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# *N*-Heterocyclic carbene containing element organic frameworks as heterogeneous organocatalysts†

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**A bifunctional imidazolium linker was used for the production of highly crosslinked element organic frameworks by Suzuki-coupling with tetrafunctional boronic acids. The resulting porous materials are good heterogeneous organocatalysts in the *N*-heterocyclic carbene-catalyzed conjugated umpolung of α,β-unsaturated cinnamaldehyde.**

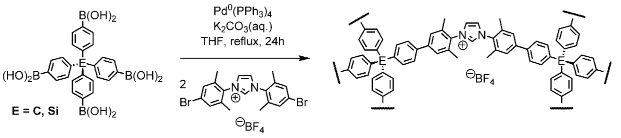
*N*-Heterocyclic carbenes (NHCs) are known for their attractive properties, being electron-rich and sterically demanding, however, also tunable over a wide range.[1] Consequently, they have found numerous applications as ligands in transition-metal catalysis[1] and as organocatalysts in their own right.[2] A preferred method for their preparation is the deprotonation of the corresponding azolium salts.

Most of this research was focussing on homogeneous processes. However, handling and separation of homogeneous catalysts exhibits significant economical and ecological disadvantages and efficient and selective heterogeneous catalyst systems would be highly desirable, especially for large scale applications. The immobilization of imidazolium-based NHCs has been investigated, like the immobilization on the surface of nanoparticles,[3] polymers[4–6] or silica-based, porous materials like SBA-15.[7] All of those publications show catalytic activity of metal species coordinated to the NHC-functionality. To our knowledge, no results have been published so far, dealing with heterogeneous NHC-compounds and their application in metal-free organocatalysis.[2]

In the last few years a lot of effort has been made in the development of metal-free organic framework materials.[8–10] The huge variety of possible reactions to crosslink multifunctional linkers for the production of porous polymers has opened new routes for the immobilization of functional organic molecules. Besides the immobilization of imidazolium species on different substrates another method is the crosslinking of multifunctional imidazolium-based linkers by convenient synthetic routes to achieve highly crosslinked, porous framework materials. As a side effect they should show a large number of accessible carbene functionalities due to an open framework structure. So far, only the approach for the production of periodic mesoporous organosilicas (PMOs)[11] was used for the immobilization of bifunctional imidazolium linkers. Nguyen *et al.* have synthesized a bifunctional bis-aryl-imidazolium linker with triethoxysilyl groups for crosslinking.[12] Polycondensation of this linker in the presence of different surfactants as structure directing agents resulted in porous materials with low specific surface areas of maximal 104 $m^2\ g^{-1}$. The co-condensation with tetraethoxysilane led to materials with a specific surface area of up to 1170 $m^2\ g^{-1}$. So far, no results from catalytic tests of these materials have been published.

Recently, we have shown the production of highly porous element organic framework materials by the Pd-catalyzed Suzuki coupling reaction of multifunctional aryl bromides and aryl boronic acids.[13] In this work, our interest was the incorporation of imidazolium linkers based on bifunctional aryl bromides by crosslinking with tetrafunctional boronic acids (Scheme 1). In the following, the resulting three-dimensional, porous element organic framework materials are used as heterogeneous organocatalysts in the NHC catalyzed conjugated umpolung of α,β-unsaturated cinnamaldehyde for the diastereoselective synthesis of γ-butyrolactones as model reaction.

The imidazolium-based linker is synthesized in two steps from 2,6-dimethylaniline similar to the previously described procedure[14] as well as the corresponding tetrafunctional linkers (silane-) and (methane-tetrayltetra-4,1-phenylene) tetrakisboronic acid.[15] The Suzuki coupling reaction of the



**Scheme 1** Syntheses of EOF-15 (E = Si) and -16 (E = C) from tetrahedral boronic acids and the bifunctional imidazolium linker by Suzuki coupling.

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linker molecules is carried out in THF solution with aqueous potassium carbonate using tetrakis(triphenyl-phosphine)-palladium(0) as a catalyst. The precipitating product is filtered off from the solution and washed at least three times with THF, water and ethanol, respectively. The pale grey powder is dried at 80 °C.

With regard to the imidazolium linker yields of about 55% could be achieved. Both compounds are amorphous in analogy to the porous organic frameworks EOF-6 to -9 synthesized by Suzuki coupling due to the kinetic controlled reaction path. FTIR and solid state NMR spectroscopy have been used for structural characterization. Both methods confirm the successful integration of the imidazolium linker in the framework material. Comparison of IR spectra of the linker molecules and the resulting polymer is shown in Fig. S1, ESI.†

A strong and broad band at 3420 $cm^{-1}$ corresponds to the hydroxy groups of the boronic acid. This band is also present in the spectrum of the polymer EOF-16, even though with a much lower intensity indicating only partial conversion of the boronic acid groups. As expected from this incomplete crosslinking, also the bromine functional groups of the imidazolium precursor indicated by a sharp band at 567 $cm^{-1}$ are present in the spectrum of the polymer, even though with a much lower intensity, too. Further proof for a successful integration is given by the bands at around 2930 $cm^{-1}$ in the spectrum of the imidazolium linker and the polymer, indicating aliphatic C–H vibrations of the methyl groups. Comparison of $^{1}H$ MAS and $^{13}C$ CP MAS NMR spectra of the imidazolium linker and the polymer EOF-15 (Fig. S2, ESI†) shows broad signals for aromatic and aliphatic carbon atoms at a chemical shift of 125–140 ppm and 16–19 ppm and the corresponding hydrogen atoms with maxima at 6.8 and 2.8 ppm, respectively. In the $^{13}C$ spectrum of the pure linker a much better resolution can be observed due to an ordered structure in contrast to the non-ordered polymer structure.

The composition of the polymer EOF-16 was determined by C, H and N combustion analysis. All experimental values (wt%, C 61.65, H 4.48, N 3.06) are significantly lower in comparison to the values calculated for an ideal structure assuming a 100% crosslinking degree (wt%, C 76.05, H 6.27, N 6.45). This difference might be attributed to the residual functional groups ($-B(OH)_2$, –Br).

EOF-16 shows a high thermal stability in air up to 300 °C (Fig. S3, ESI†). Up to that temperature a slight mass loss is observed that is attributed to volatile compounds. Under this assumption, a total mass loss of 75 wt% is observed up to a temperature of 800 °C. The decomposition occurs in two steps. We assume that at lower temperature residual functional and organic groups are decomposed, while at a higher temperature the organic framework itself is destroyed. The large residual amount of 25 wt% in comparison to the theoretical expected value of 6.7 wt% by boron oxide from the $BF_4$ counter ion might be explained by the residual boronic acid groups in the polymer.

The morphology of EOF-15 and -16 is shown to be plate-like in the upper nano- and lower micrometre range according to SEM micrographs (Fig. 1). But with higher magnification one can see highly aggregated nanoparticles with a size of 10–50 nm especially for EOF-16.

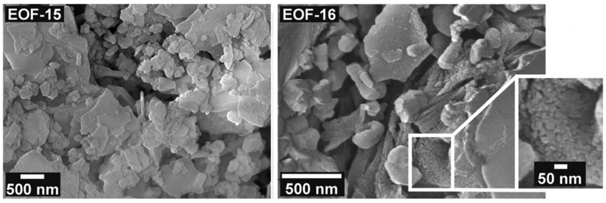


**Fig. 1** SEM micrographs of EOF-15 (left) and -16 (right) show highly aggregated particles of 10–50 nm in diameter.

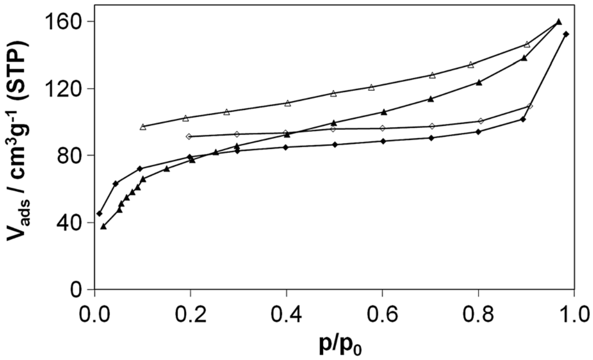


**Fig. 2** Nitrogen physisorption isotherms of EOF-15 (diamonds) and -16 (triangles) measured at −196 °C. Filled symbols denote adsorption, empty symbols denote desorption, respectively.

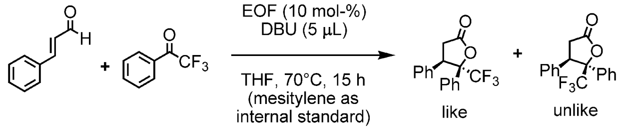
Nitrogen physisorption measurements result in a combination of type I and II isotherms that are characteristic for micro-porous polymers with an amorphous structure (Fig. 2). They show a high uptake at relative pressure below 0.2 and a hysteresis between the ad- and desorption branch indicating the flexible framework structure. The approximately linear increase of the uptake amount at $p/p_0 = 0.2–0.8$ is a result of a high external surface area due to small particles as shown by SEM. All evaluation data of the isotherms are summarized in Table 1. In comparison to other porous polymers produced by Suzuki coupling ($S_{BET}$ up to 1380 $m^2\ g^{-1}$),[13] EOF-15 and -16 show rather low specific surface areas of up to 262 $m^2\ g^{-1}$. One reason might be the large linker between the tetrahedral nodes consisting of four 1,4-connected benzene rings and one imidazolium ring. As shown before,[13] large linkers result in highly flexible frameworks allowing an effective packing in space. On the other hand such a high flexibility should result in highly swollen frameworks in certain solvents to guarantee good accessibility for substrates to catalytic active sites.

Thus, the catalytic activity of the compounds was tested in the conjugated umpolung of an α,β-unsaturated cinnamaldehyde and coupling with trifluoroacetophenone by the *in situ* generated NHC (Scheme 2).[16] The reusability of the heterogeneous catalyst was demonstrated in up to four

**Table 1** Determination of total specific surface area, external surface area, micro- and total pore volume

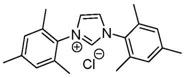
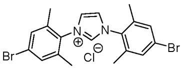
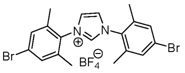
| EOF | | 15 | 16 |
|---|---|---|---|
| $S_{total}(p/p_0 = 0.3)^a$ | $m^2\ g^{-1}$ | 253 | 262 |
| $S_{extern}(p/p_0 = 0.4–0.7)^b$ | $m^2\ g^{-1}$ | 28 | 111 |
| $V_{micro}(p/p_0 = 0.2)^c$ | $cm^3\ g^{-1}$ | 0.12 | 0.12 |
| $V_{total}(p/p_0 = 0.9)^c$ | $cm^3\ g^{-1}$ | 0.16 | 0.21 |

[a] Single point BET. [b] *t*-plot. [c] *Gurvich*.



**Scheme 2** Catalytic test reaction: conjugated umpolung of an α,β-unsaturated cinnamaldehyde with trifluoroacetophenone by the *in situ* generated *N*-heterocyclic carbene. DBU = Diazabicycloundecene.

**Table 2** Results of catalytic test reaction with the reusable heterogeneous catalysts EOF-15 and -16

| Catalyst | Cycle | Isolated yield[a] (mol%) | dr (*like* : *unlike*)[b] |
|---|---|---|---|
| EOF-16(C) (ESI[1]†) | 1 | 65 (86; 81)[c] | 1.38 : 1 |
| | 2 | 60 (68; 67)[c] | 1.39 : 1 |
| | 3 | 56 | 1.43 : 1 |
| | 4 | 48 | 1.37 : 1 |
| | 5 | 46 | 1.37 : 1 |
| EOF-15(Si) | 1 | 69 | 1.33 : 1 |
| | 2 | 78 | 1.50 : 1 |
| | 3 | 84 | 1.33 : 1 |
| | 4 | 72 | 1.27 : 1 |
|  | 1 | 83 | 1.86 : 1 |
|  | 1 | 83 | 1.50 : 1 |
|  | 1 | 85 | 1.50 : 1 |

[a] Based on cinnamaldehyde. [b] Detected by $^1$H NMR. [c] Experiment repeated twice, yields given in brackets.

recycles for proof of principle, although significantly more cycles are necessary with regard to potential applications. The yields obtained with EOF-15(Si) vary from 69% to 84%, while they decrease from 65% to 46% in the case of EOF-16(C) (Table 2). The stereoselectivity (*like*/*unlike*) of the γ-butyrolactone formation is only slightly affected. The heterogeneity of EOF-16(C) was investigated by removing the catalyst by centrifugation during an ongoing reaction (ESI†). Without the catalyst, the conversion stops and no significant product formation could be observed. The yields obtained with EOF-15(Si) and EOF-16(C) are comparable with the ones obtained with homogeneous imidazolium salts.

In summary, we have presented the successful immobilization of a bifunctional imidazolium linker in highly crosslinked element organic framework materials by Suzuki coupling with tetrafunctional boronic acid linkers. The porous compounds were used as heterogeneous catalysts in an organocatalytic test reaction with similar results as compared to the molecular species in homogeneous catalysis but with the ability for catalyst recycling. In our view, these materials could prove useful in the upscaling of NHC catalysed reactions due to a higher economic and ecologic efficiency of the heterogeneous catalysed reaction.

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## Notes and references

1 Reviews: (*a*) W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1290–1309; (*b*) in N-*Heterocyclic Carbenes in Synthesis*, ed. S. P. Nolan, Wiley-VCH, Weinheim, Germany, 2006; (*c*) in N-*Heterocyclic Carbenes in Transition Metal Catalysis*, ed. F. Glorius, Springer, Berlin, 2007; (*d*) E. A. B. Kantchev, C. J. O'Brien and M. G. Organ, *Angew. Chem., Int. Ed.*, 2007, **46**, 2768–2813; (*e*) S. Würtz and F. Glorius, *Acc. Chem. Res.*, 2008, **41**, 1523–1533; (*f*) S. Díez-González, N. Marion and S. P. Nolan, *Chem. Rev.*, 2009, **109**, 3612–3676; (*g*) T. Dröge and F. Glorius, *Angew. Chem., Int. Ed.*, 2010, **49**, 6940–6952.

2 Reviews: (*a*) J. L. Moore and T. Rovis, *Top. Curr. Chem.*, 2010, **291**, 77; (*b*) V. Nair, S. Vellalath and B. Pattoorpadi Babu, *Chem. Soc. Rev.*, 2008, **37**, 2691–2698; (*c*) D. Enders, O. Niemeier and A. Henseler, *Chem. Rev.*, 2007, **107**, 5606–5655; (*d*) N. Marion, S. Díez-González and S. P. Nolan, *Angew. Chem., Int. Ed.*, 2007, **46**, 2988–3000; (*e*) U. Siemeling, C. Färber, C. Bruhn, M. Leibold, D. Selent, W. Baumann, M. V. Hopffgarten, C. Goedecke and G. Frenking, *Chem. Sci.*, 2010, **1**, 697–704.

3 (*a*) H.-J. Yoon, J.-W. Choi, H. Kang, T. Kang, S.-M. Lee and B.-H. Jun, *Synlett*, 2010, 2518–2522for the use of enantiomerically pure NHCs as chiral modifier of nanoparticles and successful application in asymmetric catalysis, see: ; (*b*) K. V. S. Ranganath, J. Kloesges, A. H. Schäfer and F. Glorius, *Angew. Chem., Int. Ed.*, 2010, **49**, 7786–7789.

4 D.-H. Lee, J.-H. Kim, B.-H. Jun, H. Kang, J. Park and Y.-S. Lee, *Org. Lett.*, 2008, **10**, 1609–1612.

5 Y. Qin, W. Wei and M. Luo, *Synlett*, 2007, 2410–2414.

6 W. J. Sommer and M. Weck, *Adv. Synth. Catal.*, 2006, **348**, 2101–2113.

7 L. Li and J.-L. Shi, *Adv. Synth. Catal.*, 2005, **347**, 1745–1749.

8 A. I. Cooper, *Adv. Mater.*, 2009, **21**, 1291–1295.

9 A. Thomas, *Angew. Chem., Int. Ed.*, 2010, **49**, 8328–8344.

10 C. Weder, *Angew. Chem., Int. Ed.*, 2008, **47**, 448–450.

11 F. Hoffmann, M. Cornelius, J. Morell and M. Fröba, *Angew. Chem., Int. Ed.*, 2006, **45**, 3216–3251.

12 T. P. Nguyen, P. Hesemann, P. Gaveau and J. J. E. Moreau, *J. Mater. Chem.*, 2009, **19**, 4164–4171.

13 M. Rose, N. Klein, W. Böhlmann, B. Böhringer, S. Fichtner and S. Kaskel, *Soft Matter*, 2010, **6**, 3918–3923.

14 S. Leuthäußer, D. Schwarz and H. Plenio, *Chem.–Eur. J.*, 2007, **13**, 7195–7203.

15 J.-H. Fournier, T. Maris, J. D. Wuest, W. Guo and E. Galoppini, *J. Am. Chem. Soc.*, 2003, **125**, 1002–1006.

16 (*a*) C. Burstein and F. Glorius, *Angew. Chem., Int. Ed.*, 2004, **43**, 6205–6208; (*b*) S. S. Sohn, E. L. Rosen and J. W. Bode, *J. Am. Chem. Soc.*, 2004, **126**, 14370–14371; (*c*) C. Burstein, S. Tschan, X. Xie and F. Glorius, *Synthesis*, 2006, 2418–2439; (*d*) K. Hirano, I. Piel and F. Glorius, *Adv. Synth. Catal.*, 2008, **350**, 984–988.