

N-Heterocyclic Carbenes Supported on Vinylic Addition Polynorbornene: A Recyclable and Recoverable Organocatalyst.

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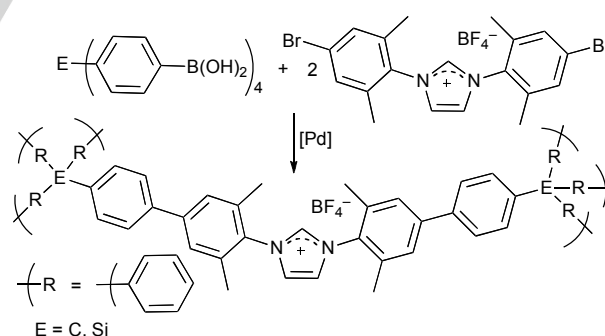
This paper is dedicated to Prof. Pablo Espinet on occasion of his 65th birthday

Abstract: A bromoalkyl functionalized vinylic addition polynorbornene has been used as an inert new scaffold to support imidazolium salts by straightforward nucleophilic substitution using different imidazoles ImR (R = Me, mesityl, 2,6-ⁱPr₂C₆H₃). These polymers, VA-PNB-(CH₂)₄ImRBr, are precursors of N-heterocyclic carbenes which are useful as heterogeneous organocatalysts. The polymeric carbenes have been tested in two model reactions: The synthesis of saturated esters from α,β -unsaturated aldehydes and the conjugate umpolung reaction of α,β -unsaturated aldehydes for the synthesis of γ -butyrolactones. The supported catalyst (R = mesityl) is fully recyclable and can be recovered as an imidazolium salt and stored for further use.

Introduction

Over the last decade N-heterocyclic carbenes (NHCs) have proved to be useful tools in organic synthesis because they are active organocatalysts in many different transformations, such as benzoin condensations, transesterifications, Stetter reactions, polymerizations, etc.^[1] Most of these reactions conventionally use soluble NHCs formed by deprotonation of the correspondingazolium salts. Although organocatalysis is considered to be free of the toxicity concerns that affect metal catalysis, these compounds are not innocuous and high catalyst loadings are used in many cases which complicate the separation protocols.^[2] Also, expensive catalysts which are difficult to prepare should not be wasted after each reaction. The use of a support allows to minimize these disadvantages, improving the separation efficiency and allowing the recyclability of the catalysts. Many different scaffolds have been used to attach NHCs as ligands to form organometallic complexes and their activity has been profusely tested in metal catalyzed reactions, most of them cross coupling processes.^[3] On the contrary, fewer examples can be found on the use of supported NHCs in organocatalysis. The functionalization of commercial polymers such as PEG or polystyrene to support NHCs has been tried,^[4] and this is probably the simplest and more convenient approach. However, their performance as organocatalysts is modest and, as far as recyclability is concerned, they show poor behavior with a decrease of 10% yield after each cycle for the polystyrene derivatives,^[4a] or a strong dependence on the reaction conditions

for the PEG-supported NHCs.^[4b] Other polymeric NHCs have been reported but they require the previous synthesis of specific monomers containing imidazolium substituents,^[5,6,7] or masked carbene functionalities.^[8] Subsequent polymerization of those monomers by a radical mechanism in the first case or a ROMP process in the second was applied. These examples show good catalytic behavior but their recyclability has either not been tested or has shown limited applicability in most cases. Recently Seo and Chung have obtained better results.^[7] Other pre-synthesizedazolium monomers have been polymerized such as thiazolium substituted styrenes; they lead to materials that can be used in a continuous flow system but cannot be reused after the first run.^[9] Better organocatalytic results have been achieved using polymeric frameworks containing imidazolium salts in the main chain. Their preparation require a several step synthesis of specially designed monomers to give the polymeric framework by condensation,^[10] or by Suzuki coupling as shown in Scheme 1.^[11] In this way symmetric or closely substituted NHCs can be generated as part of the polymeric main chain but the preparation of a carbene moiety with a different substitution pattern needs the synthesis of a new polymeric framework from scratch. NHCs have also been supported on a mesoporous MCM-41,^[12] or in a supported peptide framework for specific applications.^[13] The use of polymeric anions to recover and reuse thiazolium cations has also been explored.^[2b]



Scheme 1. Synthesis of a polymeric framework with imidazolium salts in the main chain used as carbene precursors, described in ref. [11a].

Our group has reported the synthesis of vinylic addition polynorbornenes (VA-PNB) with a completely saturated backbone and pendant bromoalkyl substituents.^[14] This polymeric backbone has two salient features that can be very convenient for the preparation of NHC organocatalysts. First, it is a completely saturated and robust scaffold with no reactive sites on the polymeric backbone, apt to be used if harsh conditions are needed. For example, it has proved to be a good support for tin reagents in the Stille reaction.^[15] On the other hand the

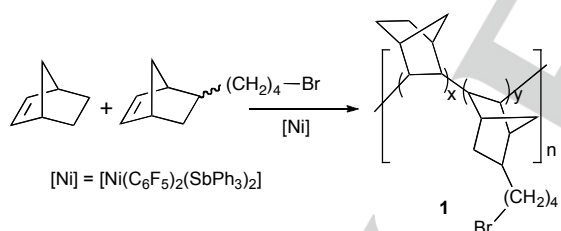
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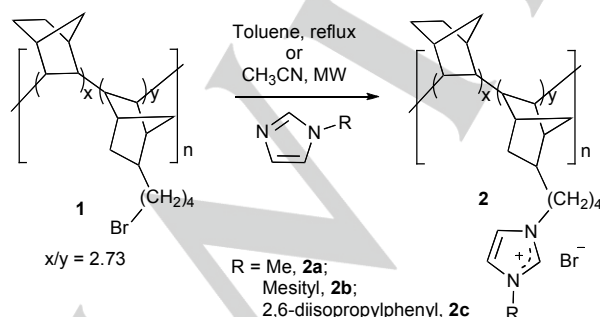
presence of the bromo substituent allow to introduce an imidazole group by a straightforward, one step nucleophilic substitution reaction. Thus, we describe here the use of this halogenated vinylic addition polynorbornene to synthesize supported NHCs and its excellent applicability and recyclability in two organocatalyzed reactions.

Results and Discussion

A vinylic addition polynorbornene with bromobutyl side chains (**1**) was used to anchor an imidazolium substituent. The polymeric support was synthesized by the Ni-catalyzed copolymerization of norbornene and bromobutylnorbornene in a chosen monomer feed ratio as we described before (Scheme 2).^[14] The bromobutylnorbornene used in this polymerization is not commercially available but can be easily synthesized by a Diels-Alder reaction of cyclopentadiene and 6-bromo, 1-hexene.^[14] A copolymer **1** of composition $x/y = 2.73$, i.e. 2.055 mmol Br/g polymer, was functionalized by nucleophilic substitution of Br by imidazole in a process that shows complete atom economy (Scheme 3). Just by selection of the desired imidazole derivative we prepared polymer-bound imidazolium salts with different steric demand. These reactions can be carried out by heating in toluene in the case of low hindered molecules like 1-methylimidazole, or in a microwave oven for bulkier imidazoles such as 1-mesityl- or 1-(2,6-diisopropylphenyl)imidazole, a method that needs shorter reaction times (cf. 60 h vs. 50 min for the microwave reaction). Thus, the tunability of one of the NHC substituent to modify its electronic behavior and steric hindrance is possible and simple.



Scheme 2. Synthesis of the halogenated vinylic addition polynorbornene VA-PNB used as support (see ref. [14]).



Scheme 3. Synthesis of polymer-bound imidazolium salts from a halogenated vinylic addition polynorbornene and different imidazole derivatives.

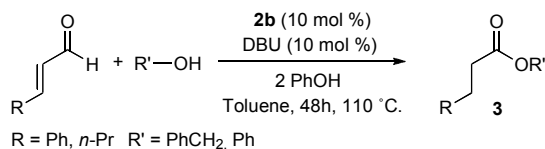
The polymer-bound imidazolium salt **2a** swells in methanol and it was characterized by NMR spectroscopy on the viscous solution. However, **2b** and **2c** are insoluble in most common solvents. Thus, they were characterized by ¹³C CP-MAS NMR and IR spectroscopy. The $\nu(\text{C-Br})$ IR absorption band in the starting polymer **1** at 562 cm^{-1} was absent in **2** and characteristic $\nu(\text{C=N})$ absorptions were found in the range $1570\text{-}1540\text{ cm}^{-1}$. The quantitative halogen and nitrogen analyses of the polymers **2a-c** is consistent with the complete substitution of the bromo and incorporation of the imidazole fragment to the pendant chains. For those reactions carried out with aryl substituted imidazoles, the excess of the imidazole used was easily recovered by filtration of the polymer and evaporation of the filtrate. This is important because many interesting imidazoles are not commercially available and, when they can be purchased, they are quite expensive.

In order to check the activity of these polymers as heterogeneous organocatalysts, **2b** was tested in two different reactions: The conversion of α,β -unsaturated aldehydes into saturated esters (Scheme 4),^[16] and the synthesis of γ -butyrolactones (Scheme 5).^[17] Both processes are umpolung reactions, quite attractive from the synthetical point of view, which are catalyzed by NHCs due to their nucleophilic behavior. α,β -unsaturated aldehydes are commonly used reagents for these transformations because of their performance like homoenolates. In the first model reaction a proton acts as electrophile whereas in the second one a carbonyl group plays that role leading to the cyclization product.

Polymer **2b** contains 1.49 mmol of imidazole per gram of polymer as determined by quantitative analyses (see above). The formation of the carbene, the catalytic active species in both model reactions, was carried out by stirring the polymer at room temperature for 30 minutes with an equivalent amount of DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene) as base before adding the corresponding reagents. Both reactions were tested without polymer **2b**, or with **2b** and no base and no reaction was observed in either case. As mentioned before, the polymers bearing the imidazolium salts are insoluble in most organic solvents and show negligible swelling in THF or toluene. The same behavior as far as solubility and swelling is concerned is observed when polymers **2** are soaked in a DBU solution in THF. Regardless the little swelling observed, the activity in the catalytic reactions is high (see below).

According to the conditions described by Chan and Scheidt for non-supported NHCs,^[16] the syntheses of saturated esters (**3**) from α,β -unsaturated aldehydes were carried out by adding an aldehyde, a twofold molar amount of phenol (used as electrophile source), and a fivefold molar amount of another alcohol to a suspension of 10% mol of the preformed carbene catalyst from **2b** in toluene (Scheme 4). After 48 h at $110\text{ }^\circ\text{C}$ complete conversion was achieved. Simple filtration and washing of the polymer with toluene under a nitrogen atmosphere allowed the recovery of the catalyst which can be reused. Table 1 collects the results obtained. Polymers **2a** and **2c** were also tested in this reaction in the conditions of entry 1, Table 1. Polymer **2c** (99% yield) turned out to be as active as **2b** whereas **2a** (73% yield) is less efficient. Thus, the presence

of a bulky R group is clearly beneficial for catalyst. The synthesis of the precursor mesityl imidazole is more convenient and affords higher yields than the preparation of 1-(2,6-diisopropylphenyl)imidazole, according to literature methods (see Experimental). Thus, the complete catalytic study was carried out with **2b**.



Scheme 4. Synthesis of saturated esters catalyzed by **2b**.

Table 1. Catalytic results on the conversion of α,β -unsaturated aldehydes into saturated esters with **2b**.^[a]

Entry	Aldehyde	Alcohol	Cycle	3 , Yield (%) ^[b]
1	PhCH=CH-C(O)H	PhCH ₂ OH	1	99
2	PhCH=CH-C(O)H	PhCH ₂ OH	2	97
3	PhCH=CH-C(O)H	PhCH ₂ OH	3	94
4	PhCH=CH-C(O)H	PhCH ₂ OH	4	99
5	PhCH=CH-C(O)H	PhCH ₂ OH	5	99
6 ^[c]	PhCH=CH-C(O)H	PhCH ₂ OH	6	99
7	C ₃ H ₇ -CH=CH-C(O)H	PhCH ₂ OH	1	80
8	C ₃ H ₇ -CH=CH-C(O)H	PhCH ₂ OH	2	82
9	C ₃ H ₇ -CH=CH-C(O)H	PhCH ₂ OH	3	92
10	C ₃ H ₇ -CH=CH-C(O)H	PhCH ₂ OH	4	87
11	C ₃ H ₇ -CH=CH-C(O)H	PhCH ₂ OH	5	85
12	PhCH=CH-C(O)H	PhOH	1	53
13 ^[d]	PhCH=CH-C(O)H	PhCH ₂ OH	1	0
14 ^[e]	PhCH=CH-C(O)H	PhCH ₂ OH	1	0

[a] Reaction conditions shown in Scheme 4. Reactions performed with 5 equiv of alcohol (R'OH). [b] Crude yields determined by ¹H NMR. [c] Catalyst recovered by protonation after cycle 5, stored for days in the air and reused. [d] Without polymer **2b**. [e] Without DBU.

In the case of cinnamaldehyde quantitative yields were achieved not only for the first use of the catalyst but also for at least four recycling experiments (Table 1, entries 1-5). As described above, after each reaction the polymer was recovered by filtration, washed with toluene and it was reused without further treatment. After these five uses, the imidazolium salt was

recovered by treatment of the polymer with an acid such as tetrafluoroboric acid in diethyl ether. This polymer was then exposed to air, stored, and reused days later in the same reaction giving again very high yields (Table 1, entry 6). β -alkyl-enals like trans-2-hexenal gave good yields which remain high when the catalyst was reused for five times (Table 1, entries 7-11). When phenol was used as both the nucleophile and electrophile source a moderate yield was obtained (entry 12). As mentioned before, the reaction is not catalyzed by either the imidazolium polymer **2b** or the base DBU alone (Table 1, entries 13 and 14). A filtration test was performed to rule out the presence of dissolved species that could catalyze the reaction. Cinnamaldehyde and benzylic alcohol were reacted under the conditions of entry 1, Table 1, for 12 h. After this time **3** had been formed in 20.6% yield. The polymer was filtered and the filtrate was kept under the same reaction conditions for an additional 12 h. The conversion did not increase noticeably (20.7% of **3**), supporting that the NHC formed from **2b** behaves as a heterogeneous catalyst. The polymeric NHC precursor **2b** works under the same reaction conditions (solvent and temperature) than the non-supported monomeric benzimidazolium salts used by Chan and Scheidt as NHC precursors in the formation of **3**.^[16] However, the reaction time needed is longer (2-6 h for the monomeric catalyst vs. 48 h for **2b**). This drawback is counterbalanced by the reusability of the catalyst precursor.

Scanning electron microscopy images of **2b** before and after its use in the synthesis of saturated esters were recorded. Polymer **2b** before use shows a granular texture with small pores (Figure 1, a). After five uses and the recovery of the imidazolium polymer by treatment with acid, the surface of the polymer is smoother and less porous (Figure 1, b). Considering the low swelling effect of the solvent, this seems to indicate that the polymeric matrix exposes enough reactive catalytic centers on the outer surface of the polymer to ensure a high catalytic activity.

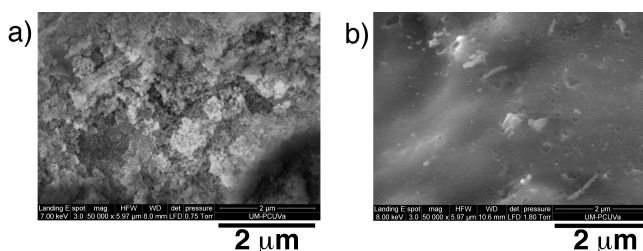
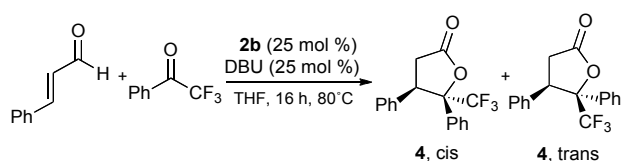


Figure 1. SEM images of polymer **2b**: a) before use; b) after five uses in the synthesis of saturated esters.

Polymer **2b** is also an efficient organocatalyst in the conjugate umpolung reaction of α,β -unsaturated aldehydes for the synthesis of γ -butyrolactones (Scheme 5).^[17] After the formation of the carbene with the base as described above, cinnamaldehyde and 2,2,2-trifluoroacetophenone were added and the mixture heated at 80 °C for 16 hours. The polymer was reused five times with almost constant yields and diastereomeric

ratios (Table 2, entries 1-5).^[18] After several reactions the polymer was recovered and, three months later, the reaction was carried out again affording good yields (Table 2, entry 6). Again, no reaction was observed when either the imidazolium precursor **2b** or DBU were used alone (Table 2, entries 7 and 8).

When compared to other catalytic systems in the synthesis of γ -butyrolactones, **2b** needs higher temperatures but similar reaction times than the reactions carried out with non-supported imidazolium salts as NHC precursors (80°C for **2b** vs. room temperature for the non-polymeric species). This has also been observed for the only example of a main chain polymeric carbene used as catalyst in this synthesis as reported before.^[11a] Again, the efficient reuse of the catalyst precursor **2b** counterbalance the temperature raise needed.



Scheme 5. Synthesis of γ -butyrolactones **4**, as a mixture of cis (like) and trans (unlike) diastereoisomers, catalyzed by **2b**.

Table 2. Catalytic results in formation of butyrolactones **4**.^[a]

Cycle	4 , Yield (%) ^[b]	dr (cis/trans) ^[b]
1	58	2.22
2	56	2.22
3	59	2.17
4	60	2.26
5	61	2.14
6	60	2.15
7 ^c	0	—
8 ^d	0	—

[a] Reaction conditions shown in Scheme 5. [b] Crude yields and diastereomeric ratios were determined by ¹⁹F NMR. d) Without **2b**. e) Without DBU.

The model reactions tested here use high temperatures and, in these conditions, the robustness of the completely saturated vinylic addition polynorbornene backbone may be quite important to explain the excellent recovery of the catalyst. As it is usually the case for supported catalysts, polymer **2b** is less active than the equivalent monomeric NHC derivatives,^[16,17] but the possibility of recycling gives an added turnover number that surpass the figures of the non-supported NHCs. Moreover, the fact that this VA-PNB imidazolium salt can be recovered and stored for future use is a most convenient feature.

Conclusions

The saturated, non-reactive vinylic addition polynorbornene scaffold (VA-PNB) has proved to be a very convenient support for N-heterocyclic carbenes in organocatalysis. These systems are advantageous in two ways. On one hand, the preparation of the precursor polymeric imidazolium salts is straightforward by the nucleophilic substitution of Br by an imidazole in the versatile bromoalkyl-substituted VA-PNB. It allows the easy introduction of different substituents on one of the imidazolium nitrogens without the need of preparing a polymer from a specific monomer for each application. On the other hand, these salts are convenient precursors of NHCs, active as organocatalysts and fully recyclable. After their use in the catalyzed reactions, the treatment with acid regenerates the imidazolium salts which can be stored for further use with no special precautions. As far as easy synthesis and performance on reuse is concerned this is a most convenient supported NHC system for organocatalysis.

Experimental Section

General Methods.

¹H and ¹⁹F NMR spectra were recorded using Bruker AV-400 and Agilent MR-500 instruments. Chemical shifts (δ) are reported in ppm and referenced to Me₄Si (¹H) or CFC₃ (¹⁹F). All of the NMR spectra were acquired at 293 K. Most of the NMR spectra were recorded in protic solvents using an acetone-d₆ capillary. The solid state NMR spectra were recorded at 293 K under magic angle spinning (MAS) in a Bruker AV-400 spectrometer using a Bruker BL-4 probe with 4mm diameter zirconia rotors spinning at 8 kHz. ¹³C CP MAS NMR spectra were measured at 100.61 MHz and recorded with proton decoupling (tpm), with a 90° pulse length of 4.5 μ s and a contact time of 3 ms and recycle delay of 3 s. The ¹³C NMR spectra were referred to glycine (CO signal at 176.1 ppm). IR spectra were recorded on a Perkin-Elmer FT/IR SPECTRUM FRONTIER spectrophotometer with Csl + ATR diamond accessory. Scanning Electron Microscopy (SEM) measurements have been carried out at the *Unidad de Microscopía Avanzada of the Parque Científico Uva* by means of an Environmental Scanning Electron Microscope (ESEM), model FEI-Quanta 200FEG provided with a Schottky-Field Emission filament. The SEM analyses were performed at Low Vacuum Mode using water vapour as auxiliary gas. This imaging mode allows working with non-conductive samples without any specific preparation or metallic coatings. The measurements were performed at a working pressure in the chamber ranging between 0.6 - 1 Torr [80 - 133 Pa] and an accelerating voltage of 7kV. The Secondary Electron SEM images were acquired with a Large Field Detector (LFD) which is the suitable one for working at Low Vacuum Mode. Microwave-promoted experiments were carried out with a CEM Discover 300W single-mode microwave instrument, with simultaneous cooling with compressed air. The reaction mixtures were prepared in 10 mL special glass reaction tubes with self-sealing septa with a pressure sensor on top of the vial. The temperature was monitored through a noncontact infrared sensor centrally located beneath the cavity floor. Magnetic stirring was provided to ensure complete mixing of the reagents. The power applied was 300 W with a ramp time of 10 min. The halogen content in the polymers was determined by oxygen-flask combustion of a sample and analysis of the residue by mercurimetric titration of the bromide.^[19] The nitrogen content was determined using a LECO CHNSO-932 microanalyzer. Solvents were dried prior to use and stored under nitrogen. The reagents used in

the organocatalytic reactions were purchased from Aldrich, Alfa-Aesar and Acros. The vinylic addition polynorbornene CopNBNB(CH₂)₄Br,^[14] 1-Mesitylimidazole and 1-(2,6-diisopropylphenyl)imidazole^[20] were prepared according to the literature procedures.

[CopNBNB(CH₂)₄IMe]Br (2a) (IMe = 1-Methyl imidazole).

In a round-bottom flask copolymer CopNBNB(CH₂)₄Br (**1**, 0.200 g, 0.411 mmol of Br) and 1-methylimidazole (0.169 g, 2.06 mmol) were stirred in toluene (30 mL) at reflux for 60 hours. The solvent was partially removed to c.a. 15 mL, the mixture was then poured onto acetone (40 mL) and stirred for 7 hours at room temperature. The polymer was filtered, washed with acetone (5 x 10 mL) and air-dried. A white solid was obtained (0.230 g, 98% yield). Elemental analysis: calcd for [(C₇H₁₀)_x{C₇H₉(CH₂)₄(C₄H₆N₂)_y}]Br (x/y = 2.73): 140.6 mg Br/g (14.06%), N 4.93%; found: Br 141.2 mg Br/g (14.12%), N 4.86%. IR (neat), ν = 1567 cm⁻¹ (C=N). ¹H NMR (400.15 MHz, δ , CD₃OD): 7.8-7.4 (br, 2H, N-CH=CH-N), 4.2 (br, 2H, -CH₂-N), 3.9 (br, 3H, N-CH₃), 2.8-0.3 (br, 25H). ¹³C CP-MAS NMR (100.61 MHz): 143-134 (br, 1C, NCHN), 130-117 (br, 2C, NCH=CHN), 67-16 (br, polyNB, Me).

[CopNBNB(CH₂)₄IMes]Br (2b) (IMes = 1-Mesityl imidazole).

Copolymer CopNBNB(CH₂)₄Br **1** (0.200 g, 0.411 mmol Br), 1-Mesitylimidazol (0.383 g, 2.06 mmol) and CH₃CN (2.0 mL) were placed in a 10 mL microwave reaction vessel. The mixture was heated to 170 °C and stirred for 50 minutes in the microwave oven using a maximum power of 300 W. The reaction mixture was poured onto Et₂O (30 mL) and stirred for four hours. The solid was filtered, washed with Et₂O (5 x 10 mL) and air-dried. The product was obtained as a white solid (0.276 g, 99% yield). This procedure can be scaled to obtain a larger amount (4.120 g, 99% yield). Elemental analysis: calcd for [(C₇H₁₀)_x{C₇H₉(CH₂)₄(C₁₂H₁₄N₂)_y}]Br (x/y = 2.73): 118.8 mg Br/g (11.88%), N 4.17%; found: Br 118.2 mg Br/g (11.82%), N 4.39%. IR (Neat): ν = 1544 cm⁻¹ (C=N). ¹³C CP-MAS NMR (100.61 MHz): 150-120 (br, 9C, aromatic, NCHN, NCH=CHN), 70-24 (br, polyNB), 24-15 (br, 3C, Me).

[CopNBNB(CH₂)₄IPr]Br (2c) (IPr = 1-(2,6-diisopropyl-phenyl)-imidazole).

Copolymer CopNBNB(CH₂)₄Br **1** (0.200 g, 0.411 mmol Br), 1-(2,6-diisopropylphenyl)-imidazol (0.470 g, 2.06 mmol) and CH₃CN (2.0 mL) were placed in a 10 mL microwave reaction vessel. The mixture was heated to 170 °C and stirred for 50 minutes in the microwave oven using a maximum power of 300 W. The reaction mixture was poured onto CH₃CN (30 mL) and stirred for four hours. The solid was filtered, washed with CH₃CN (5 x 10 mL) and air-dried. The product was obtained as a white solid (0.286 g, 97% yield). Elemental analyses: calcd for [(C₇H₁₀)_x{C₇H₉(CH₂)₄(C₁₅H₂₀N₂)_y}]Br (x/y = 2.73): 111.8 mg Br/g (11.18%), N 3.92%; found: Br 109.2 mg Br/g (10.92%), N 3.67%. IR (Neat): ν = 1541 cm⁻¹ (C=N). ¹³C CP-MAS NMR (100.61 MHz): 151-143 (br, 3C, NCHN, C_{ortho}), 142-137 (br, 1C, C_{ipso}), 136-129 (br, 2C, (CH₂)₄NCH=CHN, C_{para}), 128-119 (br, 3C, (CH₂)₄NCH=CHN, C_{meta}), 70-10 (br, polyNB, ¹Pr).

Standard procedure for conversion of α,β -unsaturated aldehydes into saturated esters.

To a suspension of **2b** (7.4 mg, 0.011 mmol of IMes) in 2 mL of dry toluene, DBU (1.52 mg, 0.01 mmol) was added. After stirring for 30 minutes at room temperature cinnamaldehyde (13.2 mg, 0.1 mmol), benzylic alcohol (54.1 mg, 0.5 mmol) and phenol (18.8 mg 0.2 mmol) were added. The reaction mixture was stirred at 110 °C for 48 h and then checked by ¹H NMR (crude yield 99%). The mixture was filtered under

nitrogen and the polymer was washed (4 x 5 mL toluene) and stored under 2 mL of dry toluene to be recycled. The filtrate was evaporated and purified by silica gel chromatography (hexane/ether 10:1) affording the ester as a light yellow oil (22.9 mg, 95%). The identity of the product was confirmed by comparison of the characterization data with those found in the literature.^[21] The other experiments collected in Table 1 were carried out in the same way.

Standard procedure for synthesis of γ -butyrolactones.

In a Schlenk tube under a nitrogen atmosphere 10 mL of dry THF, copolymer **2b** (74.0 mg, 0.11 mmol of IMes) and DBU (15.2 mg, 0.10 mmol) were added. The mixture was stirred at room temperature for 30 minutes. Then cinnamaldehyde (52.9 mg, 0.40 mmol) and 2,2,2-trifluoroacetophenone (208.9 mg, 1.2 mmol) were added and the reaction mixture was heated for 16 hours at 80 °C. Reaction was checked by ¹H and ¹⁹F NMR (crude yield 58%). The mixture was filtered and the polymer was washed (4 x 5 mL THF) and stored under 10 mL of dry THF in order to be recycled. The filtrate was evaporated and the product was purified by silica gel chromatography (hexane/ethyl acetate 20:1) to obtain a yellowish oil (69.6 mg, 56.8%). The identity of the products was confirmed by comparison of the characterization data with those found in the literature.^[17a]

Protonation of the carbene with acid.

After being used in the catalytic processes described above, a suspension of **2b** (0.011 mmol of IMes) in toluene was treated with HBF₄·Et₂O (0.0027 mL, 0.02 mmol). It was stirred at room temperature for 1 hour and the polymer was filtered, washed with toluene (4 x 5 mL) and air dried. The polymer can be stored for an indefinite period of time.

Acknowledgements

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Keywords: supported catalysts • polynorbornene • carbenes • organocatalysis • umpolung

- [1] a) V. Nair, S. Bindu, V. Sreekumar, *Angew. Chem. Int. Ed.* **2004**, *43*, 5130-5135; b) D. Enders, O. Niemeier, A. Henseler, *Chem. Rev.* **2007**, *107*, 5606-5655; c) S. Díez-González, S. P. Nolan, N. Marion, *Angew. Chem. Int. Ed.* **2007**, *46*, 2988-3000; d) M. J. Fuchter, *Chem. Eur. J.* **2010**, *16*, 12286-12294; e) M. K. Kiesewetter, E. J. Shin, J. L. Hedrick, R. M. Waymouth, *Macromolecules*, **2010**, *43*, 2093-2107; f) X. Bugaut, F. Glorius, *Chem. Soc. Rev.*, **2012**, *41*, 3511-3522; g) M. Fèvre, J. Pinaud, Y. Gnanou, J. Vignolle, D. Taton, *Chem. Soc. Rev.*, **2013**, *42*, 2142-2172; h) M. N. Hopkinson, C. Richter, M. Schedler, F. Glorius, *Nature*, **2014**, *510*, 485-496.

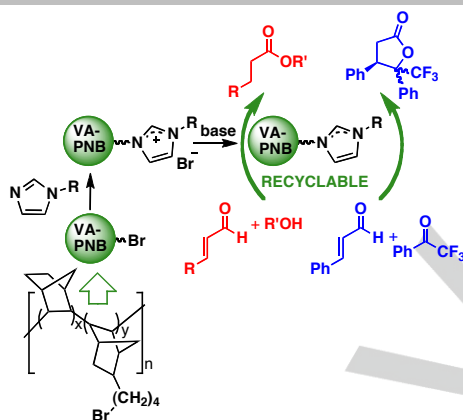
- [2] Progress has been made in the reduction of the catalyst loading in organocatalyzed reactions but only some scattered examples are known for NHCs so far. See: a) F. Giacalone, M. Gruttadauria, P.

- Agrigento, R. Noto, *Chem. Soc. Rev.* **2012**, *41*, 2406-2447. b) L. Gu, T. Lu, X. Li, Y. Zhang, *Chem. Commun.* **2014**, *50*, 12308-12310.
- [3] a) W. J. Sommer, M. Weck, *Coord. Chem. Rev.* **2007**, *251*, 860-873; b) C. S. J. Cazin, *C. R. Chimie*, **2009**, *12*, 1173-1180; c) Á. Molnár, *Chem. Rev.*, **2011**, *111*, 2251-2320; d) A. C. Albéniz, N. Carrera, *Eur. J. Inorg. Chem.* **2011**, 2347-2360; e) S. Budagumpi, R. A. Haque, A. W. Salman, *Coord. Chem. Rev.* **2012**, *256*, 1787-1830.
- [4] a) J. M. D. Storey, C. Williamson, *Tetrahedron Lett.*, **2005**, *46*, 7337-7339; b) K. Zeitler, I. Mager, *Adv. Synth. Catal.*, **2007**, *349*, 1851-1857.
- [5] a) J. Pinaud, J. Vignolle, Y. Gnanou, D. Taton, *Macromolecules* **2011**, *44*, 1900-1908; b) P. Coupillaud, J. Pinaud, N. Guidolin, J. Vignolle, M. Fèvre, E. Veaudecronne, D. Mecerreyes, D. Taton, *J. Pol. Sci. A: Pol. Chem.* **2013**, *51*, 4530-4540; c) D. Kuzmicz, P. Coupillaud, Y. Men, J. Vignolle, G. Vendraminetto, M. Ambrogi, D. Taton, J. Yuan, *Polymer*, **2014**, *55*, 3423-3430.
- [6] A. G. M. Barret, A. C. Love, L. Tedeschi, *Org. Lett.* **2004**, *6*, 3377-3380.
- [7] a) U. R. Seo, Y. K. Chung, *RSC Adv.* **2014**, *4*, 32371-32374. b) U. R. Seo, Y. K. Chung, *Adv. Synth. Catal.* **2014**, *356*, 1955-1961.
- [8] G. M. Pawar, M. R. Buchmeiser, *Adv. Synth. Catal.*, **2010**, *352*, 917-928.
- [9] a) H. J. van den Berg, G. Challa, U. K. Pandit, *React. Polym.* **1989**, *11*, 127-134; b) O. Bortolini, A. Cavazzini, P. Dambruoso, P. P. Giovannini, L. Caciolli, A. Massi, S. Pacifico, D. Ragno, *Green. Chem.* **2013**, *15*, 2981-2992.
- [10] M. Tan, Y. Zhang, J. Y. Ying, *Adv. Synth. Catal.*, **2009**, *351*, 1390-1394.
- [11] a) M. Rose, A. Notzon, M. Heitbaum, G. Nickerl, S. Paasch, E. Brunner, F. Glorius, S. Kaskel, *Chem. Commun.*, **2011**, *47*, 4814-4816; b) A. B. Powell, Y. Suzuki, M. Ueda, C. W. Bielawski, A. H. Cowley, *J. Am. Chem. Soc.* **2011**, *133*, 5218-5220.
- [12] H. Zhou, Y.-M. Wang, W.-Z. Zhang, J.-P. Qu, X.-B. Lu, *Green Chem.*, **2011**, *13*, 644-650.
- [13] C. A. Gondo, J. W. Bode, *Synlett.* **2013**, *24*, 1205-1210.
- [14] S. Martínez-Arranz, A. C. Albéniz, P. Espinet, *Macromolecules* **2010**, *43*, 7482-7487.
- [15] a) N. Carrera, E. Gutiérrez, R. Benavente, M. M. Villavieja, A. C. Albéniz, P. Espinet, *Chem. Eur. J.* **2008**, *14*, 10141-10148; b) I. Meana, A. C. Albéniz, P. Espinet, *Adv. Synth. Catal.*, **2010**, *352*, 2887-2891; c) S. Martínez-Arranz, N. Carrera, A. C. Albéniz, P. Espinet, A. Vidal-Moya, *Adv. Synth. Catal.* **2012**, *354*, 3551-3560.
- [16] A. Chan, K. A. Scheidt, *Org. Lett.* **2005**, *7*, 905-908.
- [17] a) C. Burstein, F. Glorius, *Angew. Chem. Int. Ed.* **2004**, *43*, 6205-6208; b) S. S. Sohn, E. L. Rose, J. W. Bode, *J. Am. Chem. Soc.* **2004**, *126*, 14370-14371; c) W. Ye, G. Cai, Z. Zhuang, X. Jia, H. Zhai, *Org. Lett.*, **2005**, *7*, 3769-3771.
- [18] The addition of base is needed after each cycle. A recycling experiment in the same conditions of entry 2, Table 2, but without the addition of DBU gave only 9% yield.
- [19] D. C. White, *Mikrochim. Acta* **1961**, 449-456.
- [20] Ji. Liu, J. Chen, J. Zhao, Y. Zhao, L. Li, H. Zhang, *Synthesis* **2003**, *17*, 2661-2666.
- [21] a) P. E. Peterson, M. Stepanian, *J. Org. Chem.* **1988**, *53*, 1903-1907; b) P. J. Black, G. Cami-Kobeci, M. G. Edwards, P. A. Slatford, M. K. Whittlesey, J. M. J. Williams, *Org. Biomol. Chem.* **2006**, *4*, 116-125.

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FULL PAPER

Three in one to ease organocatalysis: A robust, tunable and recyclable organocatalytic system has been prepared by anchoring N-heterocyclic carbenes on an all-aliphatic vinylic addition polynorborne (VA-PNB) scaffold. These three features makes it a most convenient heterogeneous NHC-based organocatalyst.



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N-Heterocyclic Carbenes Supported on Vinylic Addition Polynorbornene: A Recyclable and Recoverable Organocatalyst