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Biphasic dimerisation of methylacrylate—immobilisation and stabilisation of cationic Pd-catalysts in ionic liquids by an ammoniumphosphine ligand

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The first continuous, biphasic, Pd-catalysed dimerisation of methylacrylate is described. The biphasic system has been realised by using a tetrafluoroborate ionic liquid as catalyst medium and an ammoniumphosphine ligand to immobilise and stabilise the Pd-catalyst.

The dimerisation of functionalized olefins is of general technical importance. For example, the dimerisation of methylacrylate (MA) to Δ^2-dihydrodimethylmuconate (DHM) leads to a highly interesting intermediate which can be transformed to both fine chemicals (such as cyclopentenones) and adipic acid.[1] The latter reaction is of general interest since it allows the production of adipic acid from propene rather than from benzene.

Academic research has, for more than 30 years, dealt with the Pd-catalysed dimerization of MA. Barlow *et al.* described in 1970 the use of $(PhCN)_2PdCl_2$ as catalyst for this reaction.[2] They obtained the dimerisation products Δ^2- and Δ^3-DHM in a ratio of 3 : 1, but a rapid reductive decomposition of the Pd-catalyst was observed. Pracejus and Oehme could stabilise similar catalytic systems by addition of the reoxidizing agent benzoquinone.[3] In this manner, they reached a turnover number of 100 mol MA converted per mol Pd, however with low reaction rate. The reaction rate could be enhanced by the use of weakly coordinating anions (*e.g.* $[BF_4]^-$) instead of chloride, but this had a negative effect on the catalyst stability.[4] A clear improvement concerning catalyst activity and stability was published by one of us and makes use of dicationic Pd-complexes with phosphine ligands.[5–7] In pure MA these catalysts convert MA to Δ^2-DHMs in over 90% selectivity. Again, some catalyst reduction to Pd^0 was observed which afforded a complicated regeneration of the Pd after the catalytic reaction.

Ionic liquids (IL's) are low melting (< 100 °C) salts which represent a new class of non-molecular, ionic solvents.[8–10] Nowadays, IL's are widely accepted as—often greener—alternatives to classical organic solvents in chemical transformations and separation techniques. In the past years the range of known and available ILs has been expanded so that many different candidates are accessible and even commercially available today.[11]

In the past few years, several Pd-catalysed reactions have been investigated in IL's. For example, in the dimerisation of butadiene a significant rate enhancement was obtained by switching from organic solvents like THF to $[BMIM][BF_4]$.[12] Heck reactions in certain IL's demonstrated the *in situ* formation of Pd–carbene complexes.[13,14] The selectivity of some Heck reactions with aryl bromides and electron rich olefins was found to be enhanced by the use of $[BMIM][BF_4]$ as solvent.[15] Moreover, Pd-catalysed allylation reactions[16] and Trost–Tsuji-coupling reactions[17] have been carried out in a biphasic reaction mode using an IL as catalyst phase. Here, no catalyst leaching into the product layer was observed by using the ionic ligand Na_3TPPTS.

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In the present paper, we describe the first continuous, biphasic, Pd-catalysed dimerisation of MA by using a tetrafluoroborate IL as catalyst solvent. The initial idea to use tetrafluoroborate IL's as solvent for the Pd-catalyst in MA dimerisation came to us with regard to the well-known rate enhancing effect of $Li[BF_4]$ addition. The latter has been described by Nugent and Hobbs.[18] Consequently, our first experiments aimed to study the influence of an addition of $[BMIM][BF_4]$ on the dimerisation rate, in comparison to the reaction in neat MA. The results obtained after different reaction times are presented in Table 1.

Table 1 reveals a significant rate enhancement in the MA/IL mixture at comparable product selectivity. However, it is important to note that many aspects usually discussed to explain activation of transition metal catalysts in IL's do not fit here. For example, a significant influence by *in situ* formed palladium carbene complexes is rather unlikely for several reasons. a) Pd–carbene complexes (prepared separately according to a method described by Cavell *et al.*[19] and added to the ionic liquid) have been found to be inactive in the MA dimerisation reaction. b) Their *in situ* formation under the acidic reaction conditions is rather unlikely. c) We found that for the Pd-catalysed MA dimerisation pyridinium salts show the same rate enhancing effect as imidazolium salts.

Moreover, all aspects that are frequently discussed to explain activation in ionic liquids and which are related to improved solubility or *in situ* extraction effects can not be valid here since the ionic liquid addition does not change the monophasic, homogeneous reaction mode for all experiments displayed in Table 1. Finally, the neutral, weakly coordinating IL's which have been used here should not have an influence on coordination equilibria at the Pd-catalyst. From all this we speculate that the ionic medium may lower the activation barrier of the rate determining step by stabilising the cationic transition state.

In all dimerisation reactions of MA (with and without added IL) we found a maximum MA conversion of about 80% which indicated some potential product inhibition effect. To prove this, two experiments have been carried out. a) Fresh feedstock was added after the reaction had been stopped at 80% conversion; b) adipic acid dimethyl ester (a model substance for the formed product) was added at the beginning of the reaction.

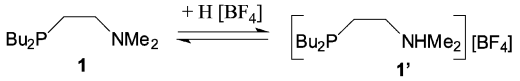
Table 1 Acceleration of the Pd-catalysed MA dimerisation by addition of the ionic liquid [BMIM] $[BF_4]$ (monophasic reaction system)

	TON after				
Catalytic system	1h	4 h	6h	12 h	24 h
PBu_3	64	216	240	559	1024
PBu_3/IL	109	384	542	1182	2986

General conditions: 100 mmol MA, 0.02 mmol $Pd(acac)_2$, 0.2 mmol $[HPBu_3][BF_4]$, $[Et_2OH][BF_4]$: 0.12 mmol at beginning, additional 0.07 mmol after 6 h and 12 h, 50 mass.-% $[BMIM][BF_4]$; 80 °C.

In the first case, the reaction started again after the addition of new substrate. In the second experiment, much lower activity of the catalyst system was found. From both experiments we concluded that product inhibition should be a major problem for the Pd-catalysed MA dimerisation.

To overcome this limitation we decided to carry out the reaction in a biphasic mode by addition of an unpolar organic solvent. We chose toluene as the organic extractant since it has a miscibility gap with [BMIM][BF$_4$], dissolves the product and is inert against the catalytic conditions. However, first recycling experiments revealed a dramatic loss in activity during the recycling if PBu$_3$ was used as the ligand [TOF = 110 (original run), TOF = 20 (third recycle); overall TON of four runs = 265]. Obviously this result was related to heavy leaching of the catalyst into the organic layer. Since even weakly coordinating anions are known to have a detrimental effect on the cationic Pd-catalyst the use of the well-known ionic ligand Na$_3$TPPTS was not a promising alternative to solve our problem. However, we found that the ammoniumphosphine ligand **1** provides a very suitable combination of properties for the biphasic, Pd-catalysed MA dimerisation in IL's.



1 **1'**

In contrast to monodentate phosphines, **1** can coordinate the catalyst in a chelating manner thus stabilizing unsaturated catalyst intermediates. From the fact that the catalytic system is more active with **1** than with PBu$_3$, we conclude that amine coordination is very labile in the acidic reaction medium. The catalytic system with **1** could be recycled four times with nearly no loss in activity (TOF = 139 (original run), 127 (third recycle), overall TON = 517). During four cycles no Pd black was formed when **1** was the ligand, in contrast to many other ligands including PBu$_3$. A possible explanation may be that **1** helps to reoxidise and reactivate Pd^0-species by bringing the acidic and reoxidizing N-H proton closely to the catalytic centre.

Finally, the biphasic reaction was transferred into a continuous flow apparatus (for a schematic view see Fig. 1). For the continuous experiment, a mixture of substrate and toluene was pumped into the bottom of a tube containing the ionic liquid catalyst solution. Driven by its lower density the feed rose in the tube and was dispersed on glass bullets to increase the exchange surface between the ionic liquid catalyst solution and the feed. A mixture of product/substrate and organic solvent is removed at the top of the reactor. This reactor concept proved to be easy to realise and to handle. However, it may be only suitable for those reactions where the rate of reaction is low in comparison to rate of mass transfer.

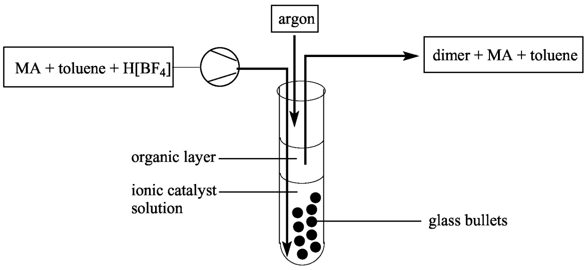


Fig. 1 Continuous apparatus as used for the biphasic Pd-catalysed dimerisation of MA.

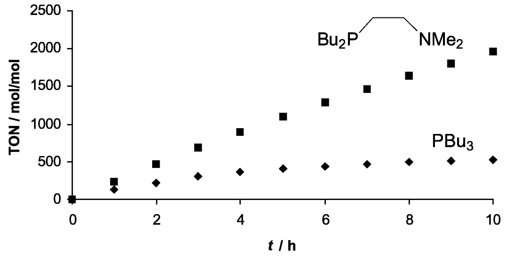


Fig. 2 †

As shown in Fig. 2, the continuous reaction confirms the fact that PBu$_3$ is efficiently extracted into the toluene/product layer during the reaction. This results in a maximum TON of about 500. In contrast, the continuous reaction with **1** is surprisingly stable indicating that **1** is immobilising the Pd-catalyst in the ionic liquid in an efficient manner. No deactivation can be observed over the first 10 h; after 50 h of continuous reaction an overall TON of more than 4000 could be realised (selectivity to Δ^2-DHM being >90%). This clearly demonstrates the potential of the biphasic ionic liquid system to bring the Pd-catalysed MA dimersation closer to a technical realisation.

Moreover, these results may be of general importance in showing that product inhibition problems can be efficiently solved by continuous extraction of the product from an ionic catalyst solution. Finally, the stabilisation and activation of Pd-catalysts in an IL by other means than the formation of Pd–carbene complexes may further inspire Pd-catalysis in IL's.

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Notes and references

† Catalyst immobilisation by use of ammoniumphosphine ligand. Conditions of the continuous experiment: the ionic catalyst solution contains 0.02 mmol Pd(acac)$_2$, 0.2 mmol ligand, 0.32 mmol H[BF$_4$] (for PBu$_3$ as the ligand), 0.52 mmol H[BF$_4$] (for **1** as the ligand); reaction system: 2.5 ml [BMIM][BF$_4$], 20 g glass bullets; feed mixture contains 40 ml MA, 60 ml toluene, 4 ml Bu$_2$O, 2.4 ml H[BF$_4$]; feed rate = 3.3 ml h^{-1}; reaction temperature 80 °C.

1 U. Onken and and A. Behr, *Lehrbuch der Technischen Chemie, Band 3: Chemische Prozesskunde*, Thieme, Stuttgart, 1996*Ullmann's Encyclopedia of Industrial Chemistry*, 6th Edition on CD-ROM, Wiley-VCH, Weinheim, 1998.
2 M. G. Barlow, M. J. Bryant, R. N. Haszeldine and A. G. Mackie, *J. Organomet. Chem.*, 1970, **21**, 215.
3 H. Pracejus, H. J. Krause and G. Oehme, *Z. Chem.*, 1980, **20**, 24.
4 G. Oehme and H. Pracejus, *J. Organomet. Chem.*, 1987, **320**, C56.
5 I. Tkatchenko, P. Grenouillet and D. Neibecker, *French Patent* 2,524,341, 1983.
6 I. Tkatchenko, P. Grenouillet and D. Neibecker, *French Patent* 2,596,390, 1987.
7 I. Tkatchenko, P. Grenouillet and D. Neibecker, *U.S. Patent* 4,889,949, 1989.
8 R. Sheldon, *Chem. Commun.*, 2001, 2399.
9 P. Wasserscheid and W. Keim, *Angew. Chem., Int. Ed.*, 2000, **39**, 3772.
10 T. Welton, *Chem. Rev.*, 1999, **99**, 2071.
11 Ionic liquids can be purchased *e.g.* from Solvent Innovation GmbH, Cologne, Germany (www.solvent-innovation.de).
12 S. M. Silvana, P. A. Z. Suarez, R. F. de Souza and J. Dupont, *Polymer Bul.*, 1998, **40**, 401.
13 L. Xu, W. Chen and J. Xiao, *Organometallics*, 2000, **19**, 1123.
14 C. J. Mathews, P. J. Smith, T. Welton, A. J. P. White and D. J. Williams, *Organometallics*, 2001, **20(18)**, 3848.
15 L. Xu, W. Chen, J. Ross and J. Xiao, *Org. Lett.*, 2001, **3**, 295.
16 W. Chen, L. Xu, C. Chatterton and J. Xiao, *Chem. Commun.*, 1999, 1247.
17 C. de Bellefon, E. Pollet and P. Grenouillet, *J. Mol. Catal. A: Chem.*, 1999, **145**, 121.
18 W. A. Nugent and F. W. Hobbs, *J. Org. Chem.*, 1983, **48**, 5364.
19 A. M. Magill, D. S. McGuinness, K. J. Cavell, G. J. P. Britovsek, V. C. Gibson, A. J. P. White, D. J. Williams, A. H. White and B. W. Skelton, *J. Organomet. Chem.*, 2001, **617–618**, 546.