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Imidazolium Hydrogen Carbonates versus Imidazolium Carboxylates as Organic Precatalysts for N-Heterocyclic Carbene Catalyzed Reactions

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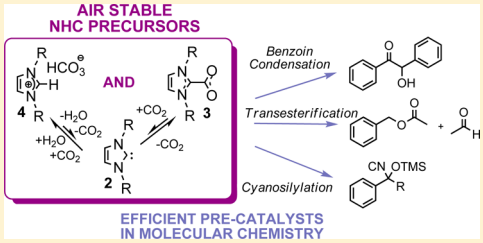
Supporting Information

ABSTRACT: Imidazolium-2-carboxylates (NHC−CO_2 adducts, **3**) and (benz)imidazolium hydrogen carbonates ([NHC(H)][HCO_3], **4**) were independently employed as organic precatalysts for various molecular N-heterocyclic carbene (NHC) catalyzed reactions. NHC−CO_2 adducts were obtained by carboxylation in THF of related free NHCs (**2**), while the synthesis of [NHC(H)][HCO_3] precursors was directly achieved by anion metathesis of imidazolium halides (**1**) using potassium hydrogen carbonate ($KHCO_3$) in methanolic solution, without the need for the prior preparation of free carbenes. Thermogravimetric analysis (TGA) and TGA coupled with mass spectrometry (TGA-MS) of most [NHC(H)][HCO_3] precursors **4** showed a degradation profile in stages, with either a concomitant or a stepwise release of H_2O and CO_2, between 108 and 280 °C, depending on the nature of the azolium and substituents. In solution, NHC generation from both [NHC(H)][HCO_3] salts and NHC−CO_2 adducts could be achieved at room temperature, most likely by a simple solvation effect. Both types of precursors proved efficient for organocatalyzed molecular reactions, including cyanosilylation, benzoin condensation, and transesterification reactions. The catalytic efficiencies of NHC−CO_2 adducts **3** were found to be approximately 3 times higher than those of their [NHC(H)][HCO_3] counterparts **4**.



INTRODUCTION

In the past few decades, N-heterocyclic carbenes (NHCs) have emerged not only as powerful ligands for transition metals[1−3] but also as true organocatalysts for various molecular reactions.[4−6] This growing interest is explained by the versatility of NHCs, their steric and/or electronic properties—hence their reactivity—being finely tuned by varying the substituents on the heterocyclic ring.[7,8] More recently, the catalytic potential of NHCs has also been exploited for several chain polymerization reactions, including the ring-opening polymerization (ROP) of heterocycles such as cyclic esters, carbonates, carbosiloxanes, *N*-carboxyanhydrides, epoxides, and the group transfer polymerization (GTP) of (meth)acrylic monomers.[9,10]

However, the relative instability of NHCs[11,12] on exposure to air makes them difficult to handle. As a matter of fact, NHCs must generally be stored and manipulated under dry and inert conditions. A general strategy to circumvent this limitation is to convert the NHC into a masked form. Various NHC adducts have thus been derived, the activation of which in situ generates free NHCs. For instance, NHC-Ag(I) complexes,[13,14] alkoxy,[15−18] trichloromethyl,[19] pentafluorophenyl,[19] carboxylic acid,[20,21] thioisocyanates (NCS),[22] thiocarboxylates (COS),[23] CO_2−NHC adducts,[24,25] and, very recently, imidazolium hydrogen carbonates[26] can serve as NHC precursors. Such masked NHCs are of practical use, either for synthesizing NHC−transition metal complexes[27] or as precatalysts for NHC-catalyzed molecular[23,28−37] and macromolecular reactions.[16−21,38−41]

Among these masked NHCs, NHC−CO_2 adducts, namely imidazol(in)ium-2-carboxylates, have attracted a great deal of attention. This is due to the fact that (i) any types of structures are virtually accessible by reaction of free NHCs with CO_2,[24,42−45] (ii) NHC−CO_2 adducts are relatively stable in the solid state under air exposure,[46] and (iii) CO_2 is the only byproduct upon NHC generation. However, synthesis of NHC−CO_2 adducts generally requires the corresponding NHC to be prepared prior to the carboxylation step.[24,42−45] Free NHCs are thought to be generated in situ upon heating such NHC−CO_2 adducts, typically between 60 and 90 °C (see Scheme 1).[24,44−51] In the context of organometallic chemistry, however, Crabtree et al.[47,48] and Sauvage et al.[51] have noticed successful NHC transfer onto transition-metal fragments at room temperature. Such imidazol(in)ium-2-carboxylates, and some polymer-supported versions, have been utilized as NHC and poly(NHC) precursors, respectively, for the purpose of organocatalysis. Related (macro)molecular reactions include

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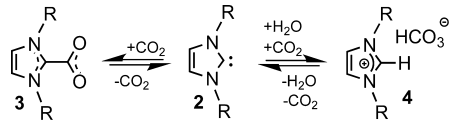
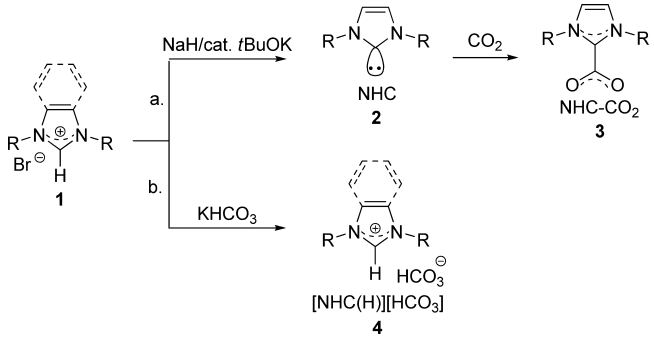
Scheme 1. Reversible Generation of NHCs 2 from [NHC(H)][HCO_3] Salts 4 and NHC−CO_2 Adducts 3



transesterification,[31,34] benzoin condensation,[34,37] cyanosilylation,[33] cyclotrimerization of isocyanates,[28,33] and synthesis of polyurethanes[39,40] and polycarbonates[41] by step-growth polymerization.

Very recently, we evidenced that imidazol(in)ium hydrogen carbonates, denoted as [NHC(H)][HCO_3], can also behave as a source of NHCs.[26] Upon formal loss of H_2CO_3 (Scheme 1), not only were NHC−transition metal complexes synthesized with no need for inert conditions but also both the NHC-catalyzed benzoin condensation and ring-opening polymerization of D,L-lactide could be achieved. Of particular interest, such [NHC(H)][HCO_3] salt precursors can be prepared by the one-step anion metathesis of commercially available imidazol(in)ium halides (Scheme 2b). In contrast to most

Scheme 2. (a) Synthesis of NHCs 2a,b by Deprotonation of the Corresponding Imidazolium Bromides (1) with a Strong Base and of Related Imidazolium-2-carboxylates 3a,b by Subsequent Carboxylation and (b) Synthesis of Imidazolium/Benzimidazolium Hydrogen Carbonates 4a−f by Anion Exchange



synthetic developments to masked NHCs, the latter method does not involve prior synthesis of the free carbene. Moreover, imidazol(in)ium hydrogen carbonates can be conveniently handled and stored in air without any particular precautions. In solution, they may coexist with their "dehydrated" imidazol(in)ium-2-carboxylate counterparts (NHC−CO_2 adducts), depending on the nature and water content of the solvent.[26,52,53] Investigation into the mechanism of the transformation [NHC(H)][HCO_3] (**4**) → NHC−CO_2 (**3**) by DFT calculations revealed the facile and reversible formation of the free NHC from both precursors.[26]

Given the small energetic barriers obtained in the gas phase at 25 °C for NHC generation from both [NHC(H)][HCO_3] salts **4** and NHC−CO_2 adducts **3**, we now wish to compare the ability of each precursor to generate the NHC **2** in solution, especially at room temperature and in the solid state. Characterization by thermogravimetric analysis (TGA) of [NHC(H)][HCO_3] salts **4** is first presented. TGA results evidence that, in the solid state, most of these precursors release H_2O and CO_2 molecules upon heating before they degrade. The catalytic efficiencies of both types of precursors (**3** and **4**) are next investigated in several reactions, including cyanosilylation, benzoin condensation, and transesterification. Both solvent and temperature effects have been studied.

RESULTS AND DISCUSSION

Synthesis and Characterization of NHC Precursors. Both types of precursors, [NHC(H)][HCO_3] salts **4** and NHC−CO_2 adducts **3**, were first synthesized following slightly modified reported procedures.[26,44,45] Briefly, 1,3-diisopropylimidazolium-2-carboxylate (**3a**) and 1,3-dimesitylimidazolium-2-carboxylate (**3b**) were obtained by direct carboxylation of the corresponding free NHCs **2** in THF (Scheme 2a) and characterized by ^{1}H and ^{13}C NMR spectroscopy (Figures S1−S4). It is worth pointing out, that unlike **2a**, **3a** was easily isolated by simple filtration of the reaction mixture. Moreover, neat **3a** was found to be relatively stable when exposed to air at room temperature, whereas its related NHC had to be stored at −30 °C under dry and inert conditions. However, **3a,b** were found to progressively hydrolyze into the corresponding [NHC(H)][HCO_3] salts **4a,b**, as already reported for similar compounds (see Scheme 1).[45,52]

Direct access to the imidazolium hydrogen carbonate salt precursors ([NHC(H)][HCO_3]) **4a−d** was achieved by anion metathesis of imidazol(in)ium bromides **1a−d**, using $KHCO_3$ in methanolic solution (Scheme 2b).[26,54−58] Characterization of **4a−d** by ^{1}H and ^{13}C NMR spectroscopy confirmed the expected structures (Figures S5−S12).

This synthetic method could also be applied to benzimidazolium hydrogen carbonates **4e,f** from the corresponding benzimidazolium bromides **1e,f** (see Figures S13−S16 for characterization by ^{1}H and ^{13}C NMR spectroscopy). In contrast, an attempt to synthesize a thiazolium hydrogen carbonate from the thiazolium bromide salt **1g** was unsuccessful: a methanolic solution of **1g** in the presence of $KHCO_3$ turned red within a few minutes, a viscous red-to-black insoluble paste progressively forming. This might be explained by the more acidic character of thiazolium salts in comparison to their imidazolium counterparts (pK_a([*i*Pr(H)][Br], **1a**) = 22 vs pK_a([MeThia(H)][Br], **1g**) = 14.5, in DMSO).[59] It is thus likely that, instead of anion metathesis, $KHCO_3$ mediated the deprotonation of **1g**, generating the corresponding NHC, which further decomposed.

It is well documented that thermal degradation of imidazolium-based ionic liquids proceeds first by dealkylation of the imidazole ring.[60,61] Likewise, studies of the thermal behavior of some NHC−CO_2 (and NHC−COS) adducts have shown that decarboxylation (or release of COS) strongly depends on the bulkiness of the substituents on the nitrogen atoms.[23,45] In contrast, and to the best of our knowledge, no report has described the thermal properties of [NHC(H)][HCO_3] salts. The thermal behavior of **4a−f** was thus investigated simultaneously by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), as summarized in Table 1.

Except for **4c,d**, no phase transition was noted on the DSC curves before these compounds started to decompose, as observed by TGA. It should be noted, however, that DSC results correspond to one heating cycle only. Hence, endotherms observed by DSC may be due to a weight loss, as seen by TGA at the same temperatures, rather than to melting peaks. In the case of **4a**, for instance, endotherms observed between 150 and 200 °C by DSC (Figure 2a) may be attributed to the melting of **4a**, to the melting of degradation

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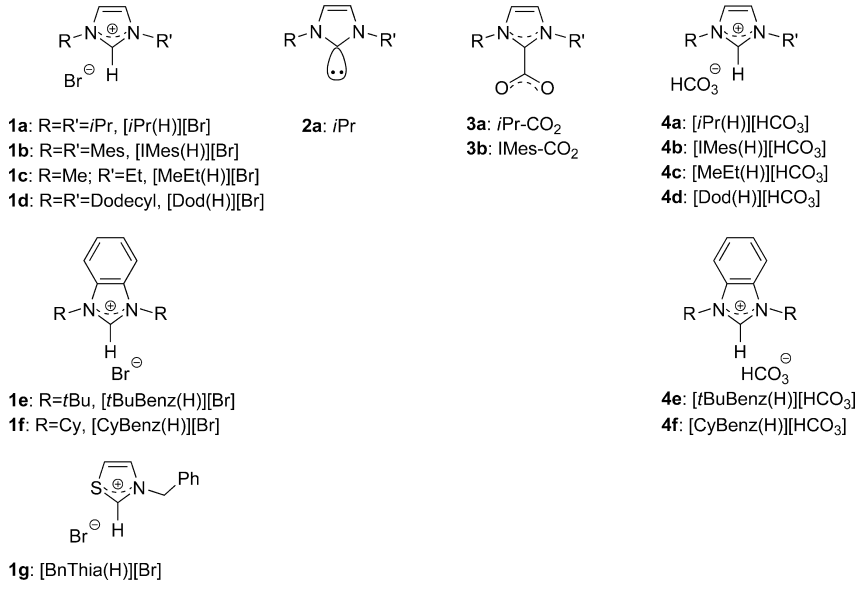

Figure 1. [NHC(H)][Br] salt precursors **1**, NHCs **2**, NHC−CO_2 adducts **3**, and [NHC(H)][HCO_3] salts **4** used in this study.

Table 1. Results of TGA and DSC Analyses of [NHC(H)][HCO_3] salts 4a−f

entry	compd	T_{onset} (°C)	WL_{exp} (%)[a]	$-H_2O_{th}$ (%)[b]	$-CO_{2,th}$ (%)[c]	T_{deg} (°C)[d]	T_m (°C)[e]
1	**4a**	110	3.1	8.4	20.6	190	
2	**4b**	134/218[f]	1.8/15.4	4.9	12.0	310	
3	**4c**	142	ND[g]			238	77
4	**4d**					280	42/126
5	**4e**	142	20.6	6.2	15.3	232	
6	**4f**	108	18.0	5.3	12.9	243	

[a]Experimental weight loss measured on TGA curves (heating rate 10 °C/min, N_2 atmosphere). [b]Theoretical weight loss for the loss of H_2O from the initial compounds **4**: $-H_2O_{th}$ (%) = $M_{H_2O}/M_4 \times 100$. [c]Theoretical weight loss for the loss of CO_2 from the initial compounds **4**: $-CO_{2,th}$ (%) = $M_{CO_2}/M_4 \times 100$. [d]Degradation temperature measured on TGA curves at the onset of their major weight losses. [e]Experimental endothermic peak temperature measured on DSC curves (when observed below T_{onset} and/or T_{deg}, heating rate 10 °C/min, N_2 atmosphere). [f]Two weight losses were observed before degradation. [g]ND = not determined because of the overlapping of the first weight loss with the major degradation.

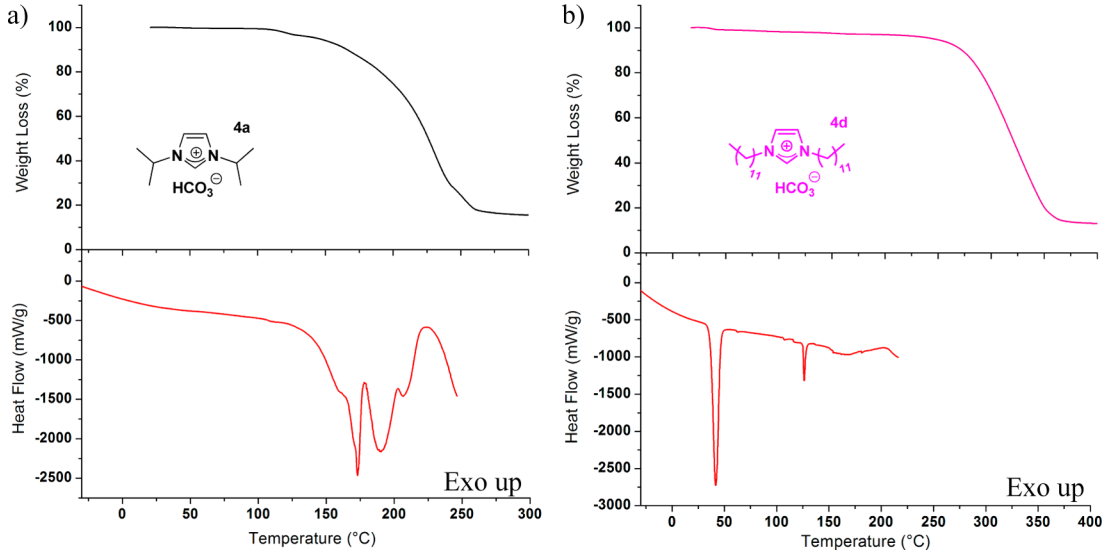

Figure 2. (a) TGA (black) and DSC (red) curves of **4a** and (b) TGA (pink) and DSC (red) curves of **4d**.

compounds, or to loss of H_2O/CO_2/alkyl chains. In contrast, the DSC curve of **4d** showed two distinct endothermic peaks below the degradation temperature (Figure 2b), owing to its liquid crystalline character. The peak observed at 42 °C can indeed be ascribed to a solid/liquid crystalline transition (S/LC), while that at 126 °C is due to a liquid crystalline/liquid transition (LC/L). A similar thermotropic behavior has already been reported for imidazolium halide homologues (1,3-

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dihexadecylimidazolium bromide: $T_{S/LC}$ = 46 °C and $T_{LC/L}$ = 143 °C).[62−64] As for precursor **4c**, its DSC analysis showed a single melting peak at 77 °C, similarly to its imidazolium bromide homologue **1c** (T_m = 79 °C). Compounds **4c,d** are thus in their melt state before they decompose, above 142 and 280 °C, respectively.

All [NHC(H)][HCO_3] **4** precursors proved stable at least up to 100 °C in the solid state (Table 1 and Figure 3). Typical

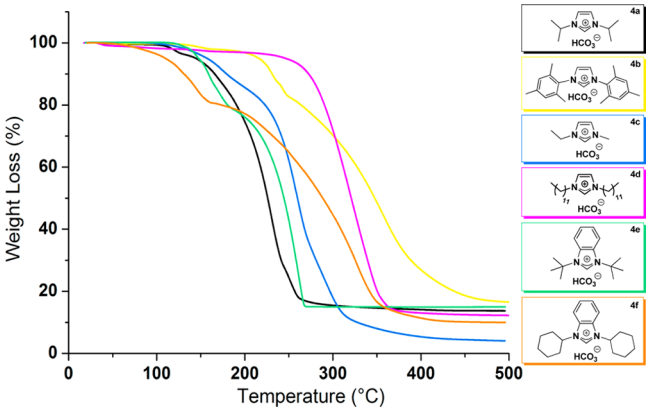

Figure 3. TGA curves of the thermal degradation of [NHC(H)]-[HCO_3] salts **4a−f**.

thermograms obtained by TGA/MS are provided in Figure 4 (in the case of precursors **4c,f**). With the exception of **4d**, featuring dodecyl chains, all compounds **4** showed a minor weight loss prior to their degradation at higher temperature.

In particular, an initial weight loss is observed at 142 and 108 °C, respectively, for both benzimidazolium hydrogen carbonates, **4e,f**, followed by their degradation at 230−240 °C. The initial weight loss can be ascribed to the loss of both H_2O and CO_2, as supported by TGA coupled with mass spectrometry (MS) analysis. In both cases, the loss of H_2O molecules (leading to mass to charge ratios at m/z 18 and 17) occurred at a slightly lower temperature than that due to the departure of CO_2 (at m/z 44 and 22). In addition, experimental weight loss (WL_{exp}) results for **4e,f** were found to be very close to the expected values (WL_{calc}) by considering a loss of H_2O + CO_2. In the case of **4e**, for instance, the results were as follows: WL_{exp} = 20.6% vs WL_{calc}(H_2O + CO_2) = 21.5%, while for **4f** WL_{exp} = 18.0% vs WL_{calc}(H_2O + CO_2) = 17.2%.

Of particular interest, a pale yellow solid could eventually be obtained after heating **4f** for 5 min at 130 °C, under a high dynamic vacuum (<10^{-7} bar). Analysis of this compound by ^{1}H NMR and ^{13}C NMR spectroscopy revealed characteristic signals of both the free benzimidazol-2-ylidene and its dimeric form, along with other signals likely attributable to degradation compounds (Figures S17 and S18).[65,66] Indeed, as can be seen on the TGA-MS curve of **4f** (Figure 4a), dealkylation of the benzimidazole backbone (yellow and green curves) starts before **4f** has completely lost its CO_2 moiety (blue and orange curves). This result nonetheless evidences that, for the first time, a free NHC can be spectroscopically detected upon heating a benzimidazolium hydrogen carbonate precursor in the solid state.

As anticipated, the size and the nature of the substituents on the nitrogen atoms significantly influenced the thermal stability of imidazolium-based [NHC(H)][HCO_3] salts **4a−d**. In contrast to the case for **4b**, the loss of H_2O/CO_2 moieties for **4a,c,d** could not be clearly distinguished from their thermal degradation (Figure 4b, case of precursor **4c**). Similar observations were made with NHC−CO_2 adducts **3a−c** undergoing decarboxylation upon heating.[45] Loss of CO_2 from **3b** could thus be discriminated from the degradation phenomenon. In contrast, **3a,c** showed concomitant degradation and loss of CO_2. This difference may be explained by the aromatic nature of the mesityl groups in **3b**, in comparison to the primary or secondary alkyl substituents in **3c** and **3a**.

In addition, the initial weight loss of **4a** was found to be lower than the expected value (3.0% vs 8.4% for −H_2O_{th} or 29.0% for −(H_2O + CO_2)$_{th}$), which might be explained by the loss of adsorbed water. Likewise, a decomposition in stages was not observed for **4c,d**. The longer the substituents of the alkyl chains, the higher the onset temperature: T_{onset} = 142 vs 280 °C for **4c,d**, respectively. In contrast, due to the higher stability of secondary cations in comparison to primary ones (iPr$^+$ vs Me$^+$ or Et$^+$), **4a** exhibited a lower degradation temperature than **4c**,

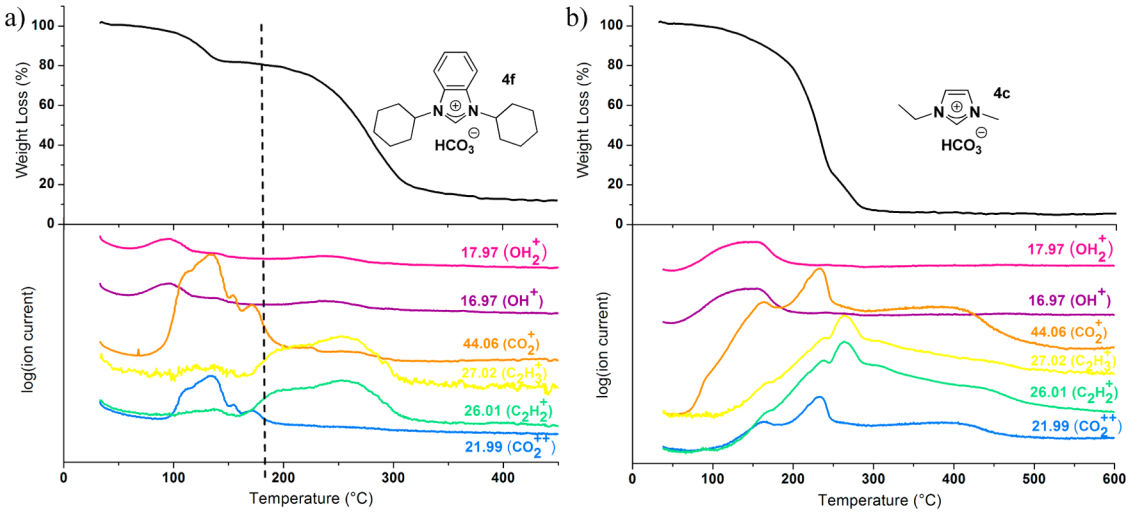

Figure 4. TGA-MS analyses (heating rate 5 °C/min, Ar atmosphere) of (a) **4f** (the dotted line denotes the end of the H_2O + CO_2 loss and the beginning of loss of alkyl chains) and (b) **4c**. log(ion current) was recorded for several mass to charge ratios corresponding to the loss of H_2O (pink and purple), CO_2 (orange and blue), and alkyl chains (yellow and green).

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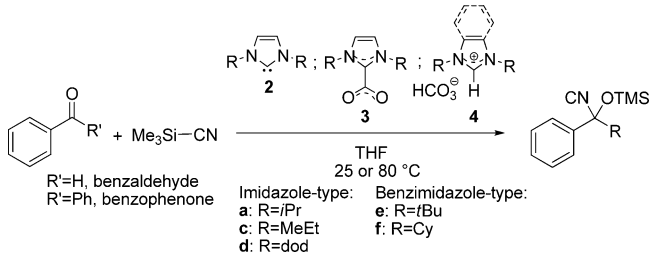
Table 2. Cyanosilylation of Benzaldehyde or Benzophenone with TMSCN in THF in the Presence of 2a, 3a, or 4a,c−f



entry	catalyst	amt of catalyst (mol %)	substrate	T (°C)	t (min)	conversn (%)[a]	TOF[b] (h^{-1})
1	**2a**	0.02	benzaldehyde	25	10	56	16 800
				80	10	95	28 500
2	**3a**	0.02	benzaldehyde	25	10	86	25 800
				80	10	100	30 000
3[c]	**4a**	0.02	benzaldehyde	25	30	86	8 600
				80	30	100	10 000
4[c]	**4c**	0.1	benzaldehyde	25	10	93	5 580
5[c]	**4d**	0.1	benzaldehyde	25	60	100	1 000
6[c]	**4e**	0.1	benzaldehyde	25	10	99	5 940
7[c]	**4f**	0.1	benzaldehyde	25	10	100	6 000
8	**2a**	0.02	benzophenone	25	20	100	15 000
				80	20	100	15 000
9	**3a**	0.02	benzophenone	25	20	100	15 000
				80	20	100	15 000

[a]Conversion was calculated by ^{1}H NMR in $CDCl_3$ (Figures S19 and S20) on comparison of the integral value of the aldehyde signal of benzaldehyde (δ 10 ppm) to that of the −C*H*− cyanide product (δ 5.5 ppm). [b]Turnover frequency. [c]3 Å molecular sieves were added.

consistent with data reported for the imidazolium bromide homologues **1a,c**.[60,61,67]

Compound **4b** exhibited the highest thermal stability in this series, which may be attributed to the aromatic nature of its aryl substituents. Similarly to benzimidazolium hydrogen carbonates, TGA curves of **4b** showed a concomitant dehydration/decarboxylation (WL_{exp} = 15.4% vs $WL_{calc}(H_2O + CO_2)$ = 16.9%), corresponding to the weight loss observed at 218 °C, followed by thermal degradation above 310 °C. The initial minor weight loss (134 °C, 1.8%) is most probably due to adsorbed water.

In summary, the solid-state behavior of [NHC(H)][HCO_3] precursors strongly depends on the nature of the azolium backbone and of the substituents on the nitrogen atoms. Benzimidazolium backbones, and more bulky substituents, lead to concomitant or stepwise losses of H_2O and CO_2 before the degradation stage, while such changes in the thermal properties cannot not be differentiated for compounds featuring short alkyl substituents.

The solution behaviors of the imidazolium/benzimidazolium hydrogen carbonates **4a−f** were also studied. As previously reported,[26] [NHC(H)][HCO_3] and their NHC−CO_2 counterparts can coexist in solution, in particular as a function of the water content of the solvent analysis. For instance, mixtures of NHC−CO_2 adducts and [NHC(H)][HCO_3] salts were observed, roughly in a molar ratio of 1:4, in the ^{1}H and ^{13}C NMR spectra of imidazolium hydrogen carbonates **4a−c** in DMSO-d_6. Analyses in MeOD showed a single population of signals attributed to the pure [NHC(H)][HCO_3] salt. In contrast, NMR spectra of imidazolium hydrogen carbonates **4d** and benzimidazolium hydrogen carbonates **4e,f** revealed the presence of the sole [NHC(H)][HCO_3] compound, irrespective of the solvent analysis (DMSO-d_6, MeOD, or CD_2Cl_2).

It is worth mentioning that compounds **4**—with the exception of **4d**—were hardly soluble in THF, which was the main solvent used for the organocatalyzed reactions of the present study. Complete solubilization of the precursors did however occur upon addition of the substrate (e.g., benzaldehyde, vinyl acetate, and benzyl alcohol; see below).

Catalytic activities of selected precursors (**3a** and **4a,c−f**, Figure 1) were next evaluated in several molecular reactions, including cyanosilylation, benzoin condensation, and transesterification reactions. All these reactions were carried out under different experimental conditions so as to investigate both solvent and temperature effects. Precursors **4a−f** being thought to generate free NHCs **2** by releasing H_2O and CO_2 (=H_2CO_3; Scheme 1),[26] molecular sieves (3 Å) were systematically added in the reaction vessel. Control experiments were also implemented from the corresponding bare NHC **2a**, which was purposely synthesized. Only **3a** and **4a** were tested as precatalysts for transesterification reactions, in order to highlight the solvent effect on the ability of imidazolium hydrogen carbonates and their NHC−CO_2 counterparts to generate the corresponding NHCs.

Benzaldehyde and Benzophenone Cyanosilylation Reaction. Hermann et al.[68] and then both Song et al.[69] and Suzuki et al.[70] have employed NHCs as organocatalysts for cyanosilylation reactions of carbonyl-containing substrates. When aldehydes or ketones react with trimethylsilyl cyanide (TMSCN) in the presence of catalytic loadings of NHC, high conversions are obtained. Although the mechanism that may involve either the activation of the carbonyl group or the silicon atom remains unclear, this is a general method to access α-hydroxyamines, α-hydroxy acids, and α-hydroxyaldehydes after derivatization.[71,72] Polymer-supported versions of NHC−CO_2 adducts have also been reported for organocatalyzed cyanosilylation reactions.[33] Here, we examined the catalytic

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activity of both molecular imidazolium hydrogen carbonates **4a,c–f** and NHC–CO_2 adduct **3a** toward the cyanosilylation reaction of benzaldehyde or benzophenone with TMSCN, both at room temperature and at 80 °C. The most significant results are collected in Table 2.

In the case of benzaldehyde as substrate, 0.02 mol % of **3a** gave almost quantitative conversions, at both room temperature and 80 °C, only after 10 min of reaction (entry 2). A control experiment employing NHC **2a** gave similar results (entry 1). Interestingly, the use of **4a** as NHC precursor only divided the turnover frequency (TOF) by a factor of 3 (entry 3), attesting to the fact that both **3a** and **4a** could generate NHC **2a** at room temperature and 80 °C.

In addition to our previous DFT calculations on the transformation **4a** → **2a**,[26] the reaction **3a** → **2a** was also investigated computationally (see the Supporting Information). As expected, a smaller activation barrier was calculated for the generation of free NHC from **3a** (6.1 kcal mol^{-1}), as compared to 10.0 kcal mol^{-1} in the case of the transformation **4a** → **2a**. The same trend was noted in the case of **4b** → **2b** and **3b** → **2b**, a 2.4 kcal mol^{-1}energy difference in activation barrier being calculated (7.5 and 5.1 kcal mol^{-1} for **4b** → **2b** and **3b** → **2b**, respectively). Moreover, all these transformations were found to be reversible (see the Supporting Information). These results are compatible with the facile generation of **2** from both precursors **3** and **4**, the formation of **2** being more favorable in the case of **3** → **2**. Moreover, the reversibility of both reactions **3** → **2** and **4** → **2** is in agreement with the absence of an induction period for the catalyst to be generated.

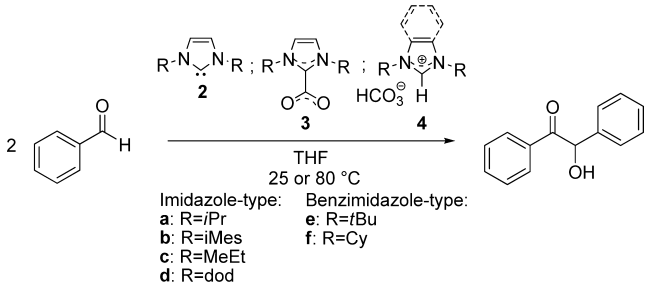
Imidazolium hydrogen carbonates **4c,d** were also efficient in triggering the cyanosilylation of benzaldehyde at room temperature (entries 4 and 5), though **4d**, bearing more bulky substituents gave a lower TOF. Benzimidazole-type salts **4e,f** were also successfully used as precatalysts at room temperature (entries 6 and 7) witnessing, for the first time, that such precursors could generate corresponding NHCs in solution at room temperature.

Song et al. have noticed that NHC-catalyzed cyanosilylation of ketones—compared to aldehydes—requires longer reaction times using 1,3-di-*tert*-butyl-imidazol-2-ylidene as catalyst, the reaction being favored in DMF in comparison to THF.[69] Here, both **2a** and **3a** catalyzed the cyanosilylation of benzophenone quantitatively, after 20 min in THF, both at room and at higher temperatures (entries 8 and 9). Hence, high temperatures are not needed to achieve high yields, suggesting in that case again that solvation effects, associated with the favorable kinetics and thermodynamics of the transformations **3a** → **2a** and **4a** → **2a**,[26] can drive the generation of the NHC catalyst from NHC–CO_2 adducts and [NHC(H)][HCO_3] precursors.

Benzoin Condensation Reaction. Pioneer works on NHC-catalyzed benzoin condensation by Breslow date back to 1958.[73] Since then, various NHCs, including thiazol-2-ylidenes, imidazol(in)-2-ylidenes, benzimidazol-2-ylidenes, and triazol-5-ylidenes, as well as NHC–COS adducts[23] have served to catalyze this C–C bond forming reaction that transforms aromatic aldehyde molecules into benzoin derivatives, the intermediate of the reaction being a resonance-stabilized enaminol-type intermediate called the "Breslow intermediate".[5] Application of this elementary reaction to polymer synthesis, that is, the NHC-catalyzed step-growth polymerization of the aromatic bis-aldehyde terephthalaldehyde to form polybenzoin, has also been reported.[74] In addition, polymer-supported NHC precursors, such as poly(NHC–CO_2) adducts[34] and poly-(imidazolium salts),[37] have been used to catalyze the benzoin condensation, the in situ generation of poly(NHCs) being triggered by a temperature increase or the addition of a base, respectively.

Masked NHCs **3a** and **4a,c–f** were thus tested as organic precatalysts for the benzoin condensation reaction (Table 3). In

Table 3. Benzoin Condensation Reaction in THF using 2a, 3a, or 4a–f



entry	catalyst	amt of catalyst (mol %)	solvent	T (°C)	t (h)	conversn (%)[a]	TOF[b] (h^{-1})
1	**2a**	1	THF	25	24	52	2.17
				80	24	72	3
2	**3a**	1	THF	25	21	28	1.3
					48	45	0.94
				80	24	72	3
3[c]	**4a**	3	THF	25	21	6	0.09
					48	11	0.08
				80	24	72	1
4[26]	**4b**	10	THF	60	24	88	0.37
5[c]	**4c**	10	THF	25	24	44	0.2
				80	24	72	0.3
6[c]	**4d**	10	THF	25	24	17	0.07
				80	24	79	0.3
7[c]	**4e**	10	THF	25	24	0	-
				80	24	0	-
8[c]	**4f**	10	THF	25	24	71	0.3
				80	24	75	0.3

[a]Conversion was calculated by ^{1}H NMR in $CDCl_3$ (Figure S21) on comparison of the integral value of the aldehyde signal of benzaldehyde (δ 10 ppm) with that of the –C*H*– benzoin signal (δ 6 ppm). [b]Turnover frequency. [c]3 Å molecular sieves were added.

contrast to cyanosilylation, the temperature has a great impact on conversion. For instance, a temperature increase, from 25 to 80 °C, led to more than 2 times higher yields upon using **3a** as precursor (Table 3, entry 2). Precatalyst **3a** gave approximately 30% conversion after 24 h at room temperature, which was 2 times lower than the result obtained with its free NHC homologue **2a**. The use of **4a** at room temperature resulted in even poorer conversions. At 80 °C, similar kinetics and yields were noted both with the free NHC **2a** and the NHC–CO_2 adduct **3a**, attesting to the quantitative generation of the NHC at this temperature. As observed in the cyanosilylation, reaction using **4a** led to similar conversions but divided the TOF by a factor of 3 at 80 °C.

While high amounts of free NHCs are generally required to achieve high yields (up to 10–30 mol % for asymmetric condensations),[5] only 1 mol % of precursor **2a** gave a rather good catalytic efficiency at room temperature (entry 1). However, complete conversion was not achieved at 80 °C using **2a**, **3a**, or **4a**, after 24 h, even with higher amounts of

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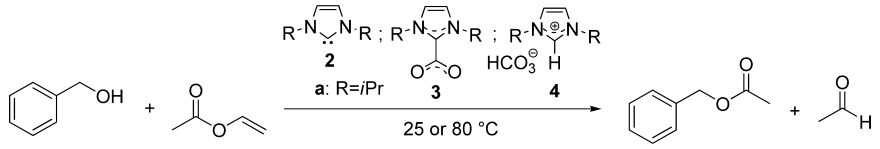
Table 4. Transesterification between Benzyl Alcohol and Vinyl Acetate using 2a, 3a, or 4a



entry	catalyst	amt of catalyst (mol %)	solvent	T (°C)	t (min)	conversn (%)[a]	TOF[b] (h^{-1})
1	**3a**	0.5	THF	25	10	100	1200
				80	10	100	1200
2[c]	**4a**	0.5	THF	25	10	81	980
				80	10	93	1120
3	**3a**	0.1	THF	25	10	30	1800
				80	10	60	3600
4	**2a**	0.1	THF	25	10	100	6000
				80	10	100	6000
5	**3a**	0.1	toluene	25	10	37	2220
				80	10	77	4620
6	**2a**	0.1	toluene	25	10	94	5640
				80	10	100	6000
7	**3a**	0.1	cyclohexane	25	10	4	240
				80	10	15	900
8	**2a**	0.1	cyclohexane	25	10	79	4740
				80	10	100	6000
9	**3a**	0.1	DMSO	25	10	0	
				80	10	7	420
10	**2a**	0.1	DMSO	25	10	5	300
				80	10	19	1140
11	**3a**	0.1	none	25	10	7	420
				80	10	10	600
12	**2a**	0.1	none	25	10	32	1920
				80	10	30	1800

[a]Conversion was calculated by ^{1}H NMR in $CDCl_3$ (Figure S22) on comparison of the integral value of the $-CH_2-$ benzyl alcohol signal (δ 4.5 ppm) to that of the $-CH_2-$ benzyl acetate signal (δ 5 ppm). conversn (%) = $(I_{\text{benzyl acetate}}/(I_{\text{benzyl acetate}} + I_{\text{benzyl alcohol}})) \times 100$. [b]Turnover frequency. [c]3 Å molecular sieves were added.

(pre)catalysts, presumably due to the temperature sensitivity of **2a**. Similar results were previously observed upon using 10 mol % of **4b** as NHC precursor (entry 4).[26] Changing the substituents of the imidazole ring to less bulky (**4c**) or to more bulky (**4d**) ones did not improve the TOF values. Benzimidazolium hydrogen carbonate **4f** exhibited catalytic efficiency similar to that of **4a–d**, whereas **4e** showed no activity at all. Indeed, the steric hindrance of *t*Bu substituents as compared to cyclohexyl substituents (**4e** vs **4f**) may slow the NHC generation by a solvation effect. Masked NHCs **3a** and **4a–d,f** are nonetheless capable of catalyzing the benzoin condensation, by generating NHCs in solution, better results being achieved at 80 °C.

Transesterification Reaction. Free NHCs,[75,76] and some masked NHCs such as imidazol(in)ium-2-thiocarboxylates[23] or polymer-supported versions of imidazolium-2-carboxylates,[34] are known to efficiently catalyze transesterification reactions. However, neither NHC–CO_2 adducts nor [NHC(H)][HCO_3] salt precursors have been evaluated as precatalysts for such reactions at room temperature. The reaction between benzyl alcohol and vinyl acetate was thus performed in the presence of **3a** or **4a**, in nonpolar solvents such as cyclohexane and toluene and in polar solvents such as THF and DMSO, both at room temperature and at 80 °C. Results obtained with the two types of NHC precursors are summarized in Table 4. The catalytic potential of free NHC **2a** was also evaluated for comparison purposes since, to the best of our knowledge, this particular NHC has never been tested for transesterification reactions.

When 0.5 mol % of 1,3-diisopropylimidazolium-2-carboxylate (**3a**) was used in THF, quantitative yields were achieved within only 10 min, at 80 °C and, more strikingly, at room temperature as well (Table 4, entry 1). Interestingly, **4a** could also serve as a precatalyst of transesterification at room temperature, although a 2 times lower TOF value was noted in comparison to its carboxylate homologue **3a** under the same conditions (entry 2 vs entry 3). These results are again consistent with the facile generation of NHC from both types of precursors at room temperature. Lower TOF values but high conversions observed with **3a** and **4a** in comparison to free NHC **2a** are also in agreement with the fact that **2a** has to be generated from its masked forms, prior to entering the catalytic cycle.

At a precatalyst **3a** concentration of 0.1 mol %, increasing the temperature from 25 to 80 °C gave 2 times higher conversions, regardless of the nature of the solvent, while almost no temperature effect was noted with the bare NHC **2a**. For example, TOF values increased from 1800 to 3600 h^{-1} in THF, from room temperature to 80 °C, using **3a** as precatalyst (entry 3). These results support that NHC **2a** is the catalytically active species, the rate of CO_2 release from **3a** being increased by increasing the temperature.

Transesterification reactions were next evaluated both in nonpolar (entries 5 and 7) and polar solvents (entry 9). Lower

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conversions were noted in THF in comparison to toluene, from both NHC precursor **3a** and free NHC **2a** (entries 3 and 4 vs 5 and 6). In addition, NHC−CO_2 **3a** gave almost no conversion in cyclohexane, most probably due to its insolubility in the reaction medium. DMSO gave lower yields than all the other tested solvents despite its high polarity, irrespective of the catalyst (entries 9 and 10). A control experiment in the absence of solvent was also attempted, which led to only poor yields, both at room temperature and at 80 °C, in the presence of either **2a** or **3a** (entries 11 and 12). Consistent with observations made by Delaude et al.[51] regarding the NHC transfer to metal complexes, the solvent may thus help the decarboxylation of NHC−CO_2 adducts, most probably by a solvation effect. The catalytic activity of **2a** in the tested solvents was thus DMSO < none ≪ cyclohexane ≈ toluene ≈ THF, while in the case of **3a**, it varied as DMSO ≈ none ≈ cyclohexane ≪ toluene ≈ THF. The influence of the solvent on the transesterification reaction was found to be similar upon using NHC−CO_2 **3a** or its corresponding bare NHC **2a**, except when cyclohexane was employed, owing to the poor solubility of **3a** in this solvent.

CONCLUSION

Various (benz)imidazolium hydrogen carbonates, [NHC(H)][HCO_3], and imidazolium-2-carboxylates, NHC−CO_2 adducts, are shown to generate related N-heterocyclic carbenes (NHCs) in situ, allowing for a use in organocatalysis for different reactions. Formation of the free carbene upon heating a benzimidazolium-type hydrogen carbonate precursor has been evidenced for the first time by NMR spectroscopy. In situ generation of NHC can be readily achieved in solution from all types of precursors at room temperature, presumably by a simple solvation effect. Solvents favoring the NHC generation include mainly THF and toluene, presumably owing to a better solvation of both the transition state and the free NHC, relative to the charged NHC−CO_2 adduct and the [NHC(H)][HCO_3] salt precursors.

Transesterification reactions can be triggered from NHC−CO_2 adducts, either in THF or in toluene, while [NHC(H)][HCO_3] precursors exhibits a good catalytic efficiency in THF. Both categories of NHC precursors, including those of benzimidazole type, proved efficient for the cyanosilylation reaction, giving excellent TOFs at room temperature in THF. They also allow catalyzing the benzoin condensation, preferentially at 80 °C.

Although [NHC(H)][HCO_3] precursors exhibit a lower catalytic activity in all reactions tested, a major advantage of these salts lies in their air stability in the solid state, combined with an easy one-step access based on anion metathesis. Thus, a variety of (benz)imidazol(in)ium hydrogen carbonates should be accessible by simple anion exchange, affording versatile precursors for various NHC-catalyzed reactions, upon formal loss of H_2CO_3. Experiments are currently ongoing in our group to highlight the potential of such precatalysts in polymer chemistry. Polymer-supported versions of these [NHC(H)][HCO_3] and their use in organocatalysis are also underway.

EXPERIMENTAL SECTION

Materials. All experiments were performed under an inert atmosphere using standard Schlenk techniques. Dry, oxygen-free solvents and reagents were employed. THF was distilled over Na/benzophenone, MeOH was distilled over Na, and toluene and cyclohexane were distilled over polystyryllithium prior to use. DMSO was distilled over CaH_2 before use following a minimum of 4 h of reflux. All reagents were purchased from commercial sources with purity ≥99% unless otherwise stated. TMSCN was used as received. Vinyl acetate (95%) was purified by distillation over CaH_2 and stored at 0 °C. Benzaldehyde and benzyl alcohol were purified by fractional distillation. Benzyl alcohol was kept over molecular sieves. Benzophenone was recrystallized twice in dry warm cyclohexane and stored in the glovebox.

Methods. NMR spectra were recorded on a 400 MHz spectrometer. The mass spectra (ESI) instrument is equipped with an ESI source, and spectra were recorded in the positive mode. The electrospray needle was maintained at 4500 V and operated at room temperature. Samples were introduced by injection through a 10 μL sample loop into a 200 μL/min flow of methanol from the LC pump. TGA experiments were performed with alumina crucibles. A constant heating rate of 10 °C/min and gas purging (N_2) at a flow rate of 100 mL/min were used for all experiments. The amount of samples used for TGA was between 9 and 10 mg. The resulting T_{onset} and T_{deg} values were determined from the step tangent. Thermogravimetric techniques coupled with mass spectrometry were employed to analyze the thermal decomposition products in situ. The TGA−MS experiments were performed from room temperature to 650 °C with a heating rate of 5 °C/min in argon gas purging. The amount of sample was ca. 12 mg. The signal intensity of gaseous products during the heating was measured in situ using mass spectroscopy. DSC experiments were performed with aluminum sealed pans. A constant heating/cooling rate of 10 °C/min and gas purging (N_2) at a flow rate of 100 mL/min was used for all experiments.

Synthesis of Imidazolium-2-carboxylates. 1,3-Diisopropylimidazolium bromide (500 mg, 2.14 mmol), synthesized using a procedure already described,[77] and 1,3-dimesitylimidazolium chloride (50 mg, 0.147 mmol), purchased from a commercial source, were first deprotonated by exposure to 1 equiv of KHMDS or 1 equiv of NaH/cat. *t*BuOK in dry THF. After being stirred overnight, solutions were filtered under inert conditions to remove metallic salts. CO_2 (99.995%) was then introduced into the flask. White precipitates were observed after a few seconds. The solutions were further exposed to CO_2 (1 atm) for 20 min before being filtered in the glovebox. The white powders were washed with dry Et_2O and dried under vacuum, affording clean 1,3-diisopropylimidazolium-2-carboxylate (**3a**; yield 295 mg, 70%) and 1,3-dimesitylimidazolium-2-carboxylate (**3b**; yield 31 mg, 60%). NMR spectra were in agreement with those already reported in the literature (Figures S1−S4).[45]

Synthesis of Imidazolium Hydrogen Carbonates. 1,3-Diisopropylimidazolium bromide (**1a**; 500 mg, 2.14 mmol), 1,3-didodecylimidazolium bromide (**1d**; 500 mg, 1.03 mmol), synthesized using a procedure already described,[77] 1,3-dimesitylimidazolium chloride (**1b**; 500 mg, 1.47 mmol), and 1-methyl-3-ethylimidazolium chloride (**1c**; 500 mg, 3.41 mmol), purchased from commercial sources, were dried under vacuum for several hours and then dissolved in 5 mL of MeOH. A 1.02 equiv portion of dry $KHCO_3$ (0.218 mg, 2.18 mmol with **1a**; 0.150 mg, 1.50 mmol with **1b**; 0.348 mg, 3.48 mmol with **1c**; 0.105 mg, 1.05 mmol with **1d**) was added. The solution was stirred under an inert atmosphere for 2 days to allow complete precipitation of KBr or KCl. After filtration of the solutions over Celite to remove the mentioned salt, MeOH was evaporated under vacuum. The powders were washed with acetone and dried under vacuum (yield: **4a**, 320 mg, 70%; **4b**, 402 mg, 75%, **4c**, 354 mg, 60%, **4d**, 313 mg, 65%). NMR spectra of **4a**,**b** were in agreement with those already reported in the literature (Figures S5−S8).[26]

In MeOD (Figures S9 and 10), **4c** was the only compound observed, while in DMSO-d_6, **4c** equilibrates with **3c** in a 1:2.5 ratio, in favor of **3c**. ^{1}H NMR (400 MHz, MeOD): δ 1.62 (t, J = 7.2 Hz, 3H, NCH_2CH_3), 3.93 (s, 3H, NCH_3), 4.26 (q, J = 7.2 Hz, 2H, NCH_2CH_3), 7.57 (s, 1H, C*H*=CH), 7.64 (s, 1H, CH=C*H*). The N_2CH and HCO_3^- protons could not be observed, while the integral of C*H*=C*H* was lowered due to rapid exchange with the deuterated solvent on the NMR time scale. ^{13}C NMR (100 MHz, MeOD): δ 15.6, 36.4, 46.0, 123.2, 124.8, 137.5, 161.4. Mp: 76−78 °C. HRMS (MALDI+): m/z calcd for $C_6H_{11}N_2$ $[M]^+$ 111.0916, found 111.0913.

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4d was the only compound observed in MeOD and DMSO-d_6 (Figures S11 and 12). ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.85 (t, J = 6.6 Hz, 6H, CH_2CH_3), 1.23 (br, 36H, $(CH_2)_9CH_3$), 1.78 (quin, J = 6.8 Hz, 4H, NCH_2CH_2), 4.16 (t, J = 7.2 Hz, 4H, NCH_2CH_2), 7.82 (s, 2H, CH=CH), 9.27 (s, 1H, NCHN). ^{13}C NMR (100 MHz, DMSO-d_6): δ 13.9, 22.1, 25.4, 28.3, 28.7, 28.8, 28.9, 29.0, 29.0, 29.2, 31.3, 48.8, 122.5, 136.0, 154.0. Mp: 40−42 °C (solid/liquid crystalline transition). HRMS (MALDI+): m/z calcd for $C_{27}H_{53}N_2$ $[M]^+$ 405.4203, found 405.4200.

Synthesis of Benzimidazolium Hydrogen Carbonates. 1,3-Di-*tert*-butyl-benzimidazolium chloride (**1e**; 500 mg, 1.71 mmol) and 1,3-dicyclohexylbenzimidazolium bromide (**1f**; 500 mg, 1.57 mmol), purchased from commercial sources, were dried under vacuum for several hours and then dissolved in 5 mL of MeOH. A 1.02 equiv portion of dry $KHCO_3$ (0.174 mg, 1.74 mmol and 0.160 mg, 1.60 mmol, respectively) was added. The solution was stirred under an inert atmosphere for 2 days to allow complete precipitation of KBr or KCl. After filtration of the solutions over Celite to remove the mentioned salt, MeOH was evaporated under vacuum. The powders were washed with acetone and dried under vacuum (yield 209 mg, 40% and 436 mg, 80%, respectively). The obtained products were soluble in MeOD, DMSO, and CD_2Cl_2, a single population of signals being observed whatever the analysis solvent.

4e (Figures S13 and S14): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 1.97 (s, 18H, $NC(CH_3)_3$), 7.62 (dd, J = 3.2 Hz, 6.4 Hz, 2H, H_{benz}), 8.00 (dd, J = 3.2 Hz, 6.8 Hz, 2H, H_{benz}), 9.82 (s, 1H, N_2CH); the HCO_3^- proton could not be observed due to rapid exchange with the deuterated solvent on the NMR time scale; ^{13}C NMR (100 MHz, CD_2Cl_2) δ 29.2, 62.3, 116.8, 126.0, 132.0, 140.6, 160.1; mp >152 °C dec; HRMS (MALDI+) m/z calcd for $C_{15}H_{23}N_2$ $[M]^+$ 231.1859, found 231.1855.

4f (Figures S15 and S16): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 1.27 (m, 2H, $CH_{2,cyclohexyl}$), 1.52 (m, 4H, $CH_{2,cyclohexyl}$), 1.74 (m, 2H, $CH_{2,cyclohexyl}$), 1.92 (m, 8H, $CH_{2,cyclohexyl}$), 2.17 (m, 4H, $CH_{2,cyclohexyl}$), 4.74 (m, 2H, $NCH_{cyclohexyl}$), 7.68 (dd, J = 2.6 Hz, 6.6 Hz, 2H, H_{benz}), 8.19 (dd, J = 3.2 Hz, 7.2 Hz, 2H, H_{benz}), 10.00 (s, 1H, N_2CH); the HCO_3^- proton could not be observed due to rapid exchange with the deuterated solvent on the NMR time scale; ^{13}C NMR (100 MHz, CD_2Cl_2) δ 24.6, 24.8, 31.8, 48.6, 50.8, 57.0, 114.0, 126.4, 130.6, 139.3, 155.6; mp >140 °C dec; HRMS (MALDI+) m/z calcd for $C_{19}H_{27}N_2$ $[M]^+$ 283.2168, found 283.2177.

Catalytic Tests. All catalytic tests were carried out under a dry and inert atmosphere using Schlenk equipment. To provide exactly similar conditions for experiments performed at room temperature and at 80 °C, one reaction medium was first prepared mixing catalyst and reagents. This solution was then equally separated into two different flasks, one being kept at room temperature and the other being transferred in an 80 °C preset oil bath. All reactions were stopped by contact with air, and small samples were immediately withdrawn for conversion analysis by NMR in $CDCl_3$.

Cyanosilylation (See Table 2). In a typical reaction, 0.5 mL (5 mmol) of benzaldehyde and 0.75 mL of TMSCN (6 mmol) were mixed with 5 mL of THF. A 23.5 μL portion (1 μmol) of a 42.5 mM solution (THF/DMSO 5/1) of **3a** was finally added. After a few seconds of homogenization at room temperature, the solution was divided as described above. Conversion was calculated by ^{1}H NMR in $CDCl_3$ (Figures S19 and S20) to compare the integral value of the aldehyde signal of benzaldehyde (δ 10 ppm) to that of the −CH− cyanide product (δ 5.5 ppm).

Benzoin Condensation (See Table 3). In a typical reaction, 31.5 mg (150 μmol) of **4a** and molecular sieves were introduced into a Schlenk tube. The powder was submitted to 30 min of vacuum and finally three Ar/vacuum cycles. A 5 mL portion of THF and then 0.5 mL (5 mmol) of benzaldehyde were added. After a few seconds at room temperature, complete solubilization of the catalyst was observed and the solution was divided as described above. Conversion was calculated by ^{1}H NMR in $CDCl_3$ (Figure S21) to compare the integral value of the aldehyde signal of benzaldehyde (δ 10 ppm) with that of the −CH− benzoin signal (δ 6 ppm).

Transesterification (See Table 4). In a typical reaction, 0.5 mL of benzyl alcohol (5 mmol) and 0.55 mL (6 mmol) of vinyl acetate were mixed in 5 mL of THF. A 4.5 mg portion (25 μmol) of precatalyst **3a** was finally added. After a few seconds at room temperature, complete solubilization of the catalyst was observed and the solution was divided as described above. After 10 min, conversion was calculated by ^{1}H NMR in $CDCl_3$ (Figure S22) to compare the integral value of the $-CH_2-$ benzyl alcohol signal (δ 4.5 ppm) to that of the $-CH_2-$ benzyl acetate signal (δ 5 ppm).

■ ASSOCIATED CONTENT

Supporting Information

Figures, text, and tables giving ^{1}H and ^{13}C NMR spectra of (benz)imidazolium hydrogen carbonates, ^{1}H and ^{13}C NMR spectra to evidence the NHC formation after heating of **4f** in the solid state, ^{1}H NMR spectra for the calculation of conversion of the tested reactions, and optimized structures of **3** and **2** with the corresponding energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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