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Basic Ionic Liquid Gels for Catalysis: Application to the Hydrogen Borrowing Mediated Dehydration of 1,3-Propanediol.

Kyra M. Bothwell, Fabio Lorenzini, Ellen Mathers, Patricia C. Marr* and Andrew C. Marr*

^a School of Chemistry and Chemical Engineering, Queen's University of Belfast, David Keir Building, Stranmillis Road, Belfast, BT9 5AG, UK.

*E-mail: p.marr@qub.ac.uk, *E-mail: a.marr@qub.ac.uk.

Dedication

This article is dedicated to our friend, the unique and brilliant Kenneth Seddon. His encouragement and enthusiasm are sorely missed.

Abstract

The application of basic ionic liquid gels (BILGs) as recyclable promoters of hydrogen borrowing chemistry was investigated. The hydrogen transfer initiated dehydration of 1,3-propanediol to propanal was catalysed by a $[\text{Cp}^*\text{IrCl}_2(\text{NHC})]$ complex promoted by BILGs containing $[\text{P}_{6,6,6,14}][\text{OH}]$. Gels comprising a mixture of basic and hydrophobic ionic liquids gave the best results. The reaction proceeded in the ionic liquid $[\text{C}_2\text{mmim}][\text{NTf}_2]$ enabling the continuous removal of propanal under reduced pressure. Tuning of the composition of the BILG led to a catalytic system that exhibited excellent conversion, selectivity and good recyclability.

Keywords: Ionic Liquid, Gel, Ionogel, Hydrogen Borrowing, 1,3-propanediol

Introduction

Hydrogen borrowing / hydrogen transfer methodologies have proven to be extremely powerful tools in sustainable chemical synthesis. In these reactions a catalyst is added that removes hydrogen from a hydrogen donor and transfers it to another molecule, or part of the same molecule. In 1981 Grigg and co-workers at Queen's University Belfast applied their platinum group metal catalysed hydrogen transfer reaction to affect the alkylation of amines.¹ Early work on Ruthenium catalysts was also performed by Watanabe and co-workers.²

40 years later a myriad of synthetic protocols have been developed that depend upon transition metal mediated hydrogen transfer, and many of them build directly on the

early work in the 1970's and early 80s. In the 21st century hydrogen transfer methods that move hydrogen from one organic functionality to another via a catalyst have been rebranded as 'hydrogen borrowing'.³

Our investigations of hydrogen borrowing mediated alkylation of amines began with an endeavour to utilise waste glycerol from biodiesel production, in collaboration with Stephens and Rebros.⁴ The whole cell biocatalytic digestion of glycerol with *Clostridium Butyricum* leads to the formation of usable quantities of 1,3-propanediol (1,3-PDO), an important bio-renewable platform chemical, and currently prepared on the large industrial scale by the fermentation of sugars.^{5,6}

Downstream chemical transformation of aliphatic alcohols such as 1,3-PDO can be challenging, and we investigated the application of modern homogeneous catalytic methods and solvent technologies. Hydrogen borrowing *N*-alkylation methods have a wide applicability for bio-derived alcohols and mono and di-amination of 1,3-PDO, initiated by [Cp*IrCl₂(NHC)] (Cp* = pentamethylcyclopentadienyl; NHC = carbene ligand) pre-catalysts was successful using aniline.^{4,7,8} An unexpected side reaction, which occurred in parallel to amination, was the partial dehydration of 1,3-PDO, this reaction was particularly prevalent in the ionic liquid methyl-trioctylammonium bis(trifluoromethylsulfonyl)imide [N_{1,8,8,8}][NTf₂], and could be performed in the presence of water, and in air.⁸

Hydrogen transfer initiated dehydration (HTID) could be performed in the absence of the amine to yield a mixture of C3 and C6 aldehydes and alcohols (Figure 1). The aldol and hydrogenation reactions to form the C6 and alcohol products respectively could be suppressed by performing the reaction under a mild vacuum.⁹ This facilitated the attainment of 84% crude isolated yield and a selectivity to propanal of 86%. The Ir(III) [Cp*IrCl₂(NHC)] catalyst **C1** (Figure 2) employed could be recycled with good retention of activity and selectivity, and exhibited excellent air and water stability; however the base (K₂CO₃) was found to require replenishment in order to achieve satisfactory recycling of the catalytic system.

Figure 1. Hydrogen Transfer Initiated Dehydration of 1,3-propanediol.

Subsequent optimisation of the solvent, conditions and catalyst led to the attainment of a quantitative crude isolated yield with 87% selectivity to propanal. This reaction was performed using a fluorinated version of the benzyl catalyst (**C2**, Figure 2) in 1-ethyl-2,3-dimethyl-imidazolium-*N,N*-bistriflimide [C₂mim][NTf₂].¹⁰

Figure 2. Hydrogen Borrowing Ir(III) Catalysts C1 and C2.

Despite the recyclability of the catalyst and facile isolation of the product, the poor stability of the base, and therefore requirement to periodically add more base, prevents HTID chemistry from being classed truly ‘green’. The resultant build-up of salts will inevitably change the process conditions and lead to the frequent requirement for reprocessing of the catalyst and ionic liquid. We therefore turned our attention to the discovery and invention of a more stable base that could be recycled under HTID conditions, and to this end combined this investigation with another ongoing research project, the preparation of basic ionic liquid gels (BILGs). Ionic liquid gels for application in sustainable chemistry have been receiving increasing attention.¹¹ Notable applications can be envisaged in energy and catalytic applications. The gel state provides heterogenized separations, but reactivity occurs in a liquid environment, entrapped within the matrix of the gel, and is therefore closely analogous to homogeneous catalysis.

One of the oldest and most successful applications of ionic liquids to chemistry is the catalytic application of acidic ILs. Two companies have declared processes in this class, China National Petroleum Corp. company Petrochina, and, more recently Chevron, with their ISOALKYL™ Process. In these processes ionic liquids with acidic anions replace conventional homogeneous acids such as H₂SO₄ and HF as catalysts in alkylation reactions. This results in greener processes with less waste, easier catalyst recycle and less danger, exactly as proposed by Earle and Seddon pre-2000.¹² Acidic ionic liquid catalysts can be heterogenized by employing gel technologies. Brønsted acidic ionic liquids entrapped within silica gels operate as solid catalysts that are simple to separate from the product mixture.¹³

The potential use of Brønsted basic ionic liquids to replace conventional basic catalysts has interested many research groups.^{14,15,16,17,18,19} Unfortunately basic ionic liquids are found to be prone to side reactions that decompose the ions over mid to long periods. Careful molecular design can overcome this problem, but the resultant ILs tend to be expensive and require multistep syntheses. An alternative method is to prepare a binary mixture of a basic ionic liquid containing hydrophobic ions. We found this approach worked well for alkoxide ionic liquids of pyrrole applied to catalytic Knoevenagel and Aldol reactions.²⁰ Another approach is to prepare an ionic liquid gel. Phosphonium hydroxide ionic liquids have been found to autocatalyse the formation of silica and titania BILGs.²¹ The application of the IL slowed down the basic sol-gel process and led to the formation of good transparent gels that could be

coated. In addition entrapment of $[P_{6,6,6,14}][OH]$ was found to significantly stabilise the cation compared to the liquid phase.

Inspired by our success applying autocatalytic acidic ionic liquid gels in dehydration reactions,¹³ we decided to attempt hydrogen borrowing initiated dehydration in the presence of BILGs.

Results and discussion

HTID Catalytic Conditions

The catalysts **C1** and **C2** (Figure 2) have been shown to be active for the HTID of 1,3-PDO to aldehydes in ionic liquids (Figure 1). The application of an Ir(III) catalysts affords a high level of air and moisture stability to the catalyst. Operating the reaction in an ionic liquid enables the product to be distilled from the mixture during the reaction on application of a vacuum (350 mbar). Such conditions are easily achievable in industry. Some typical previous results are summarised in Table 1. Under these reactions the bases tested, including K_2CO_3 and KOH, were gradually consumed. In imidazolium IL $[C_2mmim][NTf_2]$ at 150 °C **C2**¹⁰ was found to have a better tolerance for KOH than **C1**.⁹ Trifluorinated benzyl $Cp^*Ir(III)NHC$ complex **C2** was chosen as the catalyst for the HTID reaction of 1,3-propanediol using BILGs.

Table 1. Catalytic performance of C1 and C2 in the HTID of 1,3-PDO.^{a,9,10}

Entry	Catalyst	[1,3-PDO]:[Ir]	Base	% Yield ^b	2	3	4	5
1	C1	75.1	K_2CO_3	78	73.0	10.1	8.6	8.3
2	C1	219.7	K_2CO_3	70	72.7	12.5	6.1	8.6
3	C1	226.1	KOH	54	85.2	5.9	1.4	7.5
4	C2	80.3	K_2CO_3	85	83.6	4.3	0.0	12.1
5	C2	212.4	K_2CO_3	70	72.7	8.8	1.2	17.3
6	C2	208.8	KOH	85	88.8	1.5	0.0	9.7

^a Reactions performed in $[C_2mmim][NTf_2]$, T = 150 °C, P = 0.35 bar, with reaction time: 6 h, stirring speed 1000 RPM. ^b Crude isolated yield.

BILG Synthesis

The first BILGs tested were based on $[P_{6,6,6,14}][OH]$ entrapped in silica, as reported previously.²¹ These can be prepared by the simple addition of tetraethoxysilane (TEOS) to the ionic liquid; the process of gel formation is autocatalytic.

[P_{6,6,6,14}][OH] silica gels were found to give unreliable catalytic results in hydrogen borrowing experiments. In order to improve the durability of the BILGs a gel based on a mixed IL system was attempted. In order to do this an additional IL was added to the preparation. In our experience the silica gels of hydrophobic C₄ imidazolium [NTf₂] ILs exhibit good stability and so [C₄mmim][NTf₂] was chosen as the co-solvent. Maintaining a 1:1 ratio of IL and TEOS by volume, the ratio of the ionic liquids was varied (Table 2). Three gels were prepared containing [C₄mmim][NTf₂]:[P_{6,6,6,14}][OH] of 3:1 (**G1**), 1:1 (**G2**) and 1:3 (**G3**). The gels were aged for 4 weeks and extracted with ethanol to remove any IL that was not entrapped. The resultant gel was tested for leaching in toluene under reflux for 6 hours. No leaching was detected by ³¹P NMR nor by ¹⁹F NMR.

Table 2. Silica BILGs containing [P₆₆₆₁₄][OH] and [C₄mmim][NTf₂].

Entry	Gel	[C ₂ mmim][NTf ₂] ^a	[P _{6,6,6,14}][OH] ^a	TGA/ °C	BET surface area/ m ² /g	BET pore size/ nm
1	G1	0.75	0.25	274	140.9	8.1-10.5
2	G2	0.50	0.50	253	224.7	7.3-8.9
3	G3	0.25	0.75	241	222.1	10.8-14.3

^a Ratio (by volume) relative to TEOS.

The surface area of the material was found to increase as the proportion of phosphonium IL was increased from **G1** to **G2**. **G3** was found to have the highest average pore size, and similar surface area to **G2**. The thermal stability reduced slightly as the proportion of [P_{6,6,6,14}][OH] was increased, this is expected as the thermal stability of imidazolium [NTf₂] ILs far exceeds that of phosphonium hydroxides.

Hydrogen Borrowing in the presence of a BILG

The BILGS **G1-3** were tested in the HTID of 1,3-PDO catalysed by **C2**. Initial studies were carried out to optimise the quantity of gel required to promote dehydration. The results are reported in Table S1. Efficient HTID relies on the correct concentration of base, with too much or too little significantly reducing performance. The optimum quantities of gel required were 0.7g from **G1**, 0.4g for **G2** and 0.6g for **G3**. The catalytic results obtained for the three gel systems under these conditions are summarised in Table 3.

Table 3. Catalytic performance of gels G1-3 in the C2 catalysed HTID of 1,3-PDO.^a

Entry	Base	% Yield ^b	2	3	4	5
1	G1	80	88.7	3.1	0	8.3
2	G2	>99	81.9	2.8	0	15.3
3	G3	87	90.3	3.1	0	6.5

a Reactions performed in [C₂mmim][NTf₂], T = 150 °C, P = 0.35 bar, [1,3-PDO]:[Ir] = 75, with reaction time: 6 h, stirring speed 1000 RPM. **b** Crude isolated yield.

The performances of the three BILG promoted systems were highly competitive, rivalling the best results obtained for HTID of 1,3-PDO observed thus far. **G1** afforded 80% yield and 89% selectivity to propanal (**2**), **G2** over 99% yield and 82% **2** and **G3** 87% yield and 90% **2**. These results are very similar to optimised KOH and K₂CO₃ systems.^{9,10} Thus far we have been unable to achieve similar catalytic performances using homogeneous basic ionic liquids nor fully heterogenized systems containing a co-entrapped hydrogen borrowing catalyst and basic ionic liquid. The high activity of the catalytic system employing **G2** correlates with the high relative surface area of this BILG. The lower pore size of **G2** was not detrimental to the activity as a base in HTID.

Adopting BILG promoters is envisaged having a number of advantages, including increased safety of use and ease of handling. Important amongst these advantages is reusability, which will reduce costs and material consumption, and therefore the BILGs were tested in catalyst recycling experiments.

Recycling the Ir(III) BILG system

All three BILG systems exhibited better performance than KOH and K₂CO₃ in recycling experiments. For the conventional bases an additional aliquot of KOH or K₂CO₃ was required for each catalytic run, leading to a build-up of waste salts.^{9,10} The BILG promoters **G1-3** could all be reused. A comparison of five recycles of HTID catalyst **C2** in [C₂mmim][NTf₂] promoted by **G1**, **G2** and **G3** (Tables S2-4, Figure 3) revealed that there was a significant drop in the performance of the catalyst over five runs for **G1** and **G2**. In contrast the performance of **C2** promoted by **G3** was consistent over five runs in activity and selectivity. The 1:3 ratio of [C₄mmim][NTf₂]:[P_{6,6,6,14}][OH] provided the best compromise of basicity, stability and affinity for the silica matrix. This formulation also afforded the largest pore size (Table 1), which will assist diffusion and resist pore blockage.

The stability of binary mixtures of basic and hydrophobic ionic liquids was demonstrated previously for pyrrole alkoxide ionic liquids.²⁰ We suggest that hydrophobic ions protect the cation from decomposition pathways, for example the attack of hydroxide arising from absorbed moisture. The reasons behind the success of **G3** as a recyclable basic promoter of HTID are more complex, as there are many factors involved that cannot be altered independently, for example porosity, surface area, basicity and ionic liquid stability. Base activity correlates with surface area, and it is likely that the reaction occurs most efficiently near the surface of the gel. We have observed lower activities in gels incorporating hydrogen borrowing catalysts entrapped within. The lower activities of these Iridium containing basic ionic liquid

gels may arise from a combination of longer diffusion pathways for the substrate, and non-optimal basicity within the gel.

Figure 3. Recycling of HTID promoted by gels G1, G2 and G3.

Experimental

Material and equipment

TEOS ($\geq 97\%$, TCI UK), 1,3-Propanediol (98% w, Aldrich), propanal (97% w, Aldrich), 2-methyl-2-pentenal (97% w, Aldrich), 2-methyl-pentanal ($>95.0\%$ w, TCI), propanol (97% w, Sigma-Aldrich), methanol ($\geq 99.9\%$, CHROMASOLV, for HPLC, Sigma-Aldrich), CDCl_3 (99% w, Aldrich), Amberlite IRN78 hydroxide form (Sigma Aldrich), $[\text{P}_{6,6,6,14}][\text{Cl}]$ (97.7%, CYPHOS IL 101), AgNO_3 (99%, Sigma Aldrich), Nitric acid ($\geq 90\%$, Sigma Aldrich), KOH (85% w, Riedel-de Haën), 1,2-dimethylimidazole (98%, Sigma Aldrich), 1-methylimidazole (99%, Sigma Aldrich), 1-bromoethane (98%, Sigma Aldrich), 1-bromobutane (98%, Sigma Aldrich), 1-bromooctane (99%, Sigma Aldrich), Lithium bistriflimide (HQ115, 3M), Silver Oxide (99%, Sigma Aldrich), decelite (speed plus, diatomaceous filter-aid, Acros Organics), 1-benzyl-3-methylimidazolium bromide (97%, Sigma Aldrich), $[\text{Cp}^*\text{IrCl}_2]_2$ (96%, Sigma Aldrich), 2,4,6-trifluorobenzyl bromide (97%, Fluorochem), Pentafluorobenzyl bromide (99%, Fluorochem) were used as received.

^1H NMR and ^{31}P NMR spectra were measured on a Bruker Avance III HD 300 MHz. The chemical shifts are reported in ppm related to TMS. Signal multiplicities are reported as singlet (s), doublet (d), triplet (t), and multiplet (m). GC/MS spectroscopic data were collected on a MassHunter Workstation Software – Qualitative Analysis – Version B.06.00 – Build 6.0.663.10 – Service Pack 1 – © Agilent Technologies, Inc. 2012. GC/MS Column: Agilent Technologies, Inc.; 19091S-433UI; HP-5MS UI; 30 m X 0.250 mm; 0.25 Micron; -60 to $325/350^\circ\text{C}$; SN: USE137316H. GC/MS spectroscopic data were processed on MassHunter Data Analysis –

MassHunter GC/MS Acquisition B.07.01.1805 – 12-Mar-2014 – © 1989-2014 Agilent 184

Technologies. Thermogravimetric analysis (TGA) was carried out using a TGA Q5000 IR thermogravimetric analysis. The samples were heated in N_2 gas with a

balance purge flow of 25 mL/min and a sample purge flow of 10 mL/min, with a heating rate of 10 °C per minute within a temperature range of 30 °C to 600 °C. Brunauer-Emmett-Teller theory (BET) was used to determine the surface area and porosity; measured with a Tristar II 3020 instrument and using N₂ as the adsorption gas.

Synthesis

C1 and **C2** were prepared according to literature methods.^{9,10}

[C₂mim][NTf₂],²² [C₄mim][NTf₂]²² and [P_{6,6,6,14}][OH]²¹ were synthesized according to literature procedures.

Synthesis of [C₄mim][NTf₂] and [P_{6,6,6,14}][OH] containing gels G1, G2 and G3

Three ratios of [P_{6,6,6,14}][OH] and [C₄mim][NTf₂] (see Table S5) were mixed in a small sample vial, followed by the addition of TEOS (1.0 mL). The samples were stirred for 20 minutes, the magnetic stirrer bars were removed, and the mixtures left to gel (samples gelled within 16 hours). After ageing for 4 weeks, the gels were washed in refluxing ethanol (50 mL x 3) for 2 hours.

HTID of 1,3-PDO using mixed [C₄mim][NTf₂]/[P_{6,6,6,14}][OH] SiO₂ gels

HTID reactions were performed by a modification of the procedure detailed in our literature.^{9,10}

1,3-Propanediol (1.25 g, 0.0164 mol), **C2** (0.135 g, 0.236 mmol), [P_{6,6,6,14}][OH] SiO₂ gel **G1**, **G2** or **G3** (for quantities see Table S6), and [C₂mim][NTf₂] (2.9 g, 0.0071 mol) were mixed in a 50 mL round bottom flask connected, through a distillation condenser, to a 50 mL glass tube. The mixture was maintained at 150 °C, at a controlled pressure of *ca.* 0.350 bar, for six hours, stirring at 1000 RPM using a hot plate and magnetic stirrer bar. The reaction product, a colourless liquid, was isolated by distillation, it was collected for the duration of the six hours reaction, in a glass collecting tube kept at *ca.* -196 °C (N_{2(l)} bath). After separation from the water layer, the crude product was analysed by GC/MS and ¹H NMR spectroscopies.

The amount of 1-propanol (**5**) in the isolated crude product was calculated *via* GC/MS spectroscopy; then integration of the ¹H NMR spectrum was used to calculate the molar amounts of propanal (**2**), 2-methyl-2-pentenal (**3**), and 2-methyl-pentanal (**4**), relative to **5**.

The recycling reactions were carried out as follows. Another aliquot of 1,3-PDO was added to the reaction mixture resulting from the previous recycling experiment in the 10 mL round bottomed flask (full experimental details in Tables S7-9). The resulting mixture was reacted and analysed in the same way as the first reaction.

Conclusions

Cp*Ir(III)NHC hydrogen borrowing catalyst **C2** has been applied to the catalytic dehydration of 1,3-PDO promoted by Basic Ionic Liquid silica Gels containing a mixture of basic and hydrophobic ionic liquids. Operating the reaction in an ionic liquid solvent under vacuum enabled the isolation of the reaction products without extraction. The activities and selectivities towards propanal achievable rivalled, and the recycling outperformed the use of conventional bases. Basic binary ionic liquid gel **G3** was found to support the recycling of the catalytic system without intermediate treatment nor addition of further base.

Supporting Information

Details of gel syntheses, TGA and BET data, catalytic experiments and analysis methods.

Acknowledgement

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Synopsis.

Ionic liquids served as the solvent and gel base to promote HTID of 1,3-propanediol to propanal with solvent-less product separation.