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Imidazol(in)ium Hydrogen Carbonates as a Genuine Source of *N*-Heterocyclic Carbenes (NHCs): Applications to the Facile Preparation of NHC Metal Complexes and to NHC-Organocatalyzed Molecular and Macromolecular Syntheses

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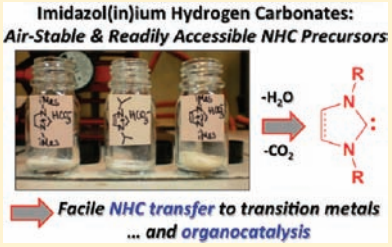
Supporting Information

ABSTRACT: Anion metathesis of imidazol(in)ium chlorides with $KHCO_3$ afforded an easy one step access to air stable imidazol(in)ium hydrogen carbonates, denoted as [NHC(H)][HCO_3]. In solution, these compounds were found to be in equilibrium with their corresponding imidazol(in)ium carboxylates, referred to as *N*-heterocyclic carbene (NHC)-CO_2 adducts. The [NHC(H)][HCO_3] salts were next shown to behave as masked NHCs, allowing for the NHC moiety to be readily transferred to both organic and organometallic substrates, without the need for dry and oxygen-free conditions. In addition, such [NHC(H)][HCO_3] precursors were successfully investigated as pre-catalysts in two selected organocatalyzed reactions of molecular chemistry and polymer synthesis, namely, the benzoin condensation reaction and the ring-opening polymerization of D,L-lactide, respectively. The generation of NHCs from [NHC(H)][HCO_3] precursors occurred *via* the formal loss of H_2CO_3 *via* a concerted low energy pathway, as substantiated by Density Functional Theory (DFT) calculations.



INTRODUCTION

In the past 20 years, stable carbenes, in particular *N*-heterocyclic carbenes (NHCs), have emerged not only as versatile ligands for transition metals[1] but also as powerful organocatalysts in molecular chemistry for a variety of transformations[2] and, more recently, in macromolecular chemistry for precision polymer synthesis.[3] NHCs are generally prepared by deprotonation of azolium salts with a strong base.[4] Because this method not only necessitates dry and air-free conditions but also provides limited tolerance to various functionalities, different approaches have been developed to circumvent these limitations. Apart from the encapsulation of free NHCs into hydrophobic silicon polymers allowing their handling in air,[5] most efforts have been focused toward the design of masked NHCs (Figure 1),[6] whose thermal activation can *in situ* generate the free carbene. Several masked NHCs such as 2-alkoxy,[7] 2-trichloromethyl,[7d,8] 2-pentafluorophenyl imidazolidines,[8,9] 5-alkxytriazolines,[7g,10] imidazolium-2-carboxylates—referred to as NHC−CO_2 adducts,[11] imidazolium-2-thioisocyanates,[12] and NHC-Ag(I) complexes[13] have been developed. Although most of these compounds have been successfully applied as NHC-transfer agents for transition metals,[7a−d,8,9,11e,14] and as (pre)catalysts for molecular[8,12,15] and macromolecular synthesis,[7f,g,8,12,16] their preparation generally involves the generation of free NHC. Structural diversity is thus often limited by the stability of the corresponding carbene and decomposition of some masked NHCs in solution, in the presence of water, has been observed. In particular, Rogers et al.[17] and Louie et al.[11g] have evidenced that the $C_{carbene}$−CO_2 bond of NHC−CO_2 adducts can hydrolyze in solution, forming stable imidazolium hydrogen carbonate salts, denoted as [NHC(H)][HCO_3] (eq 1, Scheme 1). Interestingly, this hydrolysis reaction proves reversible, suggesting a noninnocent role of the HCO_3^- counteranion toward the imidazolium cation. This behavior is reminiscent of that observed for basic anions such as AcO^- in imidazolium-based ionic liquids (ILs), which are capable of reversibly deprotonating the imidazolium cation, generating the corresponding NHC.[18] By analogy, and from a mechanistic point of view, we thus hypothesized that, in the case of [NHC(H)][HCO_3] **2**, NHC **6** could be reversibly generated by the formal loss of H_2CO_3 (eq 3, Scheme 1). It might also be anticipated that subsequent reaction of the NHC with CO_2

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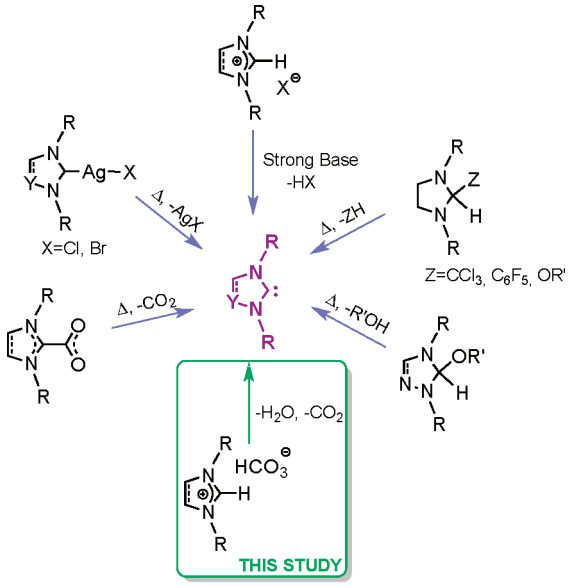
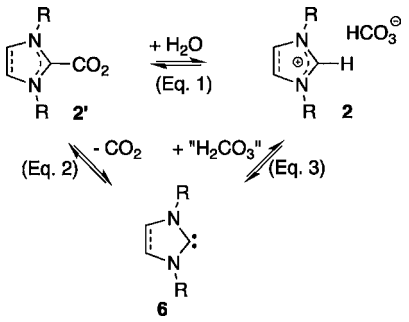


Figure 1. Masked NHC precursors reported in the literature and those described in this work.

Scheme 1. Reversible Transformation of NHC−CO_2 Adducts into [NHC(H)][HCO_3] Salts *via* the Generation of NHCs



(formed by decomposition of H_2CO_3) would afford the corresponding NHC−CO_2 adduct **2′** (eq 2, Scheme 1).

To the best of our knowledge, no report has mentioned the NHC-like behavior of imidazolium hydrogen carbonates in (macro)molecular chemistry.[19,20] We wish to report herein the facile synthesis of such [NHC(H)][HCO_3] salt precursors by a simple anion metathesis from commercially available imidazolium chlorides, [NHC(H)][Cl], using $KHCO_3$, and their use as stoichiometric transfer agents of NHCs toward organic and organometallic substrates. We also show that [NHC(H)][HCO_3] organic salts can serve as precatalysts in (macro)molecular reactions. NHC formation from its [NHC(H)][HCO_3] precursor, *via* formal loss of H_2CO_3, is investigated by Density Functional Theory (DFT) calculations.

EXPERIMENTAL SECTION

Materials. Solvents were used without any purification unless otherwise stated. Benzyl alcohol was purified by fractional distillation and stored over molecular sieves. D,L-Lactide (99%, Alfa) was recrystallized three times in warm toluene (freshly distilled from polystyryllithium prior to use), dried under vacuum, and kept in the glovebox. Benzaldehyde (99%, Alfa) was purified by fractional distillation. Carbon disulfide was used as received (99.9%, Aldrich). 1,3-Bis(isopropyl)-imidazolium chloride (Roth), 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (Strem), 1,3-bis(2,4,6-trimethylphenyl)imidazolinium chloride (Aldrich), and $KHCO_3$ (Alfa) were dried at 60 °C for 12 h under vacuum. $[Pd(allyl)Cl]_2$ and $Au(Cl)SMe_2$ were purchased from Strem Chemicals Inc. and Aldrich, respectively, and used as received.

Instrumentation. ^1H NMR (400 MHz) spectra were recorded on a Bruker AC-400 spectrometer in appropriate deuterated solvents. Molar masses were determined by size exclusion chromatography (SEC) in THF as the eluent (1 mL/min) and with trichlorobenzene as a flow marker at 25 °C, using both refractometric (RI) and UV detectors (Varian). Analyses were performed using a three-column set of TSK gel TOSOH (G4000, G3000, G2000 with pore sizes of 20, 75, and 200 Å respectively, connected in series) calibrated with polystyrene standards. The data for the crystal structure of compound **2a** have been collected on a Rigaku MM07 HF rotating anode at the Cu Kα wavelength. The system featured the Micromax microfocus X-ray source with the RAPIDII image plate detector combined with the AFC-Kappa goniometer and the osmic mirrors Varimax HF optics. The system was driven by the CrystalClear suite which was also used for the unit cell determination, integration, scaling, and absorption correction of the raw data (Reference: CrystalClear: An Integrated Program for the Collection and Processing of Area Detector Data, Rigaku Corporation, 1997−2002). MALDI-ToF spectrometry was performed using a Voyager-DE STR (Applied Biosystems) spectrometer equipped with a nitrogen laser (337 nm), a delay extraction, and a reflector. The instrument is equipped with a pulsed N_2 laser (337 nm) and a time-delayed extracted ion source. Spectra were recorded in the positive-ion mode using the reflectron and with an accelerating voltage of 20 kV. Samples were dissolved in THF at 10 mg/mL. The IAA matrix (Indole acrylic acid) solution was prepared by dissolving 10 mg in 1 mL of THF. A MeOH solution of cationization agent (NaI, 10 mg/mL) was also prepared. The solutions were combined in a 10:1:1 volume ratio of matrix to sample to cationization agent. A 1−2 μL aliquot of the obtained solution was deposited onto the sample target and vacuum-dried. Mass spectra (ESI) were obtained on a QStar Elite mass spectrometer (Applied Biosystems). The 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.

Synthesis of 1,3-Bis(isopropyl)imidazolium Hydrogen Carbonate [IiPr(H)][HCO_3] 2a. A mixture of 1,3-bis(isopropyl)-imidazolium chloride (1 g, 5.30 mmol) and 1.05 equiv of $KHCO_3$ (550 mg, 5.56 mmol) was dried at 60 °C under vacuum for 12 h. Dry MeOH (5 mL) was then added at rt, and the resulting suspension was stirred for 48 h at rt. After filtration of the suspension over Celite to remove KCl, MeOH was evaporated under vacuum to yield a sticky solid. Trituration of the solid with acetone and filtration afforded 805 mg of [**IiPr(H)**][HCO_3] **2a** as a white powder, upon drying under vacuum (yield: 71%). Recrystallization of **2a** in a MeOH/Et_2O mixture

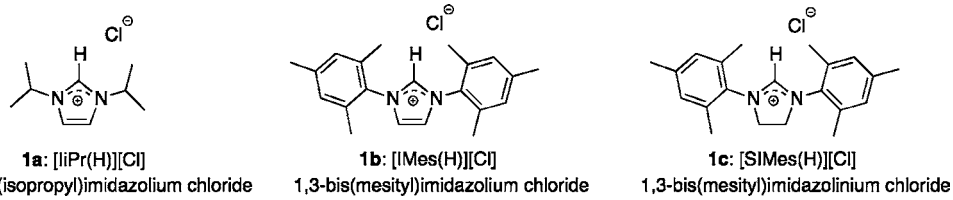


Figure 2. Structure of imidazol(in)ium chloride precursors used in this study.

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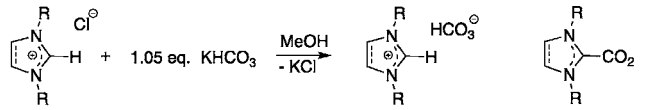
Scheme 2. Synthesis of Imidazolium Hydrogen Carbonates [NHC(H)][HCO_3] 2a–c *via* Anion Metathesis of Imidazolium Chlorides [NHC(H)][Cl] 1a–c with $KHCO_3$ in MeOH



1a: [IiPr(H)][Cl] **2a**: [IiPr(H)][HCO_3] **2'a**: IiPr-CO_2
1b: [IMes(H)][Cl] **2b**: [IMes(H)][HCO_3] **2'b**: IMes-CO_2
1c: [SIMes(H)][Cl] **2c**: [SIMes(H)][HCO_3] **2'c**: SIMes-CO_2

at 5 °C yielded colorless plate-like crystals, suitable for X-ray diffraction analysis. In MeOD, **2a** was the only compound observed, while, in dmso-d_6, **2a** equilibrates with **IiPr-CO_2 2a′** in a 1:3 ratio, in favor of **2a**. ^{1}H NMR (400 MHz, MeOD): δ = 1.62 (d, J = 6.8 Hz, 12H, CH_3*i*Pr), 4.73 (sept, J = 6.8 Hz, 2H, C*H*iPr), 7.76 (s, 2H, C*H*=C*H*). The N_2CH and HCO_3^- protons could not be observed due to their rapid exchange with the deuterated solvent on the NMR time scale. ^{13}C NMR (100 MHz, MeOD): δ = 23.0 (CH_3*i*Pr), 54.6 (C*H*iPr), 121.9 (*C*H=*C*H), 134.4 (br, N_2CH), 161.3 (HCO_3^-). In dmso-d_6, the major compound was **2a**: ^{1}H NMR (400 MHz, dmso-d_6): δ = 1.48 (d, J = 6.8 Hz, 12H, CH_3*i*Pr), 4.66 (sept, J = 6.8 Hz, 2H, C*H*iPr), 7.98 (s, 2H, C*H*=C*H*), 9.71 (s, 1H, N_2CH). ^{13}C NMR (100 MHz, dmso-d_6): δ = 23.3 (CH_3*i*Pr), 53.1 (C*H*iPr), 121.5 (*C*H=*C*H), 135.1 (N_2CH), 156.8 (HCO_3^-). Minor compound **2a′**: ^{1}H NMR (400 MHz, dmso-d_6): δ = 1.40 (d, J = 6.8 Hz, 12H, CH_3*i*Pr), 5.27 (sept, J = 6.8 Hz, 2H, C*H*iPr), 7.86 (s, 2H, C*H*=C*H*). ^{13}C NMR (100 MHz, dmso-d_6): δ = 23.3 (CH_3*i*Pr), 51.2 (C*H*iPr), 118.4 (*C*H=*C*H), 143.4 (N_2C), 155.4 (CO_2). HRMS (MALDI+): m/z calculated for $C_9H_{17}N_2$ $[M]^+$ 153.1381, found 153.1384.

Synthesis of 1,3-Bis(mesityl)imidazolium Hydrogen Carbonate [IMes(H)][HCO_3] 2b. A similar procedure to that described for the preparation of [**IiPr(H)**][**HCO_3**] **2a** was used. **2b** was obtained as a white solid (yield: 76%). In MeOD, **2b** was the only compound observed, while, in dry dmso-d_6, **2b** was only sparingly soluble. ^{1}H NMR (400 MHz, MeOD): δ = 2.20 (s, 12H, *o*-CH_3Mes), 2.40 (s, 6H, *p*-CH_3Mes), 7.20 (s, 4H, *m*-C*H*Mes), 8.06 (s, 2H, C*H*=C*H*). The N_2CH and HCO_3^- protons could not be observed due to their rapid exchange with the deuterated solvent on the NMR time scale. ^{13}C NMR (100 MHz, MeOD): δ = 17.6, 21.3, 126.5, 131.0, 132.4, 135.8, 139.8, 143.0, 161.5.

Synthesis of 1,3-Bis(mesityl)imidazolinium hydrogen carbonate [SIMes(H)][HCO_3] 2c. A similar procedure to that described for the preparation of [**IiPr(H)**][**HCO_3**] **2a** was used. **2c** was obtained as a white solid (yield: 88%). In MeOD, **2c** was the only compound observed, while, in dmso-d_6, **2c** equilibrates with **SIMes-CO_2 2c′** in a 1:1.5 ratio, in favor of **2c′**. ^{1}H NMR (400 MHz, MeOD): δ = 2.33 (s, 6H, *p*-CH_3Mes), 2.41 (s, 12H, *o*-CH_3Mes), 4.52 (s, 4H, CH_2), 7.10 (s, 4H, *m*-C*H*Mes). The N_2CH and HCO_3^- protons could not be observed due to their rapid exchange with the deuterated solvent on the NMR time scale. ^{13}C NMR (100 MHz, MeOD): δ = 17.9 (*o*-CH_3Mes), 21.2 (*p*-CH_3Mes), 52.6 (CH_2), 131.1 (*m*-CHMes), 132.1 (*p*-C_qMes), 136.7 (*o*-C_qMes), 142.1 (C_{ipso}Mes), 161.5 (N_2CH), 162.0 (br, HCO_3^-). In dmso-d_6, the ^{1}H and ^{13}C NMR data obtained for the major compound **2c′** matched those reported in the literature.[14d] Minor compound **2c**: ^{1}H NMR (400 MHz, dmso-d_6): δ = 2.27 (s, 6H, *p*-CH_3Mes), 2.33 (s, 12H, *o*-CH_3Mes), 4.44 (s, 4H, CH_2), 7.08 (s, 4H, *m*-C*H*Mes), 9.06 (s, 1H, N_2CH). ^{13}C NMR (100 MHz, dmso-d_6): δ = 17.1 (*o*-CH_3Mes), 20.6 (*p*-CH_3Mes), 51.0 (CH_2), 129.5 (*m*-CHMes), 130.9 (C_qMes), 135.4 (C_qMes), 139.7 (C_qMes), 156.3 (N_2CH), 160.3 (HCO_3^-).

Synthesis of IMes-CS_2 3b. CS_2 (10 equiv, 2.7 mmol) was added to a THF suspension (1.5 mL) of **2b** (100 mg, 0.27 mmol) at room temperature, and the reaction mixture was stirred at 60 °C in a capped vial for 2 h. After removal of all the volatiles under vacuum, 98 mg of a purple-brownish solid were isolated (yield 96%). Data from ^{1}H NMR analysis of **3b** in dmso-d_6 were found to be in good agreement with those reported in the literature.[11f]

Synthesis of SIMes-CS_2 3c. A similar procedure to that described for the synthesis of **3b** was used, yielding 95 mg of **3c** as an orange powder (yield 92%), upon removal of the volatiles. ^{1}H NMR data of **3c** in $CDCl_3$ were found to be in good agreement with those reported in the literature.[11f]

Synthesis of IiPr-Pd(allyl)Cl 4a. $[Pd(allyl)Cl]_2$ (21.3 mg, 5.8 × 10^{-5} mol), compound **2a** (29.4 mg, 1.4 × 10^{-4} mol), and THF (2 mL) were put in a capped vial (air atmosphere). After 1 d of stirring at rt, ^{1}H NMR analysis in $CDCl_3$ attested the complete disappearance of signals corresponding to $[Pd(allyl)Cl]_2$. The solution was filtered over silica to remove residual compound **2a**, and THF was finally removed under vacuum. The resulting pale yellow powder was further washed with Et_2O (yield 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.40 (pseudo t, J = 7.3 Hz, 12H, CH_3*i*Pr), 2.35 (d, J = 12.1 Hz, 1H, CH_2), 3.28 (d, J = 13.6 Hz, 1H, CH_2), 3.34 (td, J = 2.0, 7.2 Hz, 1H, CH_2), 4.24 (dd, J = 2.0, 7.2 Hz, 1H, CH_2), 4.98 (br, 2H, C*H*iPr), 5.30 (m, 1H, CH_{allyl}), 6.94 (s, 2H, C*H*=C*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.5 (CH_3*i*Pr), 23.6 (CH_3*i*Pr), 47.2 (CH_2), 52.8 (C*H*iPr), 73.0 (CH_2), 114.6 (CH_{allyl}), 116.9 (*C*H=*C*H), 177.2 ($C_{carbene}$).

Synthesis of SIMes-Pd(allyl)Cl 4b. $[Pd(allyl)Cl]_2$ (5 mg, 1.4 × 10^{-5} mol), compound **2b** (12.1 mg, 3.3 × 10^{-5} mol), and THF (0.5 mL) were put in a capped vial (air atmosphere). After 10 min of stirring at rt, ^{1}H NMR analysis in $CDCl_3$ attested the complete disappearance of $[Pd(allyl)Cl]_2$ peaks. The solution was filtered over silica to remove residual compound **2b**, and THF was finally removed

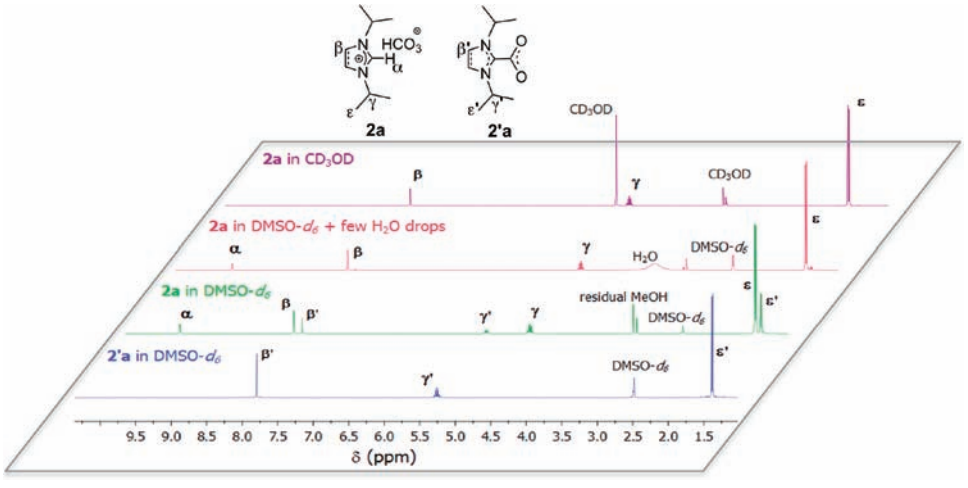


Figure 3. ^{1}H NMR spectra of **2a** in CD_3OD, DMSO-d_6 where a few drops of water were added, dry DMSO-d_6 (leading to an equilibrium between compounds **2a** and **2a′**), and ^{1}H NMR spectrum of **2a′** in dry DMSO-d_6 synthesized by carboxylation of the corresponding free NHC.

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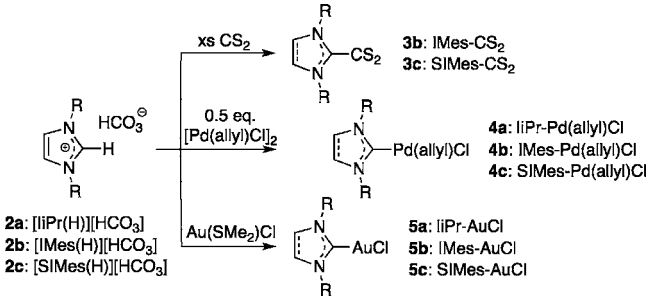
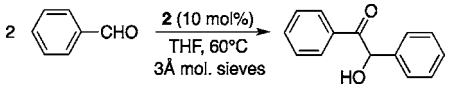
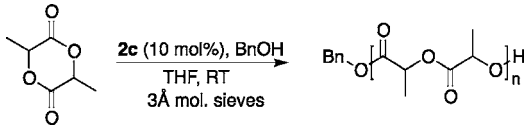
Scheme 3. Transfer of the NHC from [NHC(H)][HCO_3] Salts 2 to CS_2, [Pd(allyl)Cl]$_2$, and Au(SMe_2)Cl



Scheme 4. Benzoin Condensation Catalyzed by 10 mol % of 2b,c in THF at 60 °C



Scheme 5. RT Ring-Opening Polymerization of D,L-Lactide Using Benzyl Alcohol As Initiator and 2c as Catalyst Precursor



under vacuum. The resulting pale yellow powder was further washed with Et_2O. NMR spectra in $CDCl_3$ were in agreement with those reported in the literature (yield 95%).[21]

Synthesis of IMes-Pd(allyl)Cl 4c. A similar procedure to compound **4b** was used: 10 min of reaction between 5 mg (1.4×10^{-5} mol) of [Pd(allyl)Cl]$_2$ and 11.7 mg (3.3×10^{-5} mol) of compound **2c** in THF followed by the aforementioned purification procedures led to compound **4c** (yield 95%). NMR spectra were in agreement with those reported in the literature.[21b]

Synthesis of IiPr-AuCl 5a. Au(SMe_2)Cl (11.4 mg, 3.9×10^{-5} mol), compound **2a** (9.8 mg, 4.7×10^{-5} mol), and THF (0.7 mL) were put in a capped vial (air atmosphere). After 1 h of stirring at 50 °C, ^{1}H NMR analysis in $CDCl_3$ attested the consumption of 1 equiv of compound **2a** compared to Au(SMe_2)Cl. The solution was filtered over silica to remove residual compound **2a**, and THF was finally removed under vacuum (yield 95%). The resulting off-white powder was analyzed by NMR in $CDCl_3$. Spectra were in agreement with those reported in the literature.[22]

Synthesis of SIMes-AuCl 5b. In a similar fashion, 1 h of reaction at rt between 11.4 mg (3.9×10^{-5} mol) of Au(SMe_2)Cl and 17.2 mg (4.7×10^{-5} mol) of compound **2b** in THF followed by the aforementioned purification procedures led to compound **5b** (yield 82%). NMR spectra in $CDCl_3$ were in agreement with those reported in the literature.[23]

Synthesis of IMes-AuCl 5c. In a similar fashion, 1 h of reaction at rt between 11.4 mg (3.9×10^{-5} mol) of Au(SMe_2)Cl and 16.7 mg (4.7×10^{-5} mol) of compound **2c** in THF followed by the aforementioned purification procedures led to compound **5c** (yield 89%). NMR spectra were in agreement with those reported in the literature.[23]

Benzoin Condensation Reaction. In a typical reaction, 74 mg (0.2 mmol) of 1,3-bis(mesityl)imidazolinium hydrogen carbonate **2c** (stored in a capped vial under air) and molecular sieves were introduced into a Schlenk tube. The powder was submitted to 30 min under vacuum and finally three Ar/vacuum cycles. THF (2 mL), previously distilled from Na/benzophenone, and then benzaldehyde (0.2 mL 2 mmol) were added. The Schlenk tube was then transferred into a 60 °C preset oil bath. Conversion was calculated by ^{1}H NMR in $CDCl_3$, comparing the integral value of the C*H*O signal of benzaldehyde (δ = 10 ppm) with the integral value of the α-hydroxy C*H* signal of benzoin (δ = 6 ppm); after 24 h, 88% and 83% conversion was obtained with compounds **2b** and **2c**, respectively.

Polymerization of D,L-LA. In a typical polymerization, 3.6 mg (9.7×10^{-6} mol, 10 mol % relative to the initiator) of 1,3-bis(mesityl)-imidazolinium hydrogen carbonate **2c** (stored in a capped vial under air) were introduced into a Schlenk tube. The powder was degassed for 30 min under vacuum followed by three Ar/vacuum cycles, and then 5 mL of dry THF, previously distilled from Na/benzophenone, were added. In a glovebox, molecular sieves, 10 μL of benzyl alcohol (9.7×10^{-5} mol), and 380 mg (2.6×10^{-3} mol, targeted DP = 26) of D,L-lactide were introduced. After a the mixture was stirred for few minutes at RT complete homogenization was observed. After 3 h at rt, the conversion was calculated by ^{1}H NMR in $CDCl_3$ comparing integral values of the C*H*-signal of the polymer (broad peak around δ = 5.1 ppm) and that of the C*H*-monomer signal (quadruplet at δ = 5.0 ppm). Poly(D,L-LA) was precipitated in cold MeOH, dried under vacuum, and analyzed by ^{1}H NMR in CD_2Cl_2 to calculate DP_{NMR} (comparing benzyl protons of chain ends, δ = 7.3 ppm with C*H*-peak of the polymer, δ = 5.1 ppm). Molar masses and dispersities were obtained by SEC analysis in THF (RI detector).

RESULTS AND DISCUSSION

The synthesis of imidazolium hydrogen carbonates [NHC-(H)][HCO_3] has been scarcely investigated in the literature.[24] They can be prepared by reacting free NHCs with NH_4HCO_3,

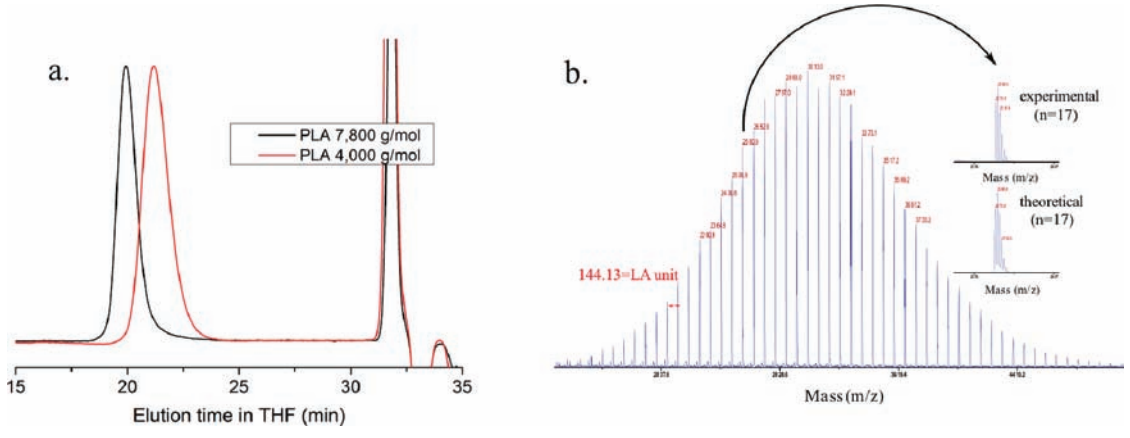


Figure 4. (a) SEC traces of PLA obtained using **2c** as NHC-precursor: in red, [LA]/[BnOH]/[**2c**] = 26/1/0.1; in black, [LA]/[BnOH]/[C] = 68/1/0.1 (SEC in THF calibrated with PS standards). (b) MALDI-ToF MS spectrum in reflector mode of PLA ([LA]/[BnOH]/[**2c**] = 26/1/0.1).

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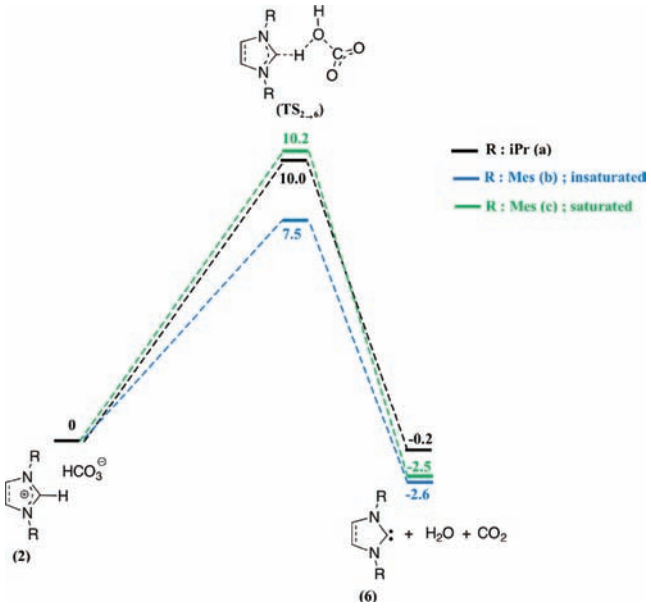

Figure 5. Energy profile computed at the B3LYP/6-31G** level (free energies *G* at 25 °C including ZPE correction in kcal/mol) for the rearrangement **2→6** + CO_2 + H_2O, noted **2→6** in the text.

as reported by Kuhn et al.,[25] or by hydrolysis of NHC−CO_2 adducts.[11g,17,24c] Note that both methods involve prior preparation of the free NHC. To avoid the manipulation of air-sensitive free carbene intermediates, and thus provide an easy access to [NHC(H)][HCO_3] salts, we turned to the anion metathesis of commercially available imidazolium halide precursors, [NHC(H)][Cl], using $KHCO_3$. This method has been employed for the synthesis of molecular,[20,24a] polymeric[24e] [NHC(H)][HCO_3]-based ILs and for the surface modification of IL-functionalized gold nanoparticles,[24d] using NH_4HCO_3,[24a] $NaHCO_3$,[20b,24d] or $KHCO_3$[24e] as a HCO_3^- source and *i*-PrOH or water as a reaction medium.[26] For this study, we selected three imidazol(in)ium chlorides (Figure 2) and resorted to a modified procedure of the aforementioned literature for anion metathesis.

Thus, reacting 1,3-bis(isopropyl)imidazolium chloride, [IiPr(H)][Cl], **1a**, with 1.05 equiv of $KHCO_3$ in MeOH for 2 days led, after workup, to a white powder in 71% yield (Scheme 2).

Analysis of the crude powder by ^{1}H NMR in CD_3OD revealed the presence of one product. As expected, the chemical shifts of the different protons of the imidazolium backbone were similar to that of the starting material **1a**, thus precluding its identification. However, in the ^{13}C NMR spectrum, the characteristic signals of both the N_2CH carbon and the HCO_3^- quaternary carbon atoms were clearly detected at 134.4 and 161.3 ppm respectively, in agreement with data from the literature.[17,24c] Note that the absence of the ^{1}H NMR signal corresponding to the N_2CH proton was attributed to the rapid exchange of this proton with the deuterated solvent, on the

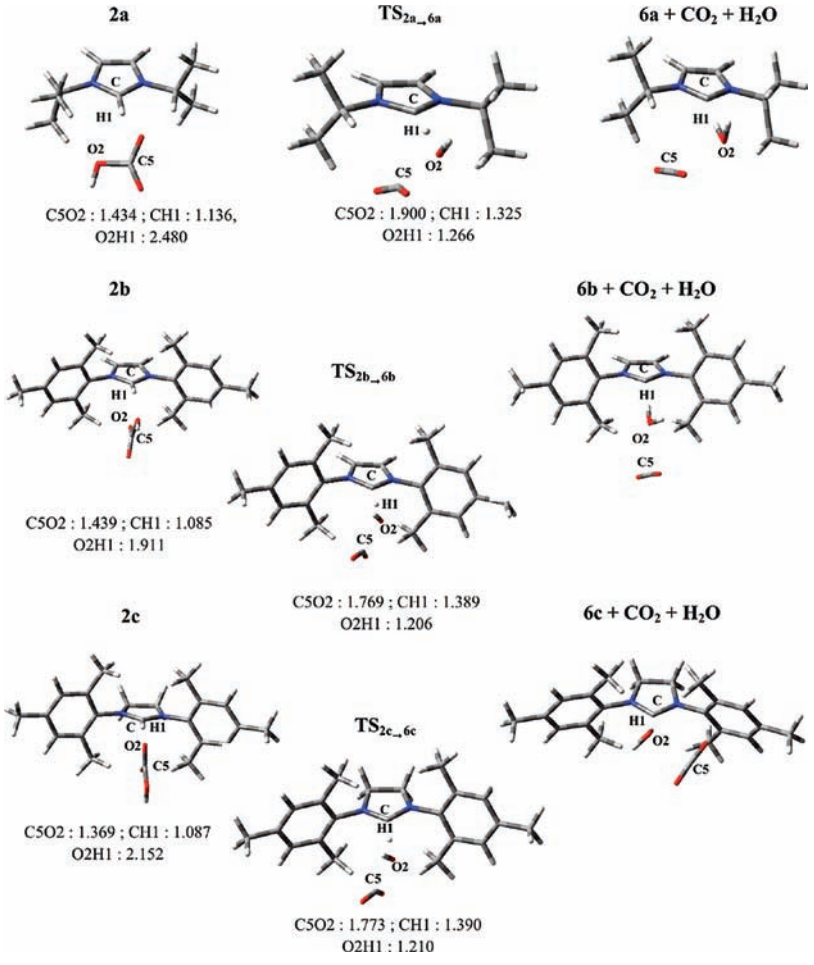

Figure 6. Geometrical structures and main bond lengths for all the compounds involved in the **2→6** rearrangement (distances in Å).

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NMR time scale.[24c] The absence of the signal due to the more acidic HCO_3^- proton is likely due to the same phenomenon.

Crystals of **2a** suitable for X-ray diffraction analysis could be obtained by cooling a solution of **2a** in a MeOH/Et_2O mixture. The modest quality of the crystallographic data precludes a discussion of the geometric parameters, but the connectivity of the complex could be unambiguously established (see Supporting Information). In particular, the asymmetric unit cell consists of one imidazolium cation and one HCO_3^- anion, the HCO_3^- anions forming hydrogen-bonded dimers around crystallographic centers of inversions, consistently with previous observations for similar structures.[17,24a,25]

In contrast to CD_3OD, **2a** was found to coexist with compound **2a′**, in a 3:1 ratio in dry DMSO-d_6, as deduced from the presence of a new set of signals in the ^1H NMR spectrum. Compound **2a′** was eventually identified as being the corresponding NHC−CO_2 adduct, by comparing its ^1H NMR spectrum with that of an authentic sample prepared by reacting the free NHC with CO_2 (see Figure 3 for a comparison between ^1H NMR spectra of **2a** in CD_3OD, dry or wet DMSO-d_6 and **2a′** in dry DMSO-d_6). Consistent with observations made by Rogers et al.[17,24c] with some [NHC(H)][HCO_3] ILs, **2a** and **2a′** are in equilibrium in DMSO. Interestingly, the equilibrium can be totally shifted toward the formation of **2a** by adding a few drops of water in DMSO or by letting the sample stand in air, while, in CD_3OD, the equilibrium is totally shifted toward the formation of **2a**.

To generalize the synthesis of imidazolium hydrogen carbonates from imidazolium chlorides, the anion metathesis method was applied to precursors featuring aryl substituents on the nitrogen atoms, namely, 1,3-bis(mesityl)imidazolium chloride [IMes(H)][Cl], **1b**, and its saturated counterpart, namely, 1,3-bis(mesityl)imidazolinium chloride [SIMes(H)][Cl], **1c**. Subjecting the two latter salts to anion metathesis in dry MeOH yielded, after the usual workup, **2b** and **2c** as off-white and white solids, in 76% and 88% yield, respectively. Given that **2b** is sparingly soluble in dry DMSO-d_6 and that **2c** is in equilibrium with **2′c** in dry DMSO-d_6, their characterization was performed in MeOD by ^1H and ^{13}C NMR spectroscopy. In particular, both the HCO_3^- anion and the N_2CH carbon atoms could be identified by ^{13}C NMR spectroscopy through the presence of signals at 161.5 and 132.4 ppm, respectively, for **2b**, and at 162.0 and 161.5 ppm, respectively, for **2c**. As in the case of **2a** discussed above, shifting the equilibrium toward the quantitative formation of the imidazolium hydrogen carbonates could be achieved by adding a few drops of water. Thus, coexistence in solution of [NHC(H)][HCO_3] and NHC−CO_2 strongly depends on the nature of the solvents and on the presence of water.

We next examined whether [NHC(H)][HCO_3] **2** could be of some practical use as a source of NHCs that either can be transferred in a stoichiometric fashion to transition metals or serve as precatalysts in selected (macro)molecular reactions. For instance, in the presence of CS_2, an organic substrate known to readily react with free NHCs,[11f,27] imidazolium hydrogen carbonates **2b,c** afforded the corresponding highly colored azolium dithiolate type betaines, denoted as NHC−CS_2 adducts **3b,c**, in high yield (92−96%; see Experimental Section). Reactions of **2** with an excess of CS_2 were carried out in THF at 50 °C for 1 to 6 h (Scheme 3). The structures of **3b−c** NHC−CS_2 adducts were authenticated by comparing their ^1H NMR spectra with those reported in the literature.[27] Although this reaction involving CS_2 has limited synthetic utility, it clearly establishes that

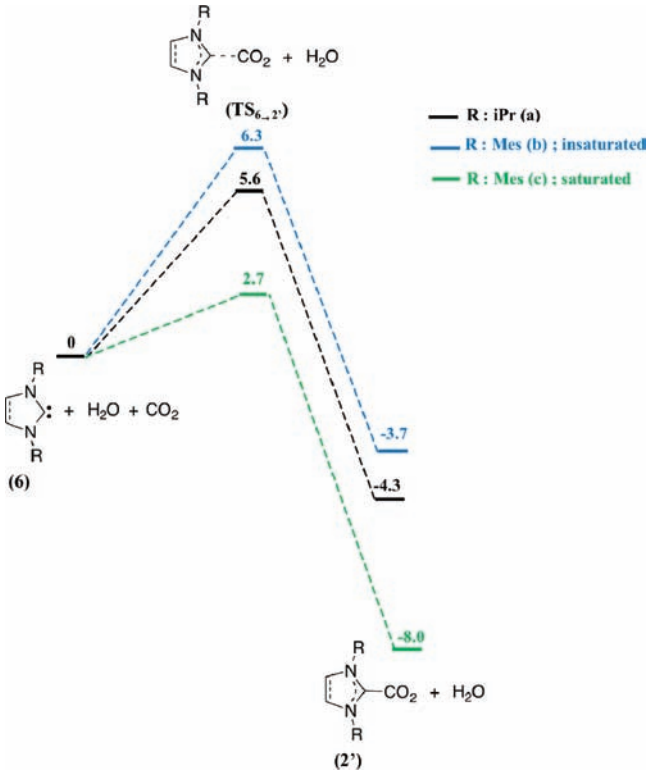

Figure 7. Energy profile computed at the B3LYP/6-31G** level (free energies *G* at 25 °C including ZPE correction in kcal/mol) for the rearrangement **6** + CO_2 + H_2O →**2′** + H_2O, noted **6→2′** in the text.

[NHC(H)][HCO_3] **2** can deliver the free carbene in solution, allowing its transfer to an organic substrate.

To further illustrate their potential as NHC precursors, the reactivity of [NHC(H)][HCO_3] salts **2** toward transition metals was investigated (Scheme 3). Thus, 1.2 equiv of **2a,b,c** was reacted with 0.5 equiv of [Pd(allyl)Cl]$_2$ in THF. The corresponding NHC−Pd(II) complexes **4a,b,c** were isolated in excellent yields (>87%), after 24 h of stirring at RT for compound **4a**, and 1 h for **4b,c**. **4b** and **4c** were identified by comparing their ^1H NMR spectra with those already reported.[21] Compound **4a** was completely characterized by ^1H and ^{13}C NMR spectroscopy. In particular, its ^1H NMR spectrum exhibited five different signals (δ = 2.35, 3.28, 3.34, 4.24, and 5.30 ppm) corresponding to the allyl fragment, indicating a dissymmetric structure around the palladium center. In ^{13}C NMR, the characteristic signal of the carbene center was observed at 177.2 ppm, in agreement with that observed for analogous palladium−NHC complexes (δ = 175.6−188.5 ppm).[21] It is worth mentioning that these transfer reactions were performed in air with nonpurified solvents. Similarly, transfer of the NHC moiety from **2** to AuCl(SMe_2) was successfully accomplished in air, giving excellent yields of the corresponding NHC−Au complexes **5**, after 1 h of stirring in THF at 50 °C for **5a** and RT for **5b,c**. Excellent agreement between the ^1H NMR spectra of **5a,b,c** synthesized from [NHC(H)][HCO_3] **2** and data reported in the literature was observed.[22,23]

To test the activity of precursors **2** as organic precatalysts, benzoin condensation, known as being selectively catalyzed by NHCs,[1,2] was implemented as a model reaction (Scheme 4). Reactions were performed in THF at 60 °C, in the presence of 10 mol % of precatalyst **2b,c**, using molecular sieves to trap the water released from the [NHC(H)][HCO_3]. After the reactions

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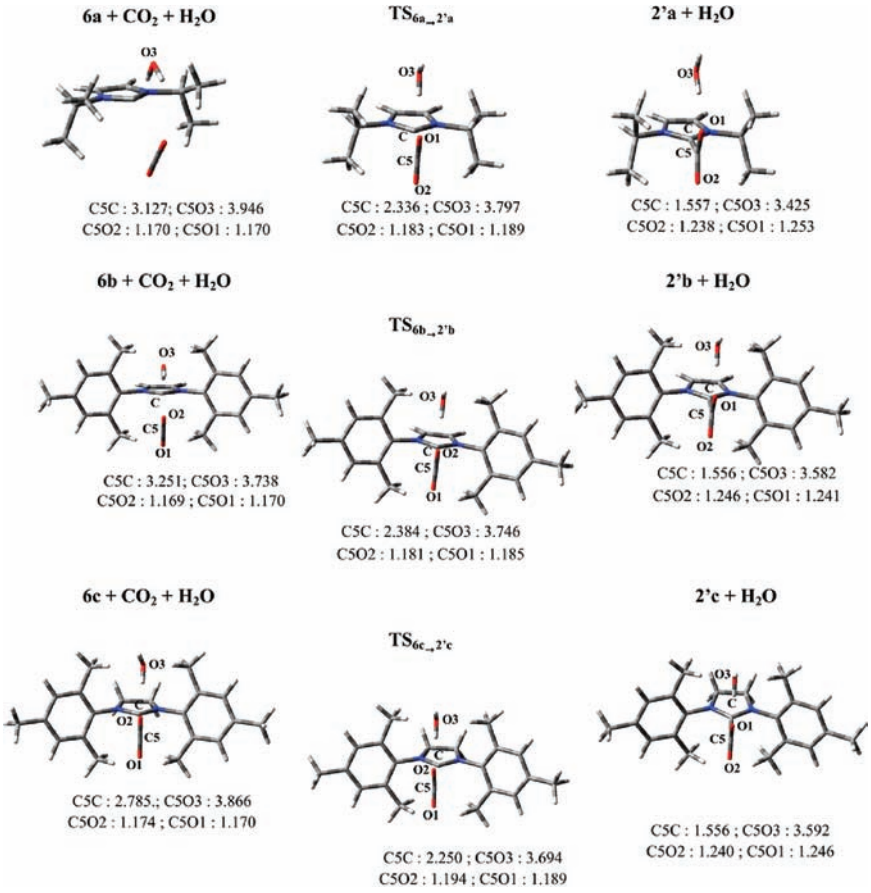

Figure 8. Geometrical structures and main bond lengths for the all the compounds involved in the **6**→**2**′ rearrangement (distances in Å).

stirred for 24 h, 88% and 83% conversion was obtained using **2b** and **2c**, respectively, attesting to the efficient NHC generation from these compounds (see Experimental Section).

Finally, given the growing attention of NHCs to trigger metal-free polymerization reactions for precision polymer synthesis,[3] the precursor **2c** [SIMes(H)][HCO_3] was evaluated as a precatalyst for the ROP of D,L-lactide (LA). It is noteworthy that this monomer was polymerized at RT in a THF solution, while others reported that masked NHCs required heating the reaction mixture (generally >60 °C).[7e−g,8] In addition, precatalyst **2c** was simply kept in air without any particular precautions. Benzyl alcohol (BnOH) was used as an initiator ([LA]/[BnOH]/[**2c**] = 26/1/0.1 and 68/1/0.1), in the presence of 10 mol % of **2c** relative to BnOH (Scheme 5). Again, 3 Å molecular sieves were added to the reaction mixture to avoid competitive initiation of the polymerization by H_2O generated from the [SIMes(H)]-[HCO_3] precatalyst. High monomer conversions (87 and 75%) were achieved in 3 to 6 h under such conditions, the resulting PLA being characterized by narrow dispersities (<1.07) and well controlled molar masses (M_{nSEC} = 4000 and 7800 g·mol^{-1}, measured by SEC in THF calibrated with PS standards; see Figure 4a), in agreement with the initial [LA]/[BnOH] feed ratio and the conversion. In the MALDI-ToF mass spectrum ([LA]/[BnOH]/[**2c**] = 26/1/0.1), only one series of signals was observed at m/z = 108.14 + 144.13 n + 23 (where 108.14 is the molar mass of the benzyloxy and H end-groups and 23 the molar mass of sodium ion), which perfectly matched the expected molar masses of the targeted BnOH-initiated [SIMes(H)]-[HCO_3]-catalyzed PLA (Figure 4b).

These results as a whole suggest that NHC−H_2CO_3 **2** do behave as masked NHCs in solution, at room temperature, regardless of the nature of the substituents on the nitrogen atoms and the presence or not of an unsaturation at C4 and C5 of the imidazole backbone. Attempts to spectroscopically characterize the generated NHCs **6** in solution so far failed, the dehydrated NHC−CO_2 adducts, **2**′, being the only product observed. To gain better insight into the generation of NHCs **6** from [NHC(H)][HCO_3] **2**, and into the facile transformation of **2** into **2**′ in solution, DFT calculations were performed at the B3LYP/6-31G** level of theory (see Supporting Information).

The reactions **2**→**6** were found to be reversible (Scheme 1, eq 3), regardless of the nature of the substituents on the nitrogen atoms. Indeed, very small energetic differences between **2** and **6** were calculated for the three transformations ($\Delta G_{2\rightarrow 6}$ = (−)0.2 − (−)2.6 kcal/mol). For each reaction, a transition state $TS_{2\rightarrow 6}$, connecting directly **2** and **6** and lying at 10.0, 7.5, and 10.2 kcal/mol above **6a**, **6b**, and **6c**, respectively, could be located on the potential energy surface (Figure 5). The geometry of the TS (Figure 6) indicates that the process is concerted for the three transformations and quasi synchronous for **2b**→**6b** and **2c**→**6c**. In the case of **2a**→**6a**, the transformation is asynchronous, the breaking of the C5−O2 bond being more advanced than the proton transfer of H1 from C to O2 in $TS_{6a\rightarrow 2a}$. The low energy barrier associated with the reversibility of this transformation agrees well with the NHC behavior of [NHC(H)][HCO_3] **2** observed in solution, at room temperature. The reactions of CO_2 with free NHCs **6** were also investigated computationally (Figure 7). Here again, the rather small differences calculated for the three

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transformations ($\Delta G_{6\rightarrow 2'}$ = (−)3.7 − (−)8.0 kcal/mol) indicate the reversibility of the process, regardless of the nature of the substituents on the nitrogen atoms. For each reaction, a transition state $TS_{6\rightarrow 2'}$ connecting directly **6** and **2′** and lying at 5.6, 6.3, and 2.7 kcal/mol above **6a**, **6b**, and **6c**, respectively, could be located on the potential energy surface (Figures 7 and 8 for geometrical parameters). The low energy barrier associated with the reversibility of the reaction accounts for the facile interconversion of [NHC(H)][HCO_3] **2** into NHC−CO_2 **2′** through the intermediacy of NHC **6**. This is also consistent with the fact that NHCs were not experimentally observed; it may be assumed that these intermediate species react very rapidly with CO_2 or (H_2O and CO_2), yielding the respective NHC−CO_2 and [NHC(H)][HCO_3] compounds, which are in equilibrium.

CONCLUSION

Anion metathesis of imidazolium chlorides with $KHCO_3$ provides a facile one step synthetic access to air stable imidazol(in)ium hydrogen carbonates ([NHC(H)][HCO_3]). On the basis of experimental NMR results, it can be evidenced that [NHC(H)][HCO_3] compounds are in equilibrium in solution with their NHC−CO_2 adduct counterparts, depending on the nature and water content of the solvent analysis. As supported by DFT calculations, these precursors can serve as a genuine source of NHCs in solution at RT, allowing an easy transfer of the carbene fragment to an organic substrate (e.g., CS_2) and to catalytically relevant transition metals (e.g., Pd, Au). We also report for the first time that these [NHC(H)]-[HCO_3] salts efficiently serve as precatalysts in both metal-free molecular and macromolecular syntheses, without any particular precautions of storage, as demonstrated by two selected organocatalyzed reactions (benzoin condensation and ring-opening polymerization of D,L-lactide). We postulate that the free NHC is generated in solution at RT from its [NHC(H)]-[HCO_3] precursor by deprotonation of the imidazolium cation and concomitant loss of H_2O and CO_2, *via* a concerted low energy pathway, as substantiated by DFT calculations.

We believe that the straightforward access to such precursors, which does not involve the generation of a free carbene at any point of their synthesis, coupled with their air and moisture stability both in the solid state and in solution should provide a competitive alternative to masked NHCs on a large scale. This opens avenues for practical use of these masked NHCs in organometallic chemistry and in various NHC-catalyzed molecular and macromolecular reactions.

ASSOCIATED CONTENT

Supporting Information

^1H and ^{13}C NMR spectra of **2a−c** and **4a**, the molecular structure, crystal data and structure refinement of **2a**, and Cartesian coordinates of all optimized structures 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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