

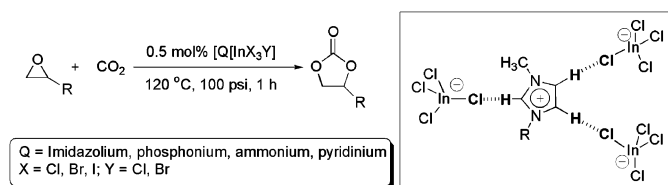
# Tetrahaloindate(III)-Based Ionic Liquids in the Coupling Reaction of Carbon Dioxide and Epoxides To Generate Cyclic Carbonates: H-Bonding and Mechanistic Studies

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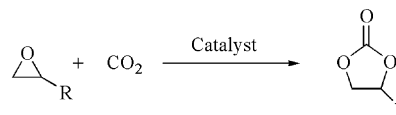


The microwave reactions of  $\text{InX}_3$  with  $[\text{Q}]\text{Y}$  produce a series of tetrahaloindate(III)-based ionic liquids (ILs) with a general formula of  $[\text{Q}][\text{InX}_3\text{Y}]$  ( $\text{Q}$  = imidazolium, phosphonium, ammonium, and pyridinium;  $\text{X}$  = Cl, Br, I;  $\text{Y}$  = Cl, Br). The reaction of  $\text{CO}_2$  with a variety of epoxides has been examined in the presence of these ILs wherein tetrahaloindate(III)-based ILs are found to exhibit high catalytic activities and evidence is presented that supports the significant role of H-bonding interactions in the  $[\text{Q}][\text{InX}_3\text{Y}]$ -catalyzed coupling reactions. The effects of various parameters such as temperature, pressure, and molar ratio of propylene oxide to catalyst have been investigated, and the plausible reaction mechanism based on the  $^1\text{H}$  and  $^{13}\text{C}$  NMR studies is presented for the formation of propylene carbonate.

## Introduction

Catalytic transformation of carbon dioxide into useful organic compounds has attracted much attention during the last two decades due to economic and environmental benefits arising from the utilization of renewable source and the growing concern on the greenhouse effect.<sup>1</sup>  $\text{CO}_2$  is an abundant, cheap, and safe  $\text{C}_1$  building block in organic synthesis; however, due to the inert nature of  $\text{CO}_2$ , efficient catalytic processes for chemical fixation remain a significant challenge. One of the most promising endeavors in this area is the coupling reaction of  $\text{CO}_2$  with epoxides affording the five-membered cyclic carbonates (Scheme 1) which find numerous applications, for example, as precursors for polymeric materials such as polyurethanes and polycarbonates, as aprotic polar solvents in various chemical processes, and as intermediates in the production of pharmaceutical and fine chemicals.<sup>2</sup> In addition, cyclic carbonates are in increasing demand

## SCHEME 1. Synthesis of Cyclic Carbonates



nowadays for use in secondary- and fuel-cell batteries and as solvents for polymer and gel electrolytes.<sup>3</sup> Substantial literature on the catalyst development for the coupling reactions has been reported.<sup>4</sup> The use of transition-metal halides ( $\text{AlCl}_3$ ,  $\text{NiCl}_2$ ,  $\text{MoCl}_3$ ) along with Lewis bases such as tetraalkylammonium halide or alkali metal halide catalyst systems have also been employed in such coupling reactions where halide ligands act as nucleophile.<sup>5</sup> While some advances have been made, most of the

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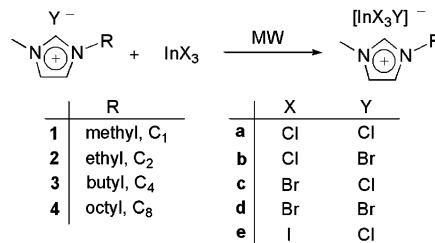
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catalyst systems still suffer from either the need for the use of cosolvent and additional Lewis bases<sup>4b</sup> or requirements for high pressures and/or temperatures.<sup>4i</sup>

Room-temperature ionic liquids (RTILs) have been developed for task-specific purposes,<sup>6</sup> including their role as active catalysts in organic synthesis.<sup>7</sup> Accordingly, imidazolium-based ILs have been employed as reaction media and/or catalysts for the above coupling reactions but the productivity was not high enough for practical purposes.<sup>8f</sup> Notable among these has been the catalyst systems comprising bisimidazolium-based halozincates that show significant improvement in the catalytic activity to be of practical value with higher turnover frequency (TOF).<sup>8a–e</sup> Although the nature of the imidazolium cation and its interaction with various anions have been explored by spectroscopic and crystallographic methods for imidazolium-based RTILs bearing AlCl<sub>4</sub><sup>−</sup>, BF<sub>4</sub><sup>−</sup>, and PF<sub>6</sub><sup>−</sup> as anionic components,<sup>9</sup> there has been no systematic study conducted that sheds some light on the enhanced catalytic activity of dialkylimidazolium metal halides in the coupling reaction of CO<sub>2</sub> with epoxides. During the course of our study on the tetrahaloindate-based RTILs for the development of their use as both solvent and catalyst,<sup>10a</sup> these were found to be less viscous and

## SCHEME 2. MW-Assisted Preparation of [C<sub>n</sub>mim][InX<sub>3</sub>Y]



thermally stable when compared to bisimidazolium halozincates. Since the catalytic performance of bisimidazolium halozincates for the coupling reaction have been well documented<sup>8a–e</sup> and in view of the fact that imidazolium tetrachloroindate(III) ILs exhibit an appropriate Lewis acidity without being reactive toward air or moisture,<sup>11</sup> we have undertaken an investigation into the H-bonding properties of these indate-based ILs as well as the effect of H-bonds on the catalytic activity for the title reaction.

Herein, we report the catalytic activities for the coupling reaction using a series of ionic liquids (Scheme 1) with a general formula of [Q][InX<sub>3</sub>Y] (Q = imidazolium, phosphonium, ammonium, and pyridinium; X = Cl, Br, I; Y = Cl, Br) including reaction mechanism specifically invoking the importance of H-bonds. These ILs are highly active, thermally stable, and easily recyclable. Furthermore, in-situ NMR studies clearly establish the reaction pathway for the formation of cyclic carbonates. More advantageously, the colorless product was obtained in contrast to the discoloration which plagued the conventional preparations requiring additional purification steps.

## Results and Discussion

### Synthesis of Tetrahaloindate(III)-Based ILs and Their Properties.

Various dialkylimidazolium tetrahaloindates(III) with a general formula, [C<sub>n</sub>mim][InX<sub>3</sub>Y], consisting of 1-alkyl-3-methylimidazolium cations, [C<sub>n</sub>mim]<sup>+</sup> (n = 1, 2, 4, 8), and tetrahaloindate [InX<sub>3</sub>Y]<sup>−</sup> (X = Cl, Br, I; Y = Cl, Br), were synthesized via modified protocol using microwave (MW) irradiation under solvent-free conditions.<sup>10</sup> Admixing equimolar amounts of InX<sub>3</sub> (X = Cl, Br, I) and 1-alkyl-3-methylimidazolium halide, [C<sub>n</sub>mim]Y (n = 1, 2, 4, 8; Y = Cl or Br), followed by MW irradiation for 15 or 30 s afforded a crude mixture of liquid and a small quantity of unreacted InX<sub>3</sub>, which was removed using a syringe filter to produce pure ionic liquid compounds 1–4 (Scheme 2).<sup>10a</sup>

Similarly, tetrabutylphosphonium- (5a), ammonium- (6a), and butylpyridinium-based [InCl<sub>4</sub>] (7a) were prepared by reacting indium trichloride (InCl<sub>3</sub>) with tetrabutylphosphonium (TBP), tetrabutylammonium (TBA), and butyl pyridinium (C<sub>4</sub>Py) chlorides, respectively (Scheme 3). Compounds 1a, 2a, 3e, 5a, 6a, and 7a were solids at room temperature with melting points of 68, 27, 49, 71, 90, and 24 °C, respectively, whereas 3a–d and 4a–c were colorless room-temperature ionic liquids with low viscosity in melting point range of −15 to −6 °C.

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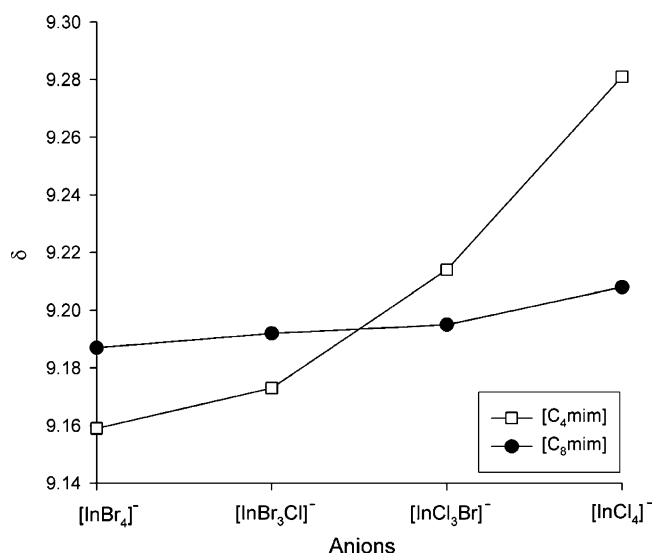
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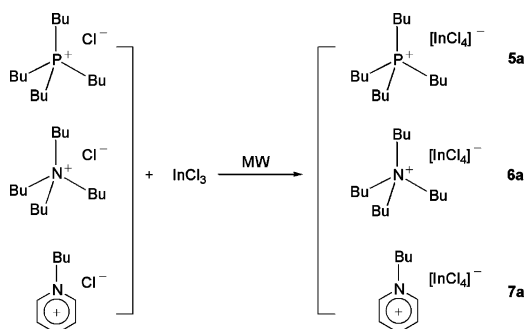
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**FIGURE 1.** Effect of anion on the C(2) proton chemical shift ( $\delta$ ) in the imidazolium ring.

**SCHEME 3. MW-Assisted Preparation of [TBP][InCl<sub>4</sub>] (5a), [TBA][InCl<sub>4</sub>] (6a), and [C<sub>4</sub>Py][InCl<sub>4</sub>] (7a)**

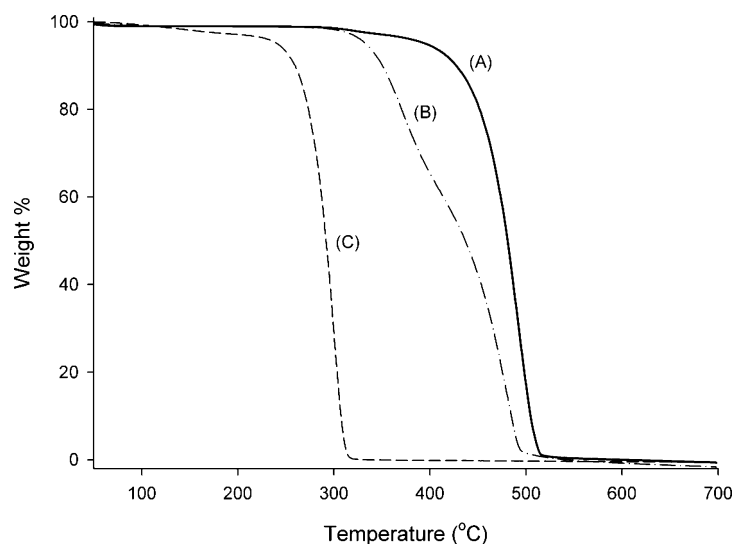


Unlike  $\text{InCl}_3$ , the ionic liquid compounds **1–7** are fairly air- and moisture-stable and highly soluble in common polar organic solvents such as dichloromethane, tetrahydrofuran (THF), acetonitrile, acetone, and dimethyl sul-

foxide (DMSO). All compounds were fully characterized by NMR spectroscopy and elemental analysis.

Figure 1 shows the effect of a variation of halides in tetrahaloindates on the  $^1\text{H}$  NMR chemical shifts of C(2) proton in the imidazolium ring constituents of the ionic liquids,  $[\text{C}_4\text{mim}][\text{InX}_3\text{Y}]$  and  $[\text{C}_8\text{mim}][\text{InX}_3\text{Y}]$ . The NMR spectra are recorded in 0.5 M solution of  $\text{DMSO-}d_6$  to eliminate concentration effect, and the listed values are the average of three NMR recordings (Supporting Information). Although the chemical shift differences are minor in the case of  $[\text{C}_8\text{mim}][\text{InX}_3\text{Y}]$ , they gradually increased with increase in the total sum of electronegativities of  $[\text{InX}_3\text{Y}]^-$ , i.e., the more  $\text{Cl}^-$  in the anion, the more downfield shift in the C(2) proton, thereby establishing the relative chemical shift order to be  $[\text{InCl}_4]^- > [\text{InCl}_3\text{Br}]^- > [\text{InBr}_3\text{Cl}]^- \approx [\text{InBr}_4]^-$ .

The thermogravimetric analysis (TGA) experiments were conducted to compare the thermal stabilities of  $[\text{C}_4\text{mim}][\text{InCl}_4]$  (**3a**) with earlier investigated catalysts,  $[\text{C}_4\text{mim}]\text{Cl}^{\text{8f}}$  and  $[\text{C}_4\text{mim}]_2[\text{ZnBr}_2\text{Cl}_2]$ .<sup>8a</sup> Recent reports have suggested that the thermal decomposition of imidazolium salts is heavily dependent on the salt structures. Generally, halide anions in imidazolium salts dramatically reduce the thermal stability with the onset of decomposition occurring at least  $100\text{ }^\circ\text{C}$  below the corresponding ILs with nonhalide anions.<sup>12</sup> The results in Figure 2 also show that the thermal stability is strongly dependent on the type of anion.  $[\text{C}_4\text{mim}]\text{Cl}$  is only stable up to  $150\text{ }^\circ\text{C}$  and started to decompose gradually and then decomposed rapidly between  $250$  and  $310\text{ }^\circ\text{C}$  at a constant rate with a temperature onset of  $301\text{ }^\circ\text{C}$ . The temperature onset for decomposition temperature of  $[\text{C}_4\text{mim}]_2[\text{ZnBr}_2\text{Cl}_2]$  showed several points ( $370$  and  $478\text{ }^\circ\text{C}$ ) as shown in Figure 2, suggesting that the decomposition mode of  $[\text{C}_4\text{mim}]_2[\text{ZnBr}_2\text{Cl}_2]$  is relatively complex. On the other hand, the compound **3a** was stable up to  $400\text{ }^\circ\text{C}$  without any loss of its original weight and decomposed rapidly between  $440$  and  $520\text{ }^\circ\text{C}$  with a temperature onset of  $494\text{ }^\circ\text{C}$  at a constant rate, thereby establishing the relative thermal stability order as  $[\text{C}_4\text{mim}][\text{InCl}_4] > [\text{C}_4\text{mim}]_2[\text{ZnBr}_2\text{Cl}_2] > [\text{C}_4\text{mim}]\text{Cl}$ . The TGA analyses for **5a**, **6a**,



**FIGURE 2.** TGA results for (A)  $[\text{C}_4\text{mim}][\text{InCl}_4]$ ; (B)  $[\text{C}_4\text{mim}]_2[\text{ZnBr}_2\text{Cl}_2]$ ; (C)  $[\text{C}_4\text{mim}]\text{Cl}$ .

**TABLE 1.** Catalytic Activities of Various Catalysts for the Coupling Reaction<sup>a</sup>

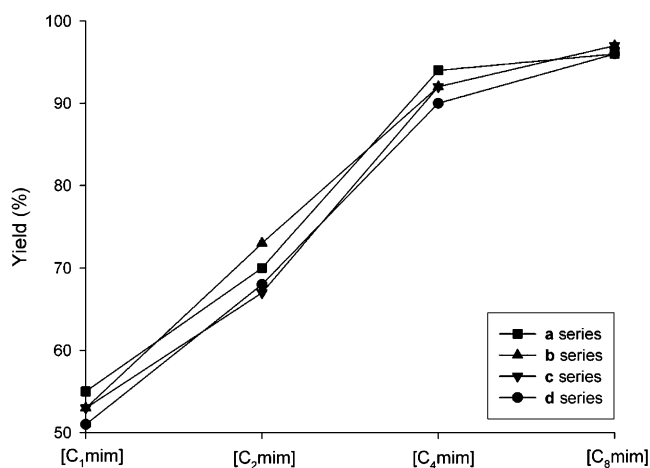
entry	catalyst	time (h)	yield <sup>b</sup> (%)	selectivity (%)	TOF <sup>c</sup> (h <sup>-1</sup> )
1	InCl <sub>3</sub>	2	0		0
2	[C <sub>4</sub> mim]Cl	1	9	100	18
3	[C <sub>4</sub> mim]Cl + InCl <sub>3</sub>	1	90	100	180
4	[C <sub>4</sub> mim][InCl <sub>4</sub> ] ( <b>3a</b> )	1	94	100	188
5	[C <sub>4</sub> mim][InCl <sub>3</sub> Br] ( <b>3b</b> )	1	92	100	184
6	[C <sub>4</sub> mim][InBr <sub>3</sub> Cl] ( <b>3c</b> )	1	92	100	184
7	[C <sub>4</sub> mim][InBr <sub>4</sub> ] ( <b>3d</b> )	1	93	100	186
8	[C <sub>4</sub> mim][InI <sub>3</sub> Cl] ( <b>3e</b> )	1	75	100	150
9	KCl + InCl <sub>3</sub>	2	trace		
10	KI + InCl <sub>3</sub>	1	70	100	140
11 <sup>d</sup>	[BDmim][InCl <sub>4</sub> ]	1	95	100	190
12 <sup>e</sup>	[TBP][InCl <sub>4</sub> ] ( <b>5a</b> )	1	65	100	130
13 <sup>f</sup>	[TBA][InCl <sub>4</sub> ] ( <b>6a</b> )	1	49 <sup>g</sup>	90	98
14 <sup>h</sup>	[C <sub>4</sub> Py][InCl <sub>4</sub> ] ( <b>7a</b> )	1	97	100	194

<sup>a</sup> Conditions: PO (3 g, 51.6 mmol), catalyst (0.252 mmol, 0.5 mol %). *T* = 120 °C, *P*<sub>CO<sub>2</sub></sub> = 100 psi. <sup>b</sup> Isolated yield. <sup>c</sup> TOF = (moles of propylene carbonate)/(moles of catalyst)<sup>-1</sup> h<sup>-1</sup>. <sup>d</sup> BDmim = 3-butyl-1,2-dimethylimidazolium. <sup>e</sup> TBP = tetra-*n*-butylphosphonium. <sup>f</sup> TBA = tetra-*n*-butylammonium. <sup>g</sup> Decomposed compounds (*n*-butyl bromide, tri-*n*-butylamine) were detected in GC-MS. <sup>h</sup> C<sub>4</sub>Py = *n*-butylpyridinium.

and **7a** were also carried out and the thermal stabilities were compared with those compounds (Supporting Information).

**Catalytic Activity.** The catalytic activities of various ionic liquids containing tetrahaloindate(III) were evaluated for the coupling reactions of CO<sub>2</sub> with propylene oxide (PO) for the formation of propylene carbonate (PC) using 0.5 mol % of specified catalyst at 120 °C and 100 psi of CO<sub>2</sub> pressure for 1 h. The results summarized in Table 1 show that [C<sub>4</sub>mim]Cl has the poorest activity (entry 2), and InCl<sub>3</sub> alone is completely inactive (entry 1). However, the combination of [C<sub>4</sub>mim]Cl and InCl<sub>3</sub> resulted in a surprisingly high activity to afford propylene carbonate in 90% yield (entry 3). This dramatic synergistic effect may be attributed to the in-situ formation of [C<sub>4</sub>mim][InCl<sub>4</sub>] which showed even higher activity in comparison with the two component system to deliver 94% yield with the turnover frequency (TOF) of 188 h<sup>-1</sup> (entry 4). All the imidazolium-based ionic liquids containing tetrahaloindates showed excellent activities for the coupling reactions to produce more than 92% yield of propylene carbonate and the usual byproducts such as polyalkylene oxides and halogenated compounds were not detected by GPC and GC analysis. Furthermore, all of the resulting products obtained using these ionic liquid catalysts are clear and colorless in contrast to the conventional preparations where discoloration has been a lingering problem due to the complicated product purification and catalyst recycling steps.

It has been reported that in the case of [C<sub>4</sub>mim]<sub>2</sub>[ZnX<sub>2</sub>Y<sub>2</sub>] (X, Y = Cl or Br)-catalyzed coupling reactions of CO<sub>2</sub> with epoxides, the dissociation of a halide ion from the zinc center and the subsequent attack of the halide ion on the carbon atom of an epoxide is facilitated with more nucleophilic bromide ions, leading to the following reactivity order: [ZnBr<sub>4</sub>]<sup>2-</sup> > [ZnBr<sub>2</sub>Cl<sub>2</sub>]<sup>2-</sup> > [ZnCl<sub>4</sub>]<sup>2-</sup>.<sup>8a-e</sup> However, it is worth noting that the variation of counteranion of the indates **3a–d** did not significantly influence the catalytic activity (entries 4–7). This unexpected result led us to explore the effects of halide ligands and

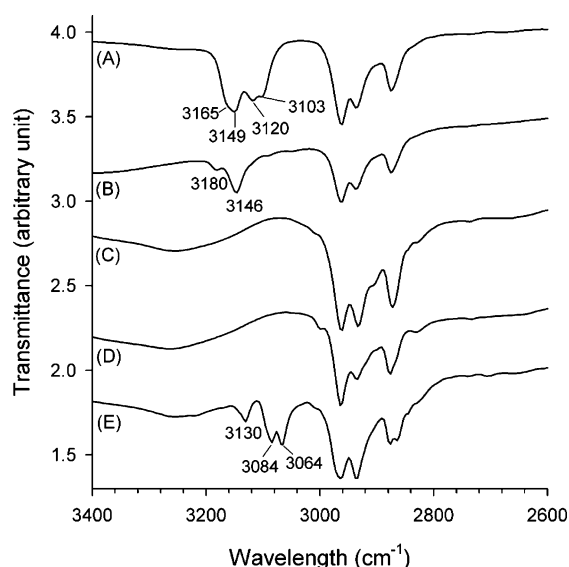


**FIGURE 3.** Effects of halide ligands and alkyl chain length of the imidazolium tetrahaloindate(III) on the catalytic activities using [C<sub>*n*</sub>mim][InX<sub>3</sub>Y] (*n* = 1, 2, 4, 8; **a** series = [InCl<sub>4</sub>]; **b** series = [InCl<sub>3</sub>Br]; **c** series = [InBr<sub>3</sub>Cl]; **d** series = [InBr<sub>4</sub>]).

the variation of alkyl chain length of the imidazolium tetrahaloindate on the catalytic activities using [C<sub>*n*</sub>mim][InX<sub>3</sub>Y] (*n* = 1, 2, 4, 8; **a** series = [InCl<sub>4</sub>]; **b** series = [InCl<sub>3</sub>Br]; **c** series = [InBr<sub>3</sub>Cl]; **d** series = [InBr<sub>4</sub>]). As shown in Figure 3, the catalytic activity again was not found to be influenced by the nature of nucleophilicity of halides, which is in accord with previous results. It is likely that once an anion dissociates from the indate(III), the catalytic activity might also be affected by the Lewis acidity of InX<sub>3</sub>. Then there are two conflicting factors: Lewis acidity and nucleophilicity. Because both the high Lewis acidity and nucleophilicity can result in the high catalytic performance, the two factors may compete with each other for the activation of the epoxide. In other words, the Lewis acidity of InCl<sub>3</sub> is stronger than that of InBr<sub>3</sub> whereas the relative nucleophilicity of Cl<sup>-</sup> is weaker than Br<sup>-</sup>, thus finally compensating the effect of halides in terms of catalytic activities. This effect might be more pronounced in the case of indate-catalyzed reaction due to the relatively stronger Lewis acidity of indium halide than that of zinc halide. Figure 3 also shows that the catalytic activities increase dramatically with increase in alkyl chain length of the imidazolium ring, possibly due to the enhanced solubility of CO<sub>2</sub> and PO in the lipophilic ionic liquid phase, which is in good agreement with the previous report.<sup>8c</sup> The relatively poor activity of [C<sub>4</sub>mim][InI<sub>3</sub>Cl] (**3e**) can be explained by the lower Lewis acidity resulting from decreased electronegativity and the steric hindrance of the iodide (entry 8).<sup>8c</sup>

To understand the effect of imidazolium cation, which might be an important factor in enhancing the catalytic activity, it is interesting to compare the activity of [C<sub>4</sub>mim][InCl<sub>4</sub>] (**3a**) with KCl + InCl<sub>3</sub> catalyst system which is isolobal with **3a** as it can be expressed as K(InCl<sub>4</sub>). However, the KCl + InCl<sub>3</sub> catalyst system is virtually devoid of any activity for the coupling reaction (entry 9 in Table 1), probably due to the lack of nucleophilicity of Cl<sup>-</sup> ion. Even a catalyst system comprising KI and InCl<sub>3</sub>

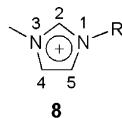
(12) (a) Ngo, H. L.; LeCompte, K.; Hargens, L.; McEwen, A. B. *Thermochim Acta*, **2000**, *357*, 97–102. (b) Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. *Green Chem.* **2001**, *3*, 156–164.



**FIGURE 4.** IR spectra of (A) **3a**; (B) [BDmim][InCl<sub>4</sub>]; (C) **5a**; (D) **6a**; (E) **7a**.

bearing strong nucleophilic component (I<sup>-</sup> ion) delivered only 70% yield (entry 10, Table 1). Therefore, the high catalytic activity of [C<sub>4</sub>mim][InCl<sub>4</sub>] (**3a**) which has no such strong nucleophilic halide ion may be explained by a central role played by the imidazolium cation. In view of this observation, a systematic study on the H-bonding interaction of the imidazolium ring hydrogens with chloride ligands in tetrahalideindate(III) was undertaken to have a better understanding of their role in the catalytic activity.

**Hydrogen Bond.** To study a possible role of hydrogen bonding (H-bonding) character in promoting the catalytic activities for this coupling reaction, FT-IR studies were carried out using **3a**, [BDmim][InCl<sub>4</sub>] (BDmim = 1-butyl-2,3-dimethylimidazolium), **5a**, **6a**, and **7a** (Figure 4) and their activities were compared (entries 11–14 in Table 1). The IR peaks in the region 2800–3000 cm<sup>-1</sup> are dominated by aliphatic C–H stretching frequency and IR frequency between 3000 and 3200 cm<sup>-1</sup> are responsible for the aromatic C–H stretching frequency, respectively.<sup>13</sup> Accordingly, the two sets of the peaks at 3165, 3149 and 3120, 3103 cm<sup>-1</sup> in Figure 4A are ascribed to the aromatic C–H frequencies which are examined carefully as this region has been used to infer the formation of H-bond in ionic liquid compounds.<sup>13</sup> There are two types of aromatic C–H stretching environment in the imidazolium ring, C(2)–H, and C(4)/C(5)–H as shown in **8**.



One way of determining the C(2)–H frequency is to replace the hydrogen with a methyl group to form 3-butyl-1,2-dimethylimidazolium tetrachloroindate(III) ([BDmim][InCl<sub>4</sub>]). The absence of the bands around 3120 and 3103 cm<sup>-1</sup> in [BDmim][InCl<sub>4</sub>] spectrum (Figure 4B)

**TABLE 2.** Effect of Mole Fraction of InCl<sub>3</sub> in **3a** on the Activity for the Coupling Reaction<sup>a</sup>

entry	catalyst	mole fraction (N) of InCl <sub>3</sub>	yield <sup>b</sup> (%)
1	[C <sub>4</sub> mim]Cl	0	9
2	[C <sub>4</sub> mim][InCl <sub>4</sub> ] <sub>0.25</sub>	0.2	39
3	[C <sub>4</sub> mim][InCl <sub>4</sub> ] <sub>0.5</sub>	0.33	65
4	[C <sub>4</sub> mim][InCl <sub>4</sub> ] <sub>0.75</sub>	0.43	67
5	[C <sub>4</sub> mim][InCl <sub>4</sub> ]	0.5	94

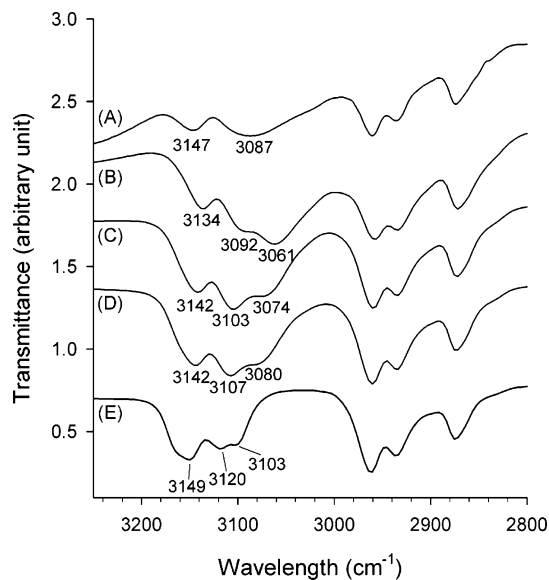
<sup>a</sup> Conditions: PO (3 g, 51.6 mmol), catalyst (0.25 mmol, 0.5 mol %). *T* = 120 °C, *P*<sub>(CO<sub>2</sub>)</sub> = 100 psi, *t* = 1 h. <sup>b</sup> Isolated yield.

confirms that these bands are identified as the C(2)–H stretching frequency. In general, the stretching frequency of the C–H...Cl (H-bond) is lower than that of C–H, suggesting that the peak at 3149 and 3103 cm<sup>-1</sup> in Figure 4A are attributed to the stretching frequency resulting from the H-bonding interaction of Cl<sup>-</sup> with C(4)/C(5) hydrogen and of Cl<sup>-</sup> with C(2) hydrogen, respectively. Dieter et al. have suggested that Cl<sup>-</sup> interacts with imidazolium cation to induce H-bonds in a fashion similar to those of C(2), C(4), and C(5) hydrogens.<sup>14</sup> The peak at 3146 cm<sup>-1</sup> in Figure 4B can be ascribed to the H-bond of C(4)/C(5) hydrogen...Cl interaction in the [BDmim][InCl<sub>4</sub>] which produced 95% yield (entry 11, Table 1). The nature of ring hydrogens in dialkylimidazolium and its interactions with various types of anions have been well documented.<sup>9,13</sup> As expected, the IR spectra of the phosphonium (Figure 4C) and ammonium (Figure 4D)-based tetrachloroindate show no such H-bonding interaction in the region between 3000 and 3200 cm<sup>-1</sup> due to lack of aromaticity;<sup>9a</sup> their catalytic activities were poor when compared with the imidazolium-based compounds (entries 12 and 13, Table 1). In contrast, pyridinium-based tetrachloroindate (**7a**) displaying the stretching frequencies at 3084, and 3064 cm<sup>-1</sup> which correspond to the H-bonding interactions of Cl<sup>-</sup> with ring hydrogens (lower compared to C–H stretching frequency of 3130 cm<sup>-1</sup>), produced 97% of product (entry 14, Table 1). From these results, it becomes clear that the presence of H-bonding interaction plays a significant role in improving the catalytic activity, when there are ring hydrogens present to interact with chloroindate moiety.

To have a better understanding of the effect of H-bonding interactions, the influence of mole fraction of InCl<sub>3</sub> on the catalytic activity was studied with a set of coupling reactions carried out using **3a** with varying mole fraction (N) of InCl<sub>3</sub> and the results are summarized in Table 2. The mole fraction of InCl<sub>3</sub> was varied from neat [C<sub>4</sub>mim]Cl to where *N* = 0.2, 0.33, 0.43, and 0.5; the viscosity increased dramatically with increasing the mole fraction of InCl<sub>3</sub>, thus providing diverse phases from solid to liquid, finally leading to the colorless liquid with low viscosity (26 mPa·s)<sup>10</sup> at the mole fraction of 0.5. Generally, the Lewis acidity increases with increasing the mole fraction of AlCl<sub>3</sub> to form a supramolecular anion like Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup>.<sup>9b,14</sup> However, the excess amount of InCl<sub>3</sub> larger than 0.5 mole fraction did not lead to the formation of supramolecules such as [C<sub>4</sub>mim][In<sub>2</sub>Cl<sub>7</sub>] in contrast to the chloroaluminates. The catalytic activity results in Table 2 show that the yield of propylene carbonate increased with increase in the mole fraction of InCl<sub>3</sub>, thus implying

(13) Tait, S.; Osteryoung, R. A. *Inorg. Chem.* **1984**, *23*, 4352–4360.

(14) Dieter, K. M.; Dymek, C. J., Jr.; Heimer, N. E.; Rovang, J. W.; Wilkes, J. S. *J. Am. Chem. Soc.* **1988**, *110*, 2722–2726.

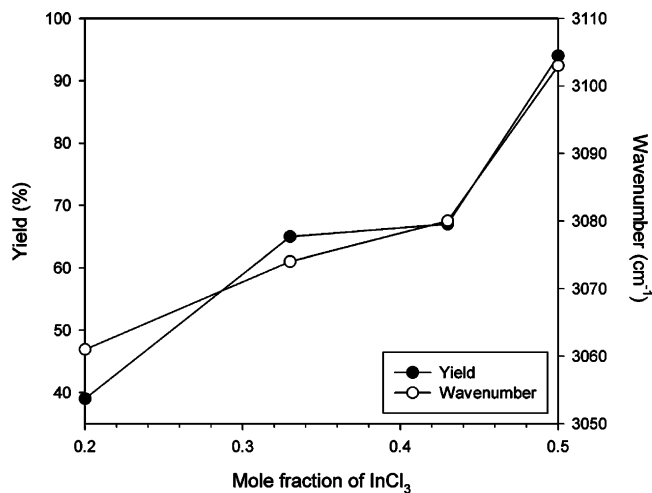


**FIGURE 5.** IR spectral change of **3a** with varying mole fraction ( $N$ ) of  $\text{InCl}_3$ : (A)  $N = 0$ , (B)  $N = 0.2$ , (C)  $N = 0.33$ , (D)  $N = 0.43$ , (E)  $N = 0.5$ .

the pivotal role of  $\text{InCl}_3$  either in rendering  $[\text{C}_4\text{mim}][\text{InCl}_4]$  more Lewis acidic to activate the PO, or in making the IL compound more amenable to H-bonding interaction to facilitate the coupling reaction.

To confirm the contribution of H-bonding effect on enhancement of the catalytic activity, a series of IR studies were carried out. Figure 5 shows the IR spectral change of **3a** with varying mole fraction of  $\text{InCl}_3$ . The peaks at 3147 and 3087  $\text{cm}^{-1}$  in Figure 5A correspond to the C(4)/C(5)-H and C(2)-H stretching frequency of  $[\text{C}_4\text{mim}]\text{Cl}$ , respectively. The H-bonding interaction started to appear at the sacrifice of the peak 3087  $\text{cm}^{-1}$  upon incorporation of 0.2 mole fraction of  $\text{InCl}_3$  (Figure 5B). Thus, the bands at 3034 and 3061  $\text{cm}^{-1}$  (Figure 5B) can be assigned to the H-bonding stretching frequencies of C(4)/C(5) and C(2) hydrogen $\cdots\text{Cl}^-$ , respectively. It is evident that shifting of these bands to the higher frequency (3134  $\rightarrow$  3142  $\rightarrow$  3142  $\rightarrow$  3149; 3061  $\rightarrow$  3074  $\rightarrow$  3080  $\rightarrow$  3103) with the increase in the mole fraction of  $\text{InCl}_3$ , suggests that the higher the  $\text{InCl}_3$  mole fraction, the stronger is the interaction of C-H $\cdots\text{Cl}$ . Interestingly, the degree of IR band shifts, corresponding to H-bonds at C(2) position, to higher frequency parallels the improvement in their catalytic activity (Figure 6). This reinforces the important role H-bonding character plays in influencing the catalytic activity of imidazolium-based tetrachloroindate(III).

Other related elements in the periodic table such as, boron-, aluminum-, and gallium-containing ionic liquids were similarly prepared by brief exposure of reactants for 15–30 s to microwave irradiation under nitrogen atmosphere. The catalytic activities of these ionic liquids were evaluated for the coupling reaction to investigate the effect of Lewis acidity on their catalytic activity. Among these,  $[\text{C}_4\text{mim}][\text{BCl}_4]$  and  $[\text{C}_4\text{mim}][\text{AlCl}_4]$  were highly air-sensitive and were very difficult to handle. The results in Table 3 show that the most Lewis acidic  $[\text{C}_4\text{mim}][\text{BCl}_4]$  delivered the product only in 6% yield with the formation of considerable amounts of 1-chloro-2-propanol as a byproduct (entry 1). Although  $[\text{C}_4\text{mim}][\text{AlCl}_4]$



**FIGURE 6.** Correlation between yields and H-bonding frequencies at the C(2) position.

**TABLE 3.** Catalytic Activities of Other Element-Containing ILS<sup>a</sup>

entry	catalyst	yield <sup>b</sup> (%)	selectivity (%)	TOF <sup>c</sup> ( $\text{h}^{-1}$ )
1	$[\text{C}_4\text{mim}][\text{BCl}_4]$	6	79 <sup>d</sup>	12
2	$[\text{C}_4\text{mim}][\text{AlCl}_4]$	56	97 <sup>d</sup>	112
3	$[\text{C}_4\text{mim}][\text{GaCl}_4]$	17	100	34
4	$[\text{C}_4\text{mim}][\text{InCl}_4]$ ( <b>3a</b> )	94	100	188

<sup>a</sup> Conditions: PO (3 g, 51.6 mmol), catalyst (0.25 mmol, 0.5 mol %).  $T = 120$  °C,  $P_{(\text{CO}_2)} = 100$  psi,  $t = 1$  h. <sup>b</sup> Isolated yield. <sup>c</sup> TOF = (moles of propylene carbonate)/(moles of catalyst)<sup>-1</sup>  $\text{h}^{-1}$ . <sup>d</sup> 1-Chloro-2-propanol was formed as byproduct.

$[\text{AlCl}_4]$  showed higher activity (entry 2) but it afforded colored product. The low activities of  $[\text{C}_4\text{mim}][\text{BCl}_4]$  and  $[\text{C}_4\text{mim}][\text{AlCl}_4]$  that have high Lewis acidity can be rationalized in terms of their lower H-bonding abilities than  $[\text{C}_4\text{mim}][\text{InCl}_4]$ , as shown by FT-IR and electrospray ionization mass spectrometry (ESI-MS).<sup>11</sup> In contrast,  $[\text{C}_4\text{mim}][\text{GaCl}_4]$  exhibiting H-bonding ability evidenced by IR (Supporting Information) also gave very low activity (entry 3), which is a somewhat unexpected result in view of the acidity of  $\text{GaCl}_3$ . From these results, it appears that both Lewis acidity and H-bonding ability are equally important factors determining the overall catalytic activity with only **3a** exhibiting the unique ability that shows high performance among other elements, presumably due to the ideal combination of Lewis acidity and H-bonding character.

**Influence of Reaction Parameters on Catalytic Activity.** Figure 7 shows the effect of temperature on the coupling reaction performed with catalyst **3a** in the temperature range 40–160 °C at 100 psi of  $\text{CO}_2$  for 1 h; at > 140 °C, PO was completely transformed to propylene carbonate (PC). The PC yield decreased sharply with decreasing temperature below 100 °C, indicating the strong dependency of the reaction on the temperature.

To our surprise, the catalyst **3a** was found to catalyze the coupling reaction at room temperature, delivering the PC quantitatively after 15 h (Figure 8).

To study the influence of  $\text{CO}_2$  pressure on the activity, the reaction was carried out with catalyst **3a** at a varying pressure range of 40–160 psi for 1 h at a constant reaction temperature of 100 °C. The results in Figure 9 show that the yield of PC increases rapidly up to 100 psi

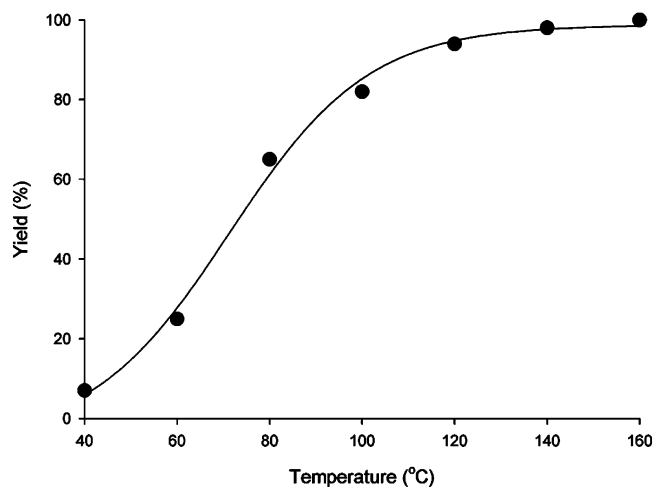


FIGURE 7. Effect of temperature on the PC yields.

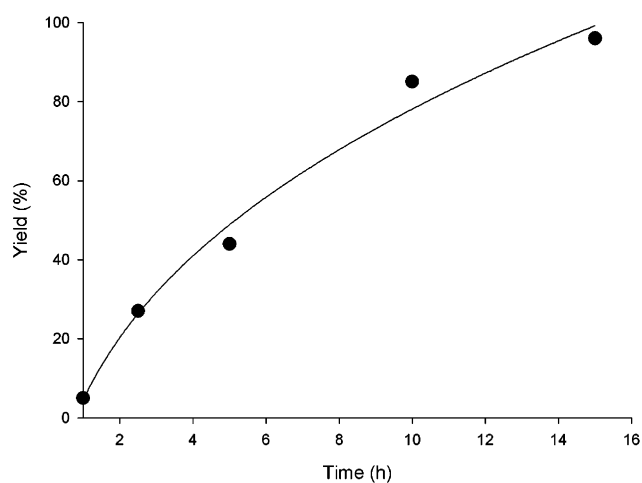


FIGURE 8. Effect of reaction time on the PC yields at room temperature in the presence of **3a** (5 mol %).

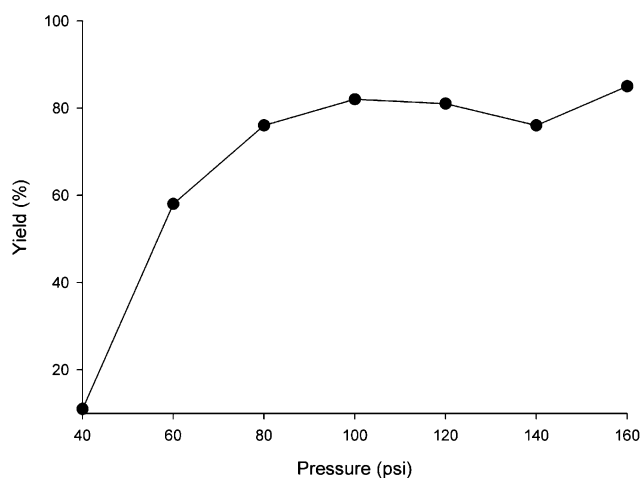


FIGURE 9. Effect of pressure on the PC yields.

and then gradually decreases and finally increases again as the pressure increases up to 160 psi. The pressure dependence is rather difficult to explain. The initial increase in yield at low pressure might be attributed to an increase in the  $\text{CO}_2$  concentration, and the decrease

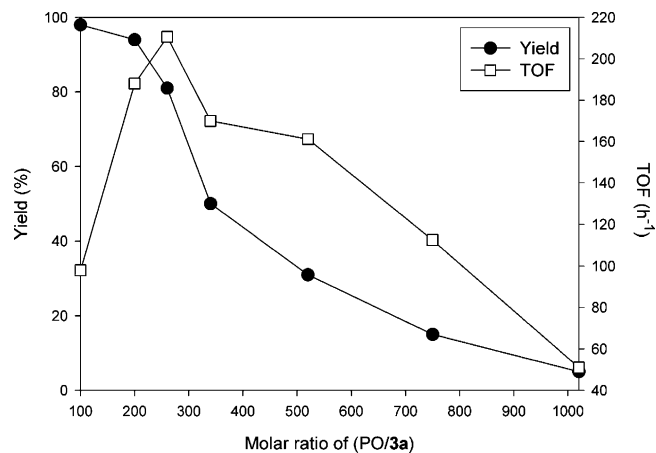







FIGURE 10. Effect of molar ratio of (PO/3a) on the PC yield and TOF.

TABLE 4. Coupling Reaction of  $\text{CO}_2$  with Various Epoxides<sup>a</sup>

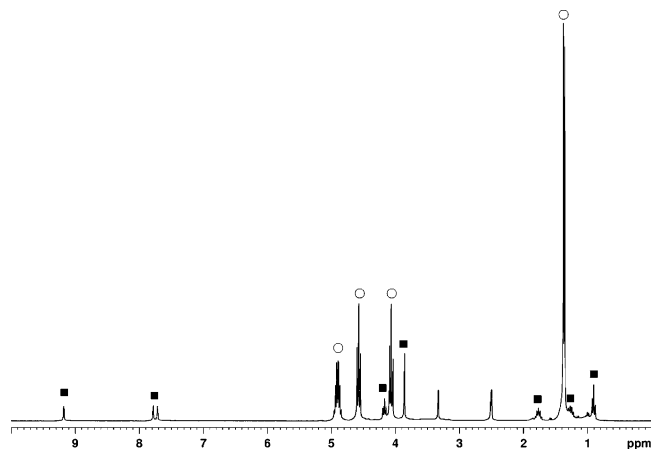
Entry	Substrate	Yield <sup>b</sup> (%)	Selectivity (%)
1		95 <sup>c</sup>	100
2		98	99
3		74	99
4		62	99
5		78	99

<sup>a</sup> Conditions: substrate (51.6 mmol), **3a** (0.1 g, 0.25 mmol, 0.5 mol %),  $T = 120\text{ }^\circ\text{C}$ ,  $P_{(\text{CO}_2)} = 100\text{ psi}$ . <sup>b</sup> Isolated yield. <sup>c</sup> Yield after five cycles.

in yield at high pressure can be ascribed to a dilution effect arising from an excessively increasing quantity of  $\text{CO}_2$ .<sup>4h,8c</sup>

The effect of varying PO/3a molar ratio on the coupling reaction was studied at  $120\text{ }^\circ\text{C}$  and 100 psi of  $\text{CO}_2$  pressure for 1 h (Figure 10). The yields of PC decreased continuously with the increase in the molar ratio and the highest turnover frequency of  $210\text{ h}^{-1}$  was obtained with catalyst **3a** at the molar ratio of 260. It is possible that interactions between catalyst with PO and/or  $\text{CO}_2$  adduct are greatly retarded at molar ratios higher than 500 under these conditions because the TOF started to decrease rapidly at this molar ratio.

To broaden the scope of the coupling reaction, various monosubstituted terminal epoxides were examined for the formation of cyclic carbonates using model catalyst, **3a** at  $120\text{ }^\circ\text{C}$  and 100 psi of  $\text{CO}_2$  pressure for 1 h. The results in Table 4 show that the monosubstituted terminal epoxides were readily converted to the corresponding cyclic carbonates but reactivity of epoxides was greatly affected by the substituent at the carbon atom of epoxide. Monosubstituted terminal epoxides with less bulky substituents afforded corresponding carbonates in high yields (entries 1 and 2) whereas epoxides with bulky substituents gave lower yields (entries 3–5). The steric hindrance around epoxide is likely to prevent the coordination of epoxides to indium center, which is presumed to be the first step in the coupling reaction. We would

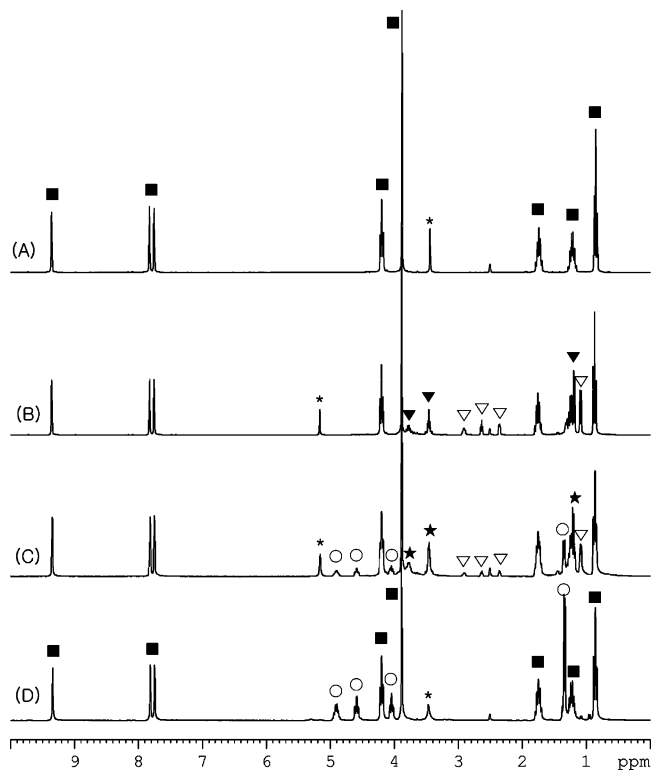


**FIGURE 11.**  $^1\text{H}$  NMR spectra of **3a** recovered after five coupling reactions of  $\text{CO}_2$  with PO performed at  $120^\circ\text{C}$  under 100 psi (■, **3a**; ○, PC).

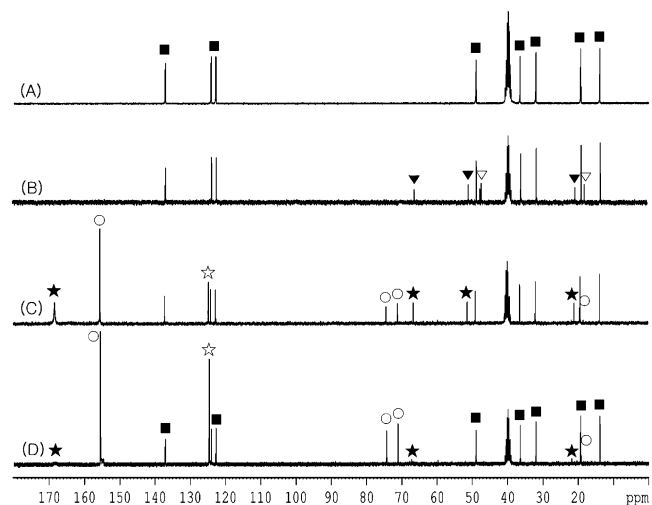
like to draw attention to the high yield obtained in the case of epichlorohydrin (entry 2) in contrast to the result reported by Kim et al. using bisimidazolium zinc compound. They ascribed the low yield to the electron-withdrawing effect of chlorine atom that prevents the coordination of epichlorohydrin to metal center due to the decrease in electron density of oxygen atom of epoxide.<sup>8b</sup> The result obtained in this case using  $[\text{C}_4\text{mim}][\text{InCl}_4]$  (**3a**) indicates the stronger Lewis acidity of our catalyst system when compared to the bisimidazolium zinc compound. Thereby, **3a** in general, was found to be an ideal catalyst applicable to a variety of terminal epoxides, producing the corresponding cyclic carbonates in moderate to high yields with more than 99% selectivities.

To test the catalyst stability and its recyclability, the coupling reactions of  $\text{CO}_2$  with PO were performed with **3a** at  $120^\circ\text{C}$  and 100 psi for 1 h. After completion of the reaction, propylene carbonate and unreacted PO were distilled off from the product mixture, and the remaining ionic liquid catalyst was reused for further reaction with a fresh charge of PO and  $\text{CO}_2$ . The recycling study with **3a** reveals that the catalyst can be recycled several times without any loss of its original reactivity (entry 1 in Table 4, after 5 cycles). The integrity of the catalyst, **3a** after five coupling reactions was confirmed by  $^1\text{H}$  NMR spectrum (Figure 11).

**$^{13}\text{C}$ -Labeling NMR Study.** To have a better understanding of the formation of active species and to study the mechanistic pathways leading to the propylene carbonate (PC), a series of  $^1\text{H}$  and  $^{13}\text{C}$  NMR experiments were carried out using  $[\text{C}_4\text{mim}][\text{InCl}_4]$  (**3a**). Figure 12A represents the  $^1\text{H}$  NMR spectrum of **3a** in  $\text{DMSO-}d_6$ . As shown in Figure 12B, the addition of 1.5 equiv of PO to the NMR tube containing **3a** generates two sets of resonance where  $\nabla$  is corresponding to PO and  $\blacktriangledown$  is believed to be ring-opened chloroalkoxy species (**3a-PO'**). When the NMR tube was pressurized with  $^{13}\text{CO}_2$  (40 psi), as expected, PC (○) started to form with the concomitant reduction in intensity of PO ( $\nabla$ ) (Figure 12C). The peaks (★) at 3.80 and 3.45 can be ascribed to indium chloroalkoxy carbonate species (**3a-PO'-CO<sub>2</sub>**) since they completely disappeared after additional introduction of  $^{13}\text{CO}_2$ , followed by the reaction at  $60^\circ\text{C}$  for 30 min (Figure 12D),



**FIGURE 12.**  $^1\text{H}$  NMR spectra: (A) **3a** in  $\text{DMSO-}d_6$ ; (B) after addition of 1.5 equiv of PO into (A); (C) after introduction of 40 psi of  $^{13}\text{CO}_2$  into (B); (D) after additional introduction of  $^{13}\text{CO}_2$ , followed by the reaction at  $60^\circ\text{C}$  for 30 min (■, **3a**; ▽, PO; ○, PC; □,  $\text{H}_2\text{O}$ ).

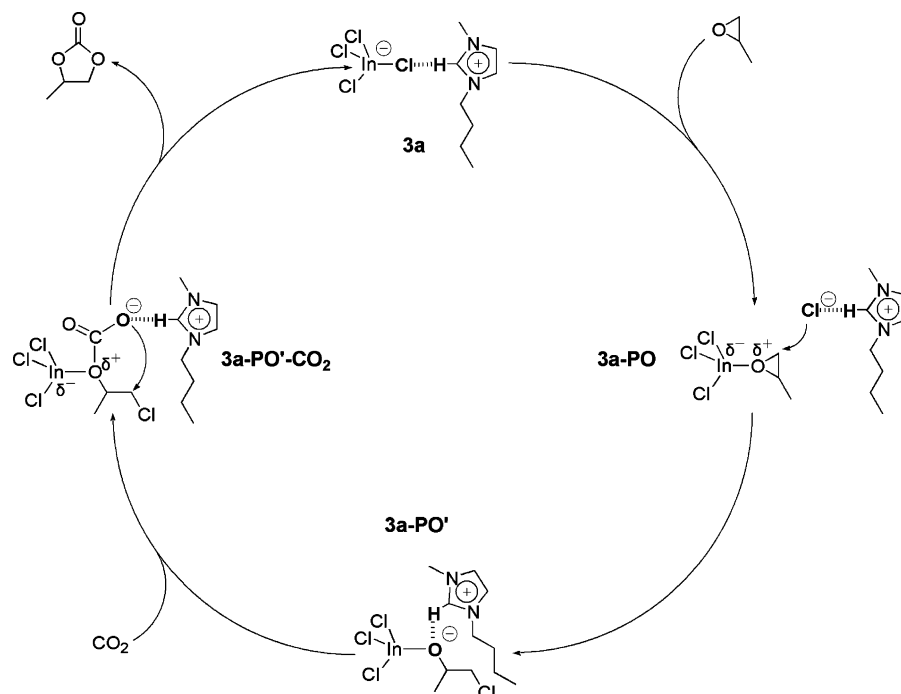


**FIGURE 13.**  $^{13}\text{C}$  NMR spectra: (A) **3a** in  $\text{DMSO-}d_6$ ; (B) after addition of 1.5 equiv of PO into (A); (C) after introduction of 40 psi of  $^{13}\text{CO}_2$  into (B); (D) after additional introduction of  $^{13}\text{CO}_2$ , followed by the reaction at  $60^\circ\text{C}$  for 30 min (■, **3a**; ▽, PO; ○, PC; ☆, free  $^{13}\text{CO}_2$ ).

indicating that **3a-PO-CO<sub>2</sub>** is the intermediate for the formation of PC.

This can be more clearly seen in  $^{13}\text{C}$  NMR spectra (Figure 13). The addition of PO to the NMR tube containing **3a** results in the formation of indium chloroalkoxy species ( $\blacktriangledown$ , **3a-PO'**, Figure 13B). Subsequent addition of 40 psi of  $^{13}\text{CO}_2$  results in the formation of



SCHEME 4. Reaction Mechanism for the Formation of Propylene Carbonate Catalyzed by **3a**

indium chloroalkoxy carbonate species ( $\star$ , **3a-PO'-CO<sub>2</sub>**) confirmed by the characteristic carbonate resonance at  $\delta = 168$  ( $\star$ ) and the formation of PC ( $\circ$ ) (Figure-13C). The peak at 124 ppm ( $\star$ ) is assigned to free <sup>13</sup>CO<sub>2</sub>. Incremental addition of <sup>13</sup>CO<sub>2</sub>, followed by the reaction at 60 °C for 30 min, results in the enhancement of peak intensity for <sup>13</sup>C-labeled PC ( $\circ$ ) (carbonyl peak for the PC at  $\delta = 155$  ppm) with the concomitant reduction in intensity of the peaks ( $\star$ ) corresponding to the intermediate species, **3a-PO'-CO<sub>2</sub>** (Figure 13D).

**Reaction Mechanism.** On the basis of the NMR spectroscopic studies delineated above, a reasonable mechanism for the coupling reaction catalyzed by **3a** is proposed (Scheme 4). The initial active catalyst can be described as **3a** in which Cl<sup>-</sup> forms H-bond with C(2) hydrogen of imidazolium cation. The coordination of PO to the Lewis acid site of indium to form the adduct, **3a-PO**, subsequent nucleophilic attack of Cl<sup>-</sup> on the less hindered carbon atom of the coordinated PO, followed by ring opening reaction leads to chloroalkoxy anion species, **3a-PO'** which is stabilized through the H-bonding interaction. The insertion of CO<sub>2</sub> into O...H of **3a-PO'** would produce chloroalkoxy carbonate intermediate, **3a-PO'-CO<sub>2</sub>** which is also stabilized via the H-bonding interaction. The intramolecular cyclic elimination thus provides PC and regenerates the catalyst, **3a**. Kisch et al. reported that the coexistence of both Lewis acid and Lewis base is required to prepare alkylene carbonates from CO<sub>2</sub> and epoxides.<sup>5a,8,15</sup> However, from a series of aforementioned experimental results using [Q][InCl<sub>4</sub>], it becomes clear that the ability to form H-bonding interaction is also an important factor influencing the catalytic activity. Therefore, it is concluded that the H-bonding property through the interaction with the halide ion and ring protons of imidazolium cation renders the dissociation of halide ion from indate(III) and the coordination of epoxide much

easier, thus facilitating the activation of coordinated epoxide to form haloalkoxy species via ring-opening, which are also stabilized by the H-bonding interactions as illustrated in Scheme 4. This explains why the imidazolium- or pyridinium-based [InCl<sub>4</sub>] display much better catalytic activities than those of potassium-, phosphonium-, or ammonium-based [InCl<sub>4</sub>] which lack the capacity to form H-bonds. These results may help to identify additional catalyst candidates for this reaction, i.e., any ionic liquid entity that inherits appropriate H-bonding property as well as Lewis acidity could be able to catalyze such coupling reactions.

**Conclusions.** A series of tetrahaloindate(III)-based ILs with the general formula of [Q][InX<sub>3</sub>Y] (Q = imidazolium, phosphonium, ammonium, and pyridinium; X = Cl, Br, I; Y = Cl, Br) were prepared by reacting InX<sub>3</sub> with the corresponding halides using microwave irradiation. The thermal stability of [C<sub>4</sub>mim][InCl<sub>4</sub>] (**3a**) was found to be much higher than that of the earlier investigated catalysts such as [C<sub>4</sub>mim]Cl and [C<sub>4</sub>mim]<sub>2</sub>[ZnBr<sub>2</sub>Cl<sub>2</sub>]. The catalytic activities of [C<sub>n</sub>mim][InX<sub>3</sub>Y] were found to increase with increasing the alkyl chain length but were not largely influenced by the halide ligands. The H-bonding interaction was also found to be an important factor affecting the catalytic activity for the coupling reaction. The formation of propylene carbonate under the catalytic influence of [C<sub>4</sub>mim][InCl<sub>4</sub>] (**3a**) was strongly dependent on both the temperature and pressure; yield increasing with increasing temperature and pressure, and the reactivities of terminal epoxides toward the coupling reaction were influenced by the substituent at the carbon atom of epoxide. From the FT-IR and <sup>13</sup>C-labeling NMR study using **3a**, it was discerned that all the intermediate species were well stabilized by the H-bonding interactions, and the chloroalkoxy carbonate species, **3a-PO'-CO<sub>2</sub>** were found to be an important intermediate in the coupling reaction. The advantageous

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features of using environmentally friendly tetrahaloindates(III) ionic liquid catalyst system includes robust catalytic performance, stability toward the air and moisture, and their efficient recycling in processes which are devoid of any volatile organic solvent usage.

## Experimental Section

**General Considerations.** All manipulations were carried out under nitrogen atmosphere except for the catalytic reaction. Propylene oxide, indium(III) chloride, indium(III) bromide, indium(III) iodide, 1-methylimidazole, 1-butyl-2,3-methylimidazole, chloromethane, chloroethane, 1-chlorobutane, 1-chlorooctane, 1-bromobutane, 1-bromooctane, KCl, KI, zinc(II) bromide, zinc(II) chloride, tetra-*n*-butylphosphonium chloride, tetra-*n*-butylammonium chloride, and *n*-butylpyridinium chloride were purchased and used without further purification. All the imidazolium chlorides and bromides were prepared according to the literature procedure.<sup>9b,16</sup> The identities of reaction products were confirmed with a MSD GC–mass spectrometer. Elemental analyses were carried out using CHNS analyzer. Good agreement between observed and calculated isotope patterns was observed in all cases, and the listed *m/z* value corresponds to the most intense peak in the isotope pattern. Microwave reactions for the preparation of ionic liquids compounds were carried out in a microwave oven (equipped with inverter technology) for 15 or 30 s. TGA analysis data was obtained in a platinum pan with heating rate of 10 °C/min under N<sub>2</sub> atmosphere. Unless otherwise noted, IR spectra were recorded for neat samples using a vessel equipped with a Di-Comp probe after the evaporation of the CH<sub>3</sub>OH under N<sub>2</sub> atmosphere. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded, and the coupling constants are reported in Hz.

**Representative Experimental Procedure for [1-*n*-Butyl-3-methylimidazolium][InCl<sub>4</sub>] (3a).** Equimolar amounts of InCl<sub>3</sub> (5.3 g, 23.9 mmol) and 1-*n*-butyl-3-methylimidazolium chloride, [C<sub>4</sub>mim]Cl (4.19 g, 23.9 mmol) were admixed in a 20 mL glass vial, followed by MW irradiation (600 W) for 15 s, and afforded a crude mixture of liquid and small quantity of unreacted InCl<sub>3</sub>, which was removed using syringe filter to give **3a**. Yield: 88%. Mp: –6 °C. <sup>1</sup>H NMR (300 MHz, DMSO-

*d*<sub>6</sub>, 25 °C): δ 9.28 (s, 1H, imidazolium ring); 7.81 (s, 1H, imidazolium ring); 7.74 (s, 1H, imidazolium ring); 4.18 (t, *J* = 7.2, H, –NCH<sub>2</sub>R); 3.86 (s, 3H, –NCH<sub>3</sub>); 1.76 (m, 2H, –CH<sub>2</sub>–); 1.24 (m, 2H, –CH<sub>2</sub>–); 0.89 (t, *J* = 7.1, 3H, –N(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>). <sup>13</sup>C-{<sup>1</sup>H} NMR (75 MHz, DMSO-*d*<sub>6</sub>, 25 °C): δ 137.1 (imidazolium ring), 124.1 (imidazolium ring), 122.7 (imidazolium ring); 48.9 (–NCH<sub>2</sub>R); 39.1 (–NCH<sub>3</sub>); 36.2 (–CH<sub>2</sub>–); 19.2 (–CH<sub>2</sub>–); 13.8 (–CH<sub>3</sub>). Anal. Calcd for C<sub>8</sub>H<sub>15</sub>Cl<sub>4</sub>InN<sub>2</sub>: C, 24.27; H, 3.82; N, 7.08. Found: C, 24.23; H, 3.84; N, 7.05.

**Coupling Reactions.** All of the coupling reactions were performed in a high-pressure glass vessel equipped with a stirring bar and a pressure gauge. In a typical procedure, the reactor was charged with the [C<sub>4</sub>mim][InCl<sub>4</sub>] (**3a**) (0.1 g, 0.25 mmol, 0.5 mol %) and propylene oxide (PO, 3.0 g, 51.7 mmol) and pressurized with CO<sub>2</sub> (~40 psi). The reactor was then heated to 100 °C with the additional CO<sub>2</sub> from a reservoir tank to maintain the pressure at 100 psi. After completion of the reaction, the reactor was cooled to room temperature and the resulting product mixtures were qualitatively analyzed by GC–MS and yields were calculated by weight of product mixtures (propylene carbonate (PC) + **3a**) after removing the residual PO under reduced pressure. For recycling experiment, the PC was isolated from the product mixture using vacuum distillation, and the remaining **3a** was reused for further reaction with a fresh charge of PO and CO<sub>2</sub>.

**In Situ NMR Study.** Compound **3a** (55 mg, 0.14 mmol) dissolved in DMSO-*d*<sub>6</sub> (0.3 mL) was placed into a thick-walled NMR tube (o.d. 5 mm) equipped with a Teflon valve. PO (2 μL, 0.28 mmol) was added, followed by the introduction of 40 psi of <sup>13</sup>CO<sub>2</sub>, and then the mixture was heated at 60 °C for 30 min. The NMR spectra were recorded at each step and were compared.

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**Supporting Information Available:** Experimental procedures and spectral copies of <sup>1</sup>H and <sup>13</sup>C NMR for all ionic liquid compounds, FT-IR spectra for **3a–d**, and TGA analysis for **5a**, **6a**, and **7a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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