Monatsh Chem (2009) 140:39–44
DOI 10.1007/s00706-008-0005-6

ORIGINAL PAPER

A diol-functionalized ionic liquid: an efficient, simple, and recoverable "capture and release" reagent for aldehydes

Yueqin Cai · Ye Liu

Received: 7 May 2008 / Accepted: 4 June 2008 / Published online: 12 September 2008

Abstract A new diol-functionalized ionic liquid, 2,2-bis(1-(1-methylimidazolium)methylpropane-1,3-diol hexafluorophosphate, was synthesized and applied as a facile, efficient, and recoverable "capture and release" reagent for aldehydes. This method has the advantages of homogeneous reaction, heterogeneous separation, and recyclable uses.

Keywords Combinatorial chemistry · Functionalized ionic liquid · Diol · Heterocycles · Aldehydes

Introduction

Over the past few years, the exploration and utilization of combinatorial chemistry in conjunction with high throughput biological screenings have rapidly evolved [1, 2]. Polymer-supported scavengers are therefore becoming widespread in chemical ensemble preparation for straightforward purification of reaction products [3–6]. One such scavenger is of the "resin capture-release" reagent, which uses the functionalized polymer scavengers to selectively trap the desired products out of solution phase [7]. However, such scavengers suffer from limited mobility as a result of restriction of the polymer matrix and the access of active sites to organic substrates, solvent dependence, as well as the difficulty in reaction monitoring. In recent years, a variety of new techniques, such as fluorous-phase [8–10], aqueous [11–13], as well as polyaromatic [14] and PEG-supported reagents [15] have been developed. These new reagents, however, have their own drawbacks, such as high cost, relatively low loading, and the need for large amounts of solvents.

Recently, ionic liquids (ILs) became of intense interest because of their unique chemical and physical characters, such as lack of vapor pressure, ease of reuse, and facile chemical modification. A wide variety of room temperature ionic liquids, especially those derived from 1-*n*-alkyl-3-methylimidazolium cations, has been demonstrated to have versatile applications in organic synthesis [16–21]. In this field, we have reported the use of amino- and carboxy-functionalized ILs as scavengers for purification of solution-phase parallel synthesis [22, 23]. It has been recognized that IL scavengers have the advantages of a homogeneous reaction process along with the recoverable and recyclable scavengers [22, 23]. Herein, as an extension of this strategy, we describe a new method that utilizes a diol-functionalized IL, 2,2-bis(1-(1-methylimidazolium) methylpropane-1,3-diol hexafluorophosphate (**1**), as an efficient and recyclable "capture-release" reagent for aldehydes from a mixture.

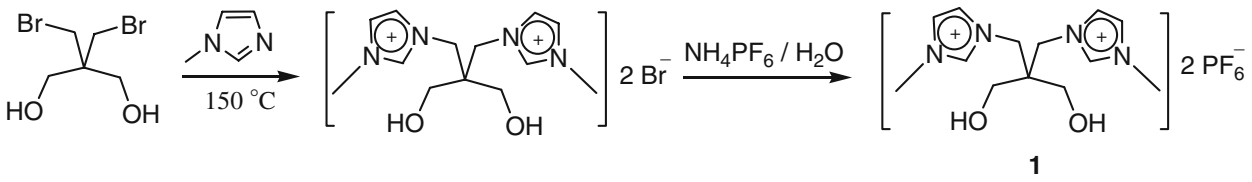
Results and discussion

*Investigation of capture and release of aldehydes via diol-functionalized IL **1***

As shown in Scheme 1, the required diol-functionalized IL **1** was simply prepared from 1-methylimidazole and

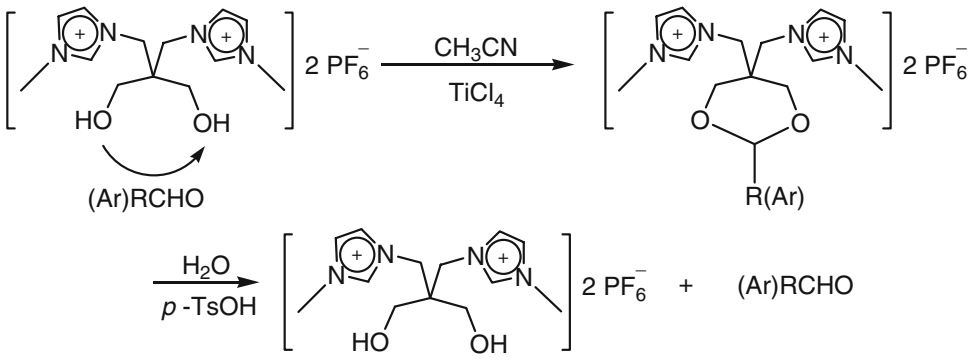
Y. Cai (✉)
School of Chemistry and Molecular Engineering,
East China University of Science and Technology,
200237 Shanghai, China
e-mail: caiyueqin2006@126.com; caiyueqin@eyou.com

Y. Liu
Shanghai Key Laboratory of Green Chemistry and Chemical Processes, East China Normal University,
200062 Shanghai, China



Scheme 1

Scheme 2



2,2-bis(bromomethyl)-1,3-propanediol, followed by anion exchange with NH_4PF_6. To illustrate that **1** is an effective "capture-release" reagent for selective and rapid isolation of aldehydes, the capture and release of different aldehydes from **1** were examined (Scheme 2).

Originally, the capture of benzaldehyde with **1** was catalyzed by *p*-TsOH with toluene as the solvent [24, 25]. Unfortunately, the poor yield of the desired acetal resulted probably from the restricted access of –OH in **1** to benzaldehyde (**1** is insoluble in toluene). Surprisingly, by replacing toluene with acetonitrile, and using $TiCl_4$ as the catalyst, the reaction of benzaldehyde with **1** occurred readily in homogeneous phase. After optimization of the reaction conditions, it was found that the reaction could be accomplished within 0.5 h with 2.0 equiv. of **1**. The resultant mixture was washed with water and ethanol to remove an excess **1** and the side-product from $TiCl_4$ hydrolysis, to yield the expected product in excellent yield (95%). The product was of high purity and required no further purification.

In order to determine the selective capture of the aldehyde group by **1**, a range of aldehydes and ketones was selected to react with **1** under the conditions established above. As shown in Table 1, all aldehydes reacted with **1** to give acetals in excellent yields (86–95%) within short time (0.5–3 h), regardless of aliphatic or aromatic aldehydes or the electronic nature of the substituents (Table 1, entries 1–9). All the products were well characterized by FT–IR and ^{1}H NMR. However, in the cases of ketones, the reactions were sluggish, and poor yields of the required products were obtained (Table 1, entries 10–14). Cyclohexanone with relatively low steric hindrance reacted with **1** providing only 37%. The formation of other aliphatic or aromatic acetals was not observed under the same conditions, even upon increasing loading of the diol-functionalized IL (Table 1, entries 15–16).

Table 1 Capture of aldehydes or ketones via diol-functionalized IL **1**

Entry	Substrate	Products	Time/h	Yield[b]/%
1	Benzaldehyde	**2**	0.5	95
2	2-Chlorobenzaldehyde	**3**	2	95
3	2,6-Dichlorobenzaldehyde	**4**	2	93
4	4-Dimethylaminobenzaldehyde	**5**	3	89
5	Cinnamaldehyde	**6**	1	86
6	3-Nitrobenzaldehyde	**7**	1	93
7	Phenyl acetaldehyde	**8**	1	91
8	Propionaldehyde	**9**	0.5	94
9	Valeraldehyde	**10**	0.5	95
10	Cyclohexanone	**11**	8	37
11	Benzophenone	**12**	8	0
12	Acetophenone	**13**	8	0
13	Butan-2-one	**14**	8	0
14	Heptan-3-one	**15**	8	0
15[a]	Butan-2-one	**16**	8	0
16[a]	Acetophenone	**17**	8	0

Substrate (5 mmol), **1** (10 mmol), $TiCl_4$ (5 mmol), and CH_3CN (5 cm^3)

[a] Substrate (5 mmol), **1** (20 mmol), $TiCl_4$ (5 mmol), and CH_3CN (5 cm^3)

[b] Isolated yield of acetals

The release of the aldehydes from **1**-supported acetals of Table 1 was investigated. (1) The acetals were hydrolyzed in water in the presence of *p*-TsOH; (2) upon completion of reaction (monitored by TLC), the mixture was extracted with

CH_2Cl_2; (3) the combined organic phase was washed with aqueous $NaHCO_3$ and brine, and then concentrated to give the aldehydes; (4) the aqueous phase was washed with CH_2Cl_2 and then concentrated in vacuo to afford the recovered **1**. It was found that the aldehydes were successfully detached from **1** without contamination of **1** (confirmed by ^{1}H NMR analysis). The recovered **1** gave FT–IR and ^{1}H NMR spectrta similar to the freshly prepared compound.

In consideration of the fact that the ILs are highly preferable in a green synthetic process due to its repeating usage, we studied the recyclability of **1** for aldehyde capture and release. As derived from Fig. 1, **1** could be recycled at least four times without obvious decrease in reactivity. Thus, benzaldehyde could be captured and then released from **1** with releasing yield of >92% per pass. These results provided strong evidence that **1** is a highly active and easily manipulatory "capture and release" reagent for aldehydes.

*Capture and release of aldehydes via diol-functionalized IL **1** from the complex mixture*

To explore the general practicability of our method, the capture and the release of aldehydes mixed with other compounds were examined (Table 2). Fortunately, it was found that 2 equiv. of **1** could capture the target aldehyde from the mixture with excellent yield (89–92%) in a short time. Most significantly, due to the higher selectivity to –CHO, **1** captured aldehydes more readily than ketones, affording acetals as the only product with yields of >90% after hydrolysis (entries 1–3). Without the competition to the –CHO, the aldehydes were captured completely and then could be released with high yields (entries 4–7). Reasonably, for the mixtures composed of two types of active aldyhydes, the specific selectivity to one individual could not be observed (Entry 8). Most importantly, compared to $NaHSO_3$,

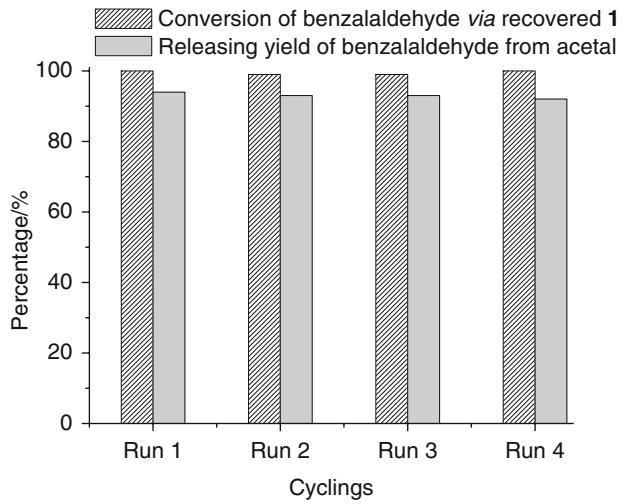


Fig. 1 Recyclability of **1** for capture and release of benzaldehyde

Table 2 Capture and release of of aldehydes via **1** from the mixture

Entry	Compounds in the mixture	Captured and released compound via diol-functionalized IL **1**	
		Percentage of captured compounds[a]/%	Releasing yield of the captured compounds[b]/%
1	Benzaldehyde	100	92
	Acetophenone	0	0
2	2,6-Dichlorobenzaldehyde	100	91
	Acetophenone	0	0
3	2,6-Dichlorobenzaldehyde	100	91
	Cyclohexanone	0	0
4	2,6-Dichlorobenzaldehyde	100	90
	Ethylbutylcetone	0	0
5	Benzaldehyde	100	93
	p-Bromoanisole	0	0
6	2-Chlorobenzaldehyde	100	92
	p-Bromoanisole	0	0
7	2,6-Dichlorobenzaldehyde	100	90
	p-Bromoanisole	0	0
8	2,6-Dichlorobenzaldehyde	63	92
	2-Chlorobenzaldehyde	37	

Compounds in the mixture (aldehyde 5 mmol and another compound 5 mmol), **1** (20 mmol), and $TiCl_4$ (10 mmol) in CH_3CN (10 cm^3) for 2 h

[a] The amount of the released compounds after hydrolysis determined by GC

[b] Isolate yield of aldehydes or ketones

which is usually used to capture aldehydes, cyclic ketones, methyl ketones, and isocyanates [26–29], the diol-functionalized IL **1** could selectively isolate aldehydes from the mixture even in the presence of ketones.

In conclusion, we describe an efficient methodology in which a diol-functionalized IL is applied to capture aldehydes from a mixture and then release pure aldehydes without further purification. Compared to the reported polymer-supported diol for aldehydes protection and isolation, the developed **1**, with the significant features of (1) homogenous reaction (**1** is soluble in CH_3CN) and heterogeneous separation (acetals from **1** are insoluble in water), (2) recoverable and recyclable nature of **1** derived from its nature of an ionic liquid, and (3) efficient and selective capture of aldehydes from a complex mixture and then release of aldehydes with high purity, presents a significant advancement over existing methodologies.

Experimental

All solvents and chemicals (aldehydes) were reagent grade purchased commercially and used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-500

(500 MHz) instrument with DMSO-d_6 as solvent. ESI-MS was detected by Agilent 1100LC/MSDVL spectrometer. FT–IR spectra were recorded on a Nicolet Nexus 670 FT–IR spectrometer (KBr pellet). Elemental analysis data were recorded on a Vario EL III instrument. Their results agreed favorably with the calculated values. GC–MS analyses were recorded on an Agilent 6890 instrument equipped with Agilent 5973 mass selective detector. GC analyses were performed on SHIMADZU-14B equipped with HP-1 capillary column (30 m × 0.25 mm).

2,2-Bis(1-(1-methylimidazolium)methylpropane-1,3-diol hexafluorophosphate (**1**, $C_{13}H_{22}N_4O_2P_2F_{12}$)

A mixture of 2.05 g 1-methylimidazole (25 mmol) and 2.60 g 2,2-bis (bromomethyl)-1, 3-propanediol (10 mmol) was heated at 150 °C for 8 h under magnetic stirring. After cooling to room temperature, the resultant solid was washed with acetonitrile, and the solution of 3.26 g NH_4PF_6 (20 mmol) in 20 cm^3 of H_2O was then added. The obtained mixture was stirred at room temperature for 1 h. After filtration, the white solid was washed with ethanol and dried, giving 4.67 g (84%) of the desired product. FT–IR (KBr) $\bar{\nu}$ = 3604, 3165, 3122, 2977, 2913, 1588, 1577, 1448, 1425, 1301, 1173, 1014, 846 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) $\delta = 3.10$ (d, 4H, $J = 4$ Hz, OH–CH_2), 3.90 (s, 6H, CH_3), 4.25 (s, 4H, N–CH_2), 5.25 (t, 2H, $J = 5$ Hz, O*H*), 7.70 (s, 2H, NC*H*), 7.80 (s, 2H, NC*H*), 9.15 (s, 2H, N*H*CN) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) $\delta = 137.8$, 123.8, 123.4, 58.5, 48.7, 45.4, 35.9 ppm; ESI–MS $m/z = 554.7$ $(M\text{-}H)^-$, 290.2 $([PF_6]_2)^{2-}$.

Typical procedure for the capture of aldehydes via diol-functionalized IL ***1***

A mixture of **1** (10 mmol), aldehyde (5 mmol), and 0.949 g $TiCl_4$ (5 mmol) in 5 cm^3 acetonitrile was refluxed under magnetic stirring (monitored by TLC). Upon completion, the obtained mixture was cooled and 10 cm^3 H_2O was added to precipitate the formed acetals. After filtration, the solid was washed with H_2O and ethanol separately to remove excess **1** and the side-product from $TiCl_4$ hydrolysis, and then dried under vacuum to give the corresponding acetal.

2-Phenyl-5,5-bis(1-(1-methylimidazolium)methyl-1,3-dioxane hexafluorophosphate (**2**, $C_{20}H_{26}N_4O_2P_2F_{12}$)

White solid (3.06 g, 95%), mp 128 °C; FT–IR (KBr) $\bar{\nu}$ = 3169, 3118, 2967, 2924, 1577, 1553, 1460, 1172, 1142, 835 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6,) δ = 3.80 (s, 6H, CH_3), 3.90 (d, 2H, $J = 10$ Hz, O–CH_2), 4.10 (d, 2H, $J = 12$ Hz, O–CH_2), 4.25 (s, 2H, N–CH_2), 4.60 (s, 2H, N–CH_2), 5.50 (s, 1H, C*H*), 7.40 (m, 5H, Ph), 7.60 (s, 2H, NC*H*), 7.80 (s, 2H, NC*H*), 9.15 (s, 1H, N (*H*) CN), 9.25 (s, 1H, N (*H*) CN) ppm.

2-(2-Chlorophenyl)-5,5-bis(1-(1-methylimidazolium) methyl-1,3-dioxane hexafluorophosphate (**3**, $C_{20}H_{25}N_4O_2ClP_2F_{12}$)

White solid (3.23 g, 95%), mp 131 °C; FT–IR (KBr) $\bar{\nu}$ = 3161, 3122, 2970, 1580, 1565, 1448, 1405, 1172, 1095, 842 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6,) $\delta = 3.85$ (s, 6H, CH_3), 4.01 (d, 2H, $J = 12$ Hz, O–CH_2), 4.10 (d, 2H, $J = 14$ Hz, O–CH_2), 4.20 (s, 2H, N–CH_2), 4.60 (s, 2H, N–CH_2), 5.75 (s, 1H, C*H*), 7.40–7.60 (m, 4H, Ph), 7.65 (s, 1H, NC*H*), 7.75 (s, 1H, NC*H*), 7.80 (s, 1H, NC*H*), 7.85 (s, 1H, NC*H*), 9.10 (s, 1H, N (*H*) CN), 9.20 (s, 1H, N (*H*) CN) ppm.

2-(2,6-Dichlorophenyl)-5,5-bis(1-(1-methylimidazolium) methyl-1,3-dioxane hexafluorophosphate (**4**, $C_{20}H_{24}N_4O_2Cl_2P_2F_{12}$)

White solid (3.31 g, 93%), mp 138 °C; FT–IR (KBr) $\bar{\nu}$ = 3165, 3122, 2967, 2935, 1584, 1561, 1436, 1401, 1173, 1099, 1067, 834 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6,) $\delta = 3.80$ (s, 6H, CH_3), 3.90 (d, 2H, $J = 11$ Hz, O–CH_2), 4.01 (d, 2H, $J = 12$ Hz, O–CH_2), 4.25 (s, 2H, N–CH_2), 4.75 (s, 2H, N–CH_2), 6.15 (s, 1H, C*H*), 7.40–7.50 (m, 3H, Ph), 7.55 (s, 1H, NC*H*), 7.65 (s, 1H, NC*H*), 7.75 (s, 1H, NC*H*), 7.85 (s, 1H, NC*H*), 9.10 (s, 1H, N (*H*) CN), 9.15 (s, 1H, N (*H*) CN) ppm.

2-(4-Dimethylamionphenyl)-5,5-bis (1-(1-methylimidazolium)methyl-1,3-dioxane hexafluorophosphate (**5**, $C_{22}H_{32}N_5O_2P_2F_{12}$)

White solid (3.05 g, 89%), mp 141 °C; FT–IR (KBr) $\bar{\nu}$ = 3168, 3126, 2967, 2908, 1580, 1561, 1448, 1367, 1173, 1091, 1029, 854 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6,) $\delta = 3.80$ (s, 6H, N-CH_3), 3.85 (s, 6H, CH_3), 3.90 (d, 2H, $J = 11$ Hz, O–CH_2), 4.01 (d, 2H, $J = 12$ Hz, O–CH_2), 4.10 (s, 2H, N–CH_2), 4.60 (s, 2H, N–CH_2), 5.48 (s, 1H, C*H*), 7.35 (m, 4H, Ph), 7.70 (s, 1H, NC*H*), 7.75 (s, 1H, NC*H*), 7.80 (s, 1H, NC*H*), 7.85 (s, 1H, NC*H*), 9.10 (s, 1H, N (*H*) CN), 9.15 (s, 1H, N (*H*) CN) ppm.

2-Styryl-5,5-bis(1-(1-methylimidazolium)methyl-1,3-dioxane hexafluorophosphate (**6**, $C_{22}H_{28}N_4O_2P_2F_{12}$)

White solid (2.88 g, 86%), mp 121 °C; FT–IR (KBr) $\bar{\nu}$ = 3169, 3118, 2967, 2924, 1577, 1553, 1460, 1172, 1142, 835 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6,) $\delta = 3.63$ (t, 2H, $J = 8$ Hz, O–CH_2), 3.75 (t, 2H, $J = 7$ Hz, O–CH_2), 3.80 (s, 3H, CH_3), 3.83 (s, 3H, CH_3), 4.20 (s, 2H, N–CH_2), 4.50 (s, 2H, N–CH_2), 5.10 (s, 1H, C*H*), 7.25–7.35 (m, 5H, Ph), 7.45 (s, 1H, =C*H*), 7.47 (s, 1H, =C*H*), 7.60 (s, 1H, NC*H*), 7.65 (s, 1H, NC*H*), 7.75 (s, 1H, NC*H*), 7.80 (s, 1H, NC*H*), 9.01 (s, 1H, N (*H*) CN), 9.10 (s, 1H, N (*H*) CN) ppm.

2-(3-Nitrophenyl)-5,5-bis(1-(1-methylimidazolium)methyl-1,3-dioxane hexafluorophosphate (**7**, $C_{20}H_{25}N_5O_4P_2F_{12}$) White solid (3.20 g, 93%), mp 143 °C; FT–IR (KBr) $\bar{\nu}$ = 3173, 3118, 2982, 2916, 1565, 1452, 1176, 1009, 862 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6,) δ = 3.75 (s, 6H, N–CH_3), 4.05 (d, 2H, J = 11 Hz, O–CH_2), 4.20 (d, 2H, J = 12 Hz, O–CH_2), 4.45 (s, 2H, N–CH_2), 4.55 (s, 2H, N–CH_2), 5.80 (s, 1H, C*H*), 7.60–7.85 (m, 4H, Ph), 8.15 (s, 1H, NC*H*), 8.11 (s, 1H, NC*H*), 8.25 (s, 1H, NC*H*), 8.30 (s, 1H, NC*H*), 9.10 (s, 2H, N (*H*) CN) ppm.

2-Benzyl-5,5-bis(1-(1-methylimidazolium)methyl-1,3-dioxane hexafluorophosphate (**8**, $C_{21}H_{28}N_4O_2P_2F_{12}$) White solid (2.99 g, 91%), mp 123 °C; FT–IR (KBr) $\bar{\nu}$ = 3169, 3126, 2980, 2898, 1580, 1565, 1389, 1173, 1126, 1079, 1017, 850 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6,) δ = 2.65 (d, J = 6 Hz, 2H, Ph–CH_2), 3.75 (s, 6H, N–CH_3), 3.90 (d, 2H, J = 11 Hz, O–CH_2), 4.05 (d, 2H, J = 10 Hz, O–CH_2), 4.15 (s, 2H, N–CH_2), 4.65 (s, 2H, N–CH_2), 5.35 (s, 1H, C*H*), 7.35–7.45 (m, 5H, Ph), 7.65 (s, 1H, NC*H*), 7.70 (s, 1H, NC*H*), 7.85 (s, 1H, NC*H*), 7.90 (s, 1H, NC*H*), 9.05 (s, 1H, N (*H*) CN), 9.10 (s, 1H, N (*H*) CN) ppm.

2-Ethyl-5,5-bis(1-(1-methylimidazolium)methyl-1,3-dioxane hexafluorophosphate (**9**, $C_{16}H_{26}N_4O_2P_2F_{12}$) White solid (2.80 g, 94%), mp 94 °C; FT–IR (KBr) $\bar{\nu}$ = 3161, 3122, 2935, 2897, 1569, 1445, 1417, 1304, 1176, 1017, 846 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6,) δ = 0.95 (t, 3H, J = 8 Hz, CH_3), 1.30 (m, 2H, CH_2–CH_3), 3.85 (s, 6H, N–CH_3), 3.95 (d, 2H, J = 12 Hz, O–CH_2), 4.03 (d, 2H, J = 12 Hz, O–CH_2), 4.15 (s, 2H, N–CH_2), 4.55 (s, 2H, N–CH_2), 5.50 (s, 1H, C*H*), 7.65 (s, 1H, NC*H*), 7.70 (s, 1H, NC*H*), 7.75 (s, 1H, NC*H*), 7.80 (s, 1H, NC*H*), 9.01 (s, 1H, N (*H*) CN), 9.06 (s, 1H, N (*H*) CN) ppm.

2-Butyl-5,5-bis(1-(1-methylimidazolium)methyl-1,3-dioxane hexafluorophosphate (**10**, $C_{18}H_{30}N_4O_2P_2F_{12}$) White solid (2.96 g, 95%), mp 99 °C; FT–IR (KBr); $\bar{\nu}$ = 3168, 3134, 2924, 2897, 1565, 1448, 1429, 1180, 1021, 854 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6,) δ = 1.05 (t, 3H, J = 7 Hz, CH_3), 1.40 (m, 2H, CH_2–CH_3), 1.75 (m, 2H, CH_2–CH_2), 1.95 (m, 2H, CH_2–CH), 3.90 (s, 6H, N–CH_3), 3.95 (d, 2H, J = 11 Hz, O–CH_2), 4.05 (d, 2H, J = 11 Hz, O–CH_2), 4.20 (s, 2H, N–CH_2), 4.55 (s, 2H, N–CH_2), 5.55 (s, 1H, C*H*), 7.65 (s, 1H, NC*H*), 7.70 (s, 1H, NC*H*), 7.75 (s, 1H, NC*H*), 7.80 (s, 1H, NC*H*), 9.10 (s, 1H, N (*H*) CN), 9.15 (s, 1H, N (*H*) CN) ppm.

2-Cyclohexyl-5,5-bis(1-(1-methylimidazolium)methyl-1,3-dioxane hexafluorophosphate (**11**, $C_{19}H_{30}N_4O_2P_2F_{12}$) White solid (1.17 g, 37%), mp 117 °C; FT–IR (KBr); $\bar{\nu}$ = 3157, 3122, 2932, 2846, 1573, 1448, 1277, 1181, 1095, 1029, 854 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6,) δ = 1.45 (m, 4H, CH_2), 1.60 (m, 2H, CH_2), 3.10 (m, 4H, CH_2), 3.65 (s, 2H, O–CH_2), 3.80 (s, 6H, N–CH_3), 4.20 (s, 4H, N–CH_2), 4.30 (s, 2H, O–CH_2), 7.55 (s, 2H, NC*H*), 7.75 (s, 2H, NC*H*), 8.90 (s, 2H, N (*H*) CN) ppm.

Typical procedure for release of aldehydes from diol-functionalized IL ***1***

Acetal **2** (3.06 g, 0.48 mmol) and 2 mg *p*-TsOH (0.01 mmol) were mixed with 10 cm^3 H_2O and refluxed under magnetic stirring for 2 h. After cooling to room temperature, the reaction mixture was extracted with CH_2Cl_2 (10 cm^3 × 3). The combined organic layers were washed with 10 cm^3 saturated aqu. $NaHCO_3$ and 10 cm^3 brine. After drying (Na_2SO_4) and filtration, the organic phase was concentrated in vacuo. Due to the fact that the aldehydes are commercial products, it is only necessary to state that 0.49 g (98%) benzaldehyde identical with the educt was obtained.

The recovery of diol-functionalized IL ***1***

Only the recipe to obtain **1** from the de-acetalization has to be given here. After hydrolysis of the formed acetal, benzaldehyde and *p*-TsOH were extracted out with CH_2Cl_2. The left aqueous layer was concentrated to afford the white solid as the released diol-functionalized IL **1** with high purity after washing ethanol and dryness in vacuo.

Acknowledgments We acknowledge the National Natural Science Foundation of China (no. 20673039, 20533010, 20590366), China Postdoctoral Science Po-undation (no. 44021220), and the Science and Technology Commission of Shanghai Municipality (no. 06JC14023) for financial support.

References

1. Hermkens PHH, Ottenheijm HC, Rees JD (1996) Tetrahedron 52:4527
2. Hermkens PHH, Ottenheijm HCJ, Rees D (1996) Tetrahedron 32:5643
3. Eames J, Watkinson M (2001) Eur J Org Chem 7:1213
4. Bhattacharyya S (2001) Indian J Chem Sect B 40:878
5. Ley SV, Baxendale IR, Bream RN, Ackson PS, Leach JAG, Longbottom DA, Nosi M, Scott JS, Storer RI, Taylor SJ (2000) J Chem Soc Perkin Trans I 23:3815
6. Warmus JS, Silva MI (2000) Org Lett 13:1807
7. Kischning A, Monenschein H, Wittenberg R (2000) Chem Eur J 6:4445
8. Linclau B, Singh AK, Curran DP (1999) J Org Chem 64:2835
9. Lindsley CW, Zhao ZY, Leister WH (2002) Tetrahedron Lett 43:4225
10. Zhang W, Chen CHT, Nagashima T (2003) Tetrahedron Lett 44:2065
11. Kim S, Ko H, Lee T (2002) J Comb Chem 4:549
12. Ghanem N, Martinez J, Stien D (2002) Tetrahedron Lett 43:1693

13. Lin CE, Richardson SK, Garvey DS (2002) Tetrahedron Lett 43:4531
14. Warmus JS, Da Silva MI (2002) Org Lett 2:1807
15. Falchi A, Taddei M (2000) Org Lett 2:3429
16. Seddon KR (1997) J Chem Technol Biotechnol 68:351
17. Welton T (1999) Chem Rev 99:2071
18. Wasserscheid P, Keim W (2000) Angew Chem Int Ed 39:3772
19. Seddon KR, Stark A, Torres MJ (2000) Pure Appl Chem 72:2275
20. Sheldon R (2001) Chem Commun 2399
21. Dupont J, de Souza RF, Suarez PAZ (2002) Chem Rev 102:3667
22. Song GH, Cai YQ, Peng YQ (2005) J Comb Chem 7:561
23. Cai YQ, Zhang Y, Peng YQ, Lu F, Huang XL, Song GH (2006) J Comb Chem 8:638
24. Young PR, Jencks WP (1978) J Am Chem Soc 100:1228
25. Chihara T, Wakabayashi T, Taya K (1981) Chem Lett 10:1657
26. Hodge P, Waterhouse J (1983) J Chem Soc Perkin Trans I 20:2319
27. Leznoff CC, Greenberg S (1973) Can J Chem 51:3765
28. Leznoff CC, Wong JY (1976) Can J Chem 54:3765
29. Leznoff CC, Sywanyk W (1977) J Org Chem 42:3203