incorporation of *o*-carborane anion resulted in significantly lowered melting point of the obtained IL. This would be useful for further design of carborane anion based ILs showing lower melting point.

In conclusion, a series of novel organoboron ILs including *o*-carborane anion were facilely prepared via carbene formation of *N,N'*-dialkylimidazolium halides. Their structures were confirmed by ¹H and ¹¹B NMR spectra. The obtained ILs were soluble in H₂O/THF (v/v = 1/1) at room temperature. $[\text{EMIm}]^+[\textit{closo-1,2-C}_2\text{B}_{10}\text{H}_{11}]^-$ (**4a**) showed its melting point at 30.4 °C, which was significantly lower than those for carborane anion based imidazolium type molten salts reported in Ref. [11] ($[\text{EMIm}]^+[\text{1-C}_3\text{H}_7\text{-CB}_{11}\text{H}_{11}]^-$, m.p. 45 °C; $[\text{EMIm}]^+[\text{1-C}_4\text{H}_9\text{-CB}_{11}\text{H}_{11}]^-$, m.p. 49 °C).

This indicated potential utility of these ILs as reaction media for a variety of nucleophilic substitution reactions. The ionic conductivity of $[\text{EMIm}]^+[\textit{closo-1,2-C}_2\text{B}_{10}\text{H}_{11}]^-$ (**4a**) was found to be $2.9 \times 10^{-5} \text{ S cm}^{-1}$ at 51 °C.

3. Experimental section

3.1. Instruments and materials

o-Carborane (Wako. Co. Ltd.), *n*-butyllithium in *n*-hexane (1.63 M; Kanto Reagents. Co. Ltd.), 2-propanol (Kanto Reagents. Co. Ltd.) were purchased and used without further purification. Tetrahydrofuran was purchased from Kishida Chemicals Co. Ltd. and used after distilled over sodium. *N,N'*-Dialkylimidazolium halides were prepared according to the reported method [24].

¹H and ¹¹B NMR spectra were recorded on Bruker ARX-400 or JEOL-A400 Win Alipha FT-NMR system. DSC (differential scanning calorimetry) measurements were made on DSC-6200 (Seiko Instruments. Co. Ltd.). Ionic conductivity of ionic liquids was measured by ac impedance method using Solartron 1260. Thin layer chromatography (TLC) analysis for ILs was carried out using PdCl₂/HCl aq. solution that is capable of detecting boron cluster derivatives [22].

All the reactions were carried out under inert atmosphere.

3.2. Synthesis of $[\text{EMIm}]^+[\textit{closo-1,2-C}_2\text{B}_{10}\text{H}_{11}]^-$ (**4a**)

To a 1-ethyl-3-methylimidazolium bromide (204 mg, 1.07 mmol), 1.20 mmol of *n*-butyllithium (1.63 M in *n*-hexane) was added at 0 °C, and the reaction mixture was stirred for 1 h

while the reaction mixture was gradually warmed up to room temperature. Then a THF solution (0.4 ml) of *o*-carborane (145 mg, 1.01 mmol) was added to the reaction mixture, and the resulting mixture was stirred for 12 h at room temperature. After the solvents were removed under reduced pressure, the resulting solid was extracted with 2-propanol. The insoluble part was removed by filtration. Then, the solvent of the soluble part was removed, and the obtained crude product was purified by reprecipitation into diethylether. $[\text{EMIm}]^+[\textit{closo-1,2-C}_2\text{B}_{10}\text{H}_{11}]^-$ was obtained as a yellowish soft solid (249 mg, 91% yield).

¹H NMR (CD₃OD, δ, ppm) 0.8–3.0 (br, 14H, NCH₂CH₃ and C₂B₁₀H₁₁), 3.8 (3H, NCH₃), 4.3 (2H, NCH₂CH₃), 7.5 (2H, NCHCHN).

¹¹B NMR (CD₃OD, δ, ppm) –21.8 (d, 2B), –28.3 (d, 4B), –32.3 (d, 4B).

3.3. Synthesis of $[\text{BMIm}]^+[\textit{closo-1,2-C}_2\text{B}_{10}\text{H}_{11}]^-$ (**4b**)

To a 1-butyl-3-methylimidazolium bromide (269 mg, 1.70 mmol), 1.80 mmol of *n*-butyllithium (1.63 M in *n*-hexane) was added at 0 °C, and the reaction mixture was stirred for 10 min. Then a THF solution (0.8 ml) of *o*-carborane (245 mg, 1.70 mmol) was added to the reaction mixture, and the resulting mixture was stirred for 12 h at room temperature. After the solvents were removed under reduced pressure, the resulting solid was extracted with 2-propanol. The insoluble part was removed by filtration. Then, the solvent of the soluble part was removed, and the obtained crude product was purified by reprecipitation into diethylether. $[\text{BMIm}]^+[\textit{closo-1,2-C}_2\text{B}_{10}\text{H}_{11}]^-$ was obtained as a yellowish soft solid (232 mg, 49% yield).

¹H NMR (CD₃OD, δ, ppm) 0.8–3.0 (br, 18H, NCH₂CH₂CH₂CH₃, C₂B₁₀H₁₁), 3.8 (3H, NCH₃), 4.2 (2H, NCH₂CH₂CH₂CH₃), 7.6 (2H, NCHCHN).

3.4. Synthesis of $[\text{BEIm}]^+[\textit{closo-1,2-C}_2\text{B}_{10}\text{H}_{11}]^-$ (**4c**)

To a 1-butyl-3-ethylimidazolium bromide (189 mg, 1.00 mmol), 1.00 mmol of *n*-butyllithium (1.63 M in *n*-hexane) was added at 0 °C, and the reaction mixture was stirred for 30 min. Then a THF solution (0.4 ml) of *o*-carborane (144 mg, 1.00 mmol) was added to the reaction mixture, and the resulting mixture was stirred for 19 h at room temperature. After the solvents were removed under reduced pressure, the resulting solid was extracted with 2-propanol. The insoluble part was removed by filtration. Then, the solvent of the soluble part was removed, and the obtained crude product was purified by reprecipitation into diethylether. $[\text{BEIm}]^+[\textit{closo-1,2-C}_2\text{B}_{10}\text{H}_{11}]^-$ was obtained as a yellowish soft solid (187 mg, 69% yield).

¹H NMR (CD₃OD, δ, ppm) 0.8–3.0 (br, 21H, NCH₂CH₃, NCH₂CH₂CH₂CH₃ and C₂B₁₀H₁₁), 4.3 (2H, NCH₂CH₂CH₂CH₃), 4.5–4.6 (2H, –NCH₂CH₃), 7.4 (2H, NCHCHN).

Acknowledgements

The present study was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan (#20031013).

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