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A Systematic Investigation of Factors Influencing the Decarboxylation of Imidazolium Carboxylates

Bret R. Van Ausdall, Jeremy L. Glass, Kelly M. Wiggins, Atta M. Aarif, and Janis Louie*

Department of Chemistry, Henry Eyring Building, University of Utah, 315 S. 1400 East, Salt Lake City, Utah 84112-0850

louie@chem.utah.edu

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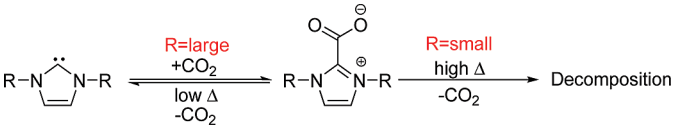

A series of 1,3-disubstituted-2-imidazolium carboxylates, an adduct of CO_2 and *N*-heterocyclic carbenes, were synthesized and characterized using single crystal X-ray, thermogravimetric, IR, and NMR analysis. The TGA analysis of the NHC-CO_2's shows that as steric bulk on the *N*-substituent increases, the ability of the NHC-CO_2 to decarboxylate increases. The comparison of NHC-CO_2's with and without methyls at the 4,5-position indicate that extra electron density in the imidazolium ring enhances the stability of an NHC-CO_2 thereby making it less prone to decarboxylation. Single crystal X-ray analysis shows that the torsional angle of the carboxylate group and the C−CO_2 bond length with respect to the imidazolium ring is dependent on the steric bulk of the *N*-substituent. Rotamers in the unit cell of a single crystal of I′BuPrCO$_2$ (**2f**) indicate that the C−CO_2 bond length increases as the *N*-substituents rotate toward the carboxylate moiety, which suggests that rotation of the *N*-substituents through the plane of the C−CO_2 bond may be involved in the bond breaking event to release CO_2.

Introduction

The capture of carbon dioxide by organic compounds has been a long-standing interest in organic chemistry.[1−4] Although the discovery of the reactivity of imidazolidenes to capture CO_2 was discovered a decade ago (eq 1),[5,6] this reaction and the resulting imidazolium carboxylates remain under-utilized. Initially, imidazolium carboxylates have been used as an air-stable precursor to imidazolidenes,[7] which are both highly synthetically useful ligands for transition metal catalysts[8] and potent nucleophilic organocatalysts.[9] In addition, the ability for NHCs to react with carbon dioxide (and other heterocumulenes) to afford stable zwitterions has been exploited to quench polymerizations catalyzed by NHCs.[10] More recently, imidazolium carboxylates themselves have demonstrated the ability to catalyze reactions such as the cyclotrimerization of isocyanates[11] and the coupling of epoxides and carbon dioxide.[12] Finally, imidazolium

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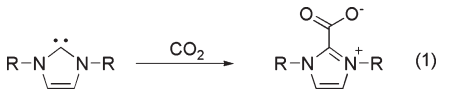
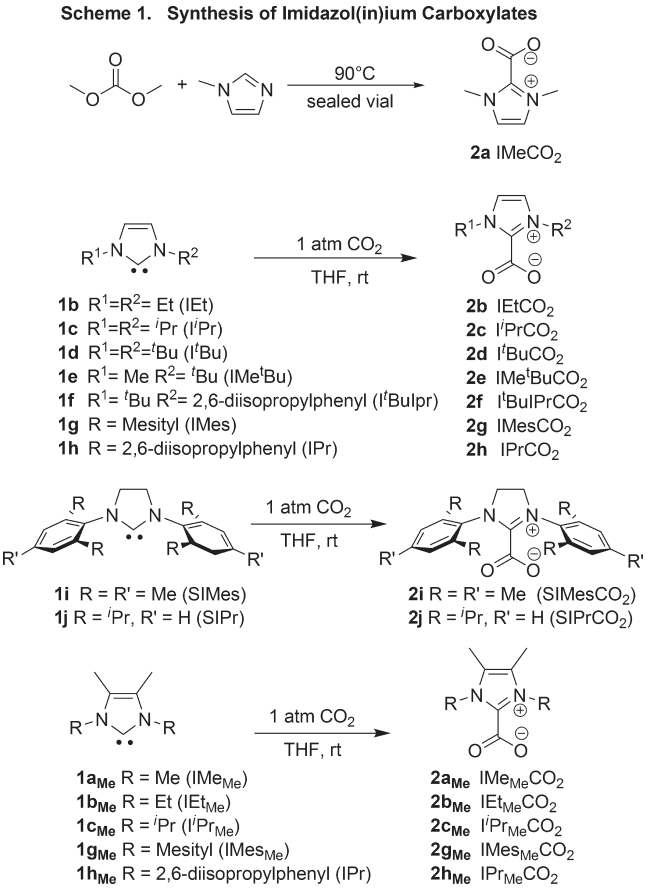
carboxylates have been shown to act as a CO_2 delivery agent in the carboxylation of acetophenone.[13] Despite these advances, the utility of imidazolium carboxylates remains sparse. In an effort to increase the function of these interesting carboxylates, we have synthesized a large array of imidazolium carboxylates where we have systematically altered the *N*-substituent and studied their propensity to undergo thermal decarboxylation.



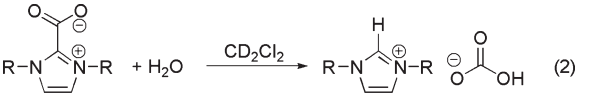
Results and Discussion

Synthesis of Imidazolium Carboxylates. A series of imidazolium carboxylates were prepared (Scheme 1). The smallest carboxylate (**2a**) was synthesized using Crabtree's modification of a literature procedure.[7] In all other cases, we found imidazolium carboxylates (**2b**−**2h**) were generated cleanly and in excellent yields from direct carboxylation of the NHC precursors. Simple *N*-alkyl (**1b**−**1e**) and -aryl imidazole (**1f**−**1h**) and -aryl imidazolin (**1i**−**1j**) carbenes were generated in situ from deprotonation of the corresponding imidazol(in)-ium salt with potassium hexamethyldisilylazide (KHMDS) in toluene. Interestingly, the standard deprotonation methods such as catalytic amounts of KO^{t}Bu with NaH[14] generally led to contaminated carboxylate. Furthermore, when 1 equiv of KO^{t}Bu was used to deprotonate the imidazolium salts, the *tert*-butanol that was produced could not be separated effectively from the carbene. Ultimately, carboxylates that were determined to be pure by elemental analysis were obtained through the reaction of carbon dioxide and carbenes that were prepared in situ via the deprotonation of the imidazol(in)ium salts in toluene with KHMDS. Importantly, the carbenes were filtered away from the potassium halide salt byproduct before exposure to carbon dioxide. This step is critical to obtain pure, salt-free imidazoylium carboxylates (**2b**−**2j**, vide infra). *N*-Alkyl carbenes that possess a methylated backbone (**1a$_{Me}$**−**1c$_{Me}$**) were prepared from the reduction of the corresponding thiourea with potassium and isolated prior to carboxylation.[15]

SCHEME 1. Synthesis of Imidazo(in)ium Carboxylates



Reactions with Water. The stability of the imidazolium carboxylates toward water was evaluated. When H_2O was introduced to a CD_2Cl_2 solution of $IMeCO_2$ (**2a**), $IEtCO_2$ (**2b**), I^iPrCO_2 (**2c**), or I^tBuCO_2 (**2d**), protonation occurred within minutes as indicated by the appearance of a new singlet at 9.10 ppm in the respective ^1H NMR spectra. Interestingly, an imidazolium carbonate[16] was formed that resulted from decarboxylation in addition to protonation (eq 2). Rogers and co-workers have prepared **3a$_{OCOOH}$** through a two-step reaction of **2a** and aqueous carbonic acid.



In contrast to *N*-alkyl imidazolium carboxylates, decarboxylation does not readily occur when water is added to

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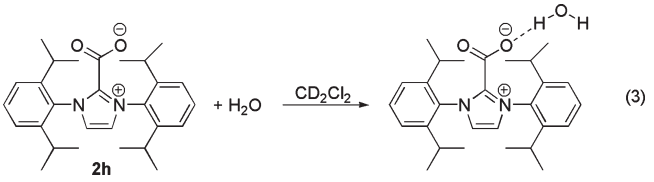
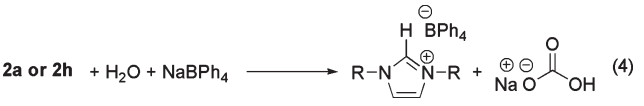
N-aryl imidazolium carboxylates. Specifically, when H_2O was added to a solution of **2h** in CD_2Cl_2, the signature imidazolium proton signal at 9.10 ppm that was observed with the alkyl carboxylates **2a**−**2d** did not appear. Instead, a new set of signals for the aryl and backbone protons was observed alongside the original signals for starting carboxylate, **2h**. The backbone, *ortho*, and *meta* aryl protons all moved downfield, shifting from 7.17 to 7.83 ppm, 7.28 to 7.37 ppm, and 7.51 to 7.6 ppm, respectively. We tentatively assign this species to an imidazolium carboxylate where the carboxylate is hydrogen-bonded to a water molecule (eq 3). The same phenomenon was observed when H_2O was added to aryl carboxylate $IMesCO_2$ (**2g**).



(3)

The addition of water to **2h** and **2a** in the presence of $NaBPh_4$ led to rapid and smooth decarboxylation (eq 4). $IPrBPh_4$ and $IMeBPh_4$, which both possess a distinct acidic proton (~9 ppm in the ^1H NMR spectrum), and sodium carbonate were formed quantitatively.



(4)

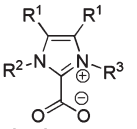
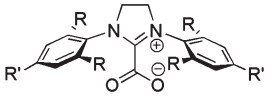
IR Frequency Analysis. The imidazolium carboxylates display distinct carbonyl stretching frequencies (Table 1). *N*-Alkyl imidazolium carboxylates (**2a**−**2e**) have COO^- asymmetric stretching frequencies that are in the low to mid 1600 cm^{-1}. A slight trend between the stretching frequencies and the size of the *N*-substituent was observed. As the alkyl substituent changes from Me to Et to *i*Pr (**2a**, **2b**, **2c**), the C=O stretching frequencies gradually increase. However, when the alkyl substituent is replaced with the bulky ^{t}Bu group (**2d**), the C=O stretching dramatically decreases by 37 cm^{-1}. The hybrid NHC-CO_2 **2e** has an intermediate frequency of 1647 cm^{-1}, between $IMeCO_2$ (**2a**) and I^tBuCO_2 (**2d**).

N-Aryl imidazolium carboxylates have higher C=O stretching frequencies than their *N*-alkyl counterparts. Interestingly, the stretching frequencies of $IMesCO_2$ (**2g**) and $IPrCO_2$ (**2h**) are almost identical, which suggests that the carbon−oxygen bond is less affected by the *ortho* substituents (i.e., the methyl of the $IMesCO_2$ and the *i*Pr of the $IPrCO_2$) than in the *N*-alkyl series (i.e., **2a** vs **2c**).

Modification of the imidazolium backbone, through either methylation or saturation, does not have a large influence on the C=O stretching frequencies. For example, the stretching frequency of **2b** and $\mathbf{2b_{Me}}$ differ by only 3 cm^{-1}. In addition, methylation of the backbone causes the C=O stretching frequency to increase for $\mathbf{2a_{Me}}$ (relative to **2a**) but causes a decrease for $\mathbf{2c_{Me}}$ (relative to **2c**). Imidazolinium carboxylates (**2i** and **2j**) displayed stretching frequencies that were only 5 cm^{-1} higher than their unsaturated analogues.

Thermogravimetric Analysis. The imidazolium carboxylates were each evaluated by thermogravimetric analysis

TABLE 1. IR Stretching Frequencies of Imidazol(in)ium Carboxylates

Entry	Carboxylate	ν_{COasym} (cm^{-1})
		
1	**2a** R^1=H R^2=R^3=Me ($IMeCO_2$)	1653
2	**2b** R^1=H R^2=R^3=Et ($IEtCO_2$)	1654
3	**2c** R^1=H R^2=R^3=^{i}Pr (I^iPrCO_2)	1666
4	**2d** R^1=H R^2=R^3=^{t}Bu (I^tBuCO_2)	1629
5	**2e** R^1=H R^2=Me R^3= ^{t}Bu (IMe^tBuCO_2)	1647
6	$\mathbf{2a_{Me}}$ R^1=Me R^2=R^3=Me ($IMe_{Me}CO_2$)	1669
7	$\mathbf{2b_{Me}}$ R^1=Me R^2=R^3=Et ($IEt_{Me}CO_2$)	1657
8	$\mathbf{2c_{Me}}$ R^1=Me R^2=R^3=*i*Pr (I*i*$Pr_{Me}CO_2$)	1662
9	**2f** R^1=^{t}Bu R^2= 2,6-diisopropylphenyl ($I^tBuIprCO_2$)	1675
10	**2g** R^1=H R^2=R^3=Me ($IMesCO_2$)	1675
11	$\mathbf{2g_{Me}}$ R^1=Me R^2=R^3=Me ($IMes_{Me}CO_2$)	1674
12	**2h** R^1=H R^2=R^3=2,6-diisopropylphenyl ($IPrCO_2$)	1678
13	$\mathbf{2h_{Me}}$ R^1=Me R^2=R^3=2,6-diisopropylphenyl ($IPr_{Me}CO_2$)	1683
		
11	**2i** R = R' = Me ($SIMesCO_2$)	1680
12	**2j** R = *i*Pr, R' = H ($SIPrCO_2$)	1683

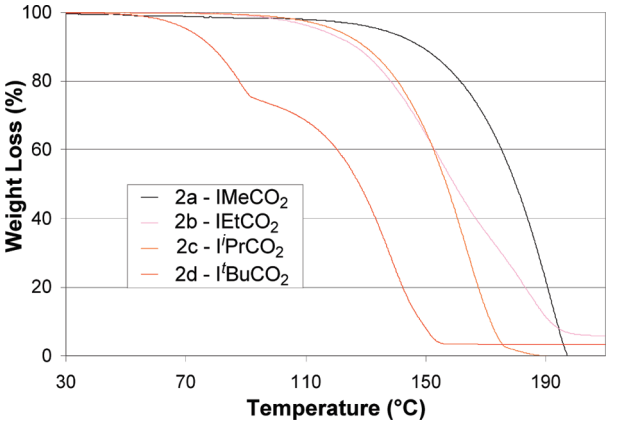


FIGURE 1. TGA of alkyl NHC-CO_2's **2a**−**2d**.

(TGA). During the investigation, we found that the amount of imidazolium carboxylate that was subjected to TGA had a profound effect on the results. For example, the TGA analysis of larger samples of $IPrCO_2$ (**2h**) afforded higher decarboxylation temperatures than smaller samples.[17] As such, subsequent TGAs were consistently performed with 3.5 mg of imidazolium carboxylate.

TGA of *N*-Alkyl Imidazolium Carboxylates (2a−2d). The TGA of a series of *N*-alkyl NHC-CO_2's where the size of the *N*-alkyl substituent was increased in size (i.e., Me (**2a**), Et (**2b**), *i*Pr (**2c**), and ^{t}Bu (**2d**)) is shown in Figure 1. It is clear that an increase in substituent size leads to a decrease in decarboxylation temperature. At the two extremes, $IMeCO_2$ (**2a**) begins to decompose at 162 °C, whereas I^tBuCO_2 (**2d**) loses CO_2 and decomposes at a much lower temperature

(17) See Supporting Information for the TGA data with $IPrCO_2$ at varied masses.

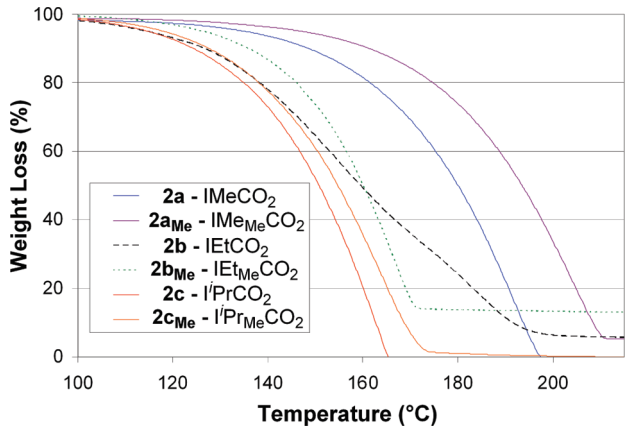


FIGURE 2. TGA analysis of alkyl NHC-CO_2's $\mathbf{2a_{Me}}$–$\mathbf{2c_{Me}}$ and **2a**–**2c**.

(71 °C) for a difference in decarboxylation temperatures of 91 °C. Only $IEtCO_2$ (**2b**) does not seem to follow this trend and undergoes decarboxylation at 128 °C, i.e., 12 °C lower than the decarboxylation temperature of I^iPrCO_2 (**2c**). Interestingly, only I^tBuCO_2 displays a biphasic TGA curve suggesting that a short-lived intermediate, presumably I^tBu, is generated. Nevertheless, CO_2 was detected via mass spectrometry at the onset of weight loss in each TGA analysis of **2a**–**2d**.

TGA of *N*-Alkyl Imidazolium Carboxylates Possessing a Methylated Backbone ($\mathbf{2a_{Me}}$–$\mathbf{2d_{Me}}$). The collective TGA spectra of the 4,5-dimethyl *N*-alkyl NHC-CO_2 compounds $\mathbf{2a_{Me}}$–$\mathbf{2c_{Me}}$ as well as **2a**–**2c** are shown in Figure 2 and are summarized in Table 2. In general, imidazolium carboxylates possessing increasing steric hindrance of the *N*-alkyl substituent displayed lower decarboxylation temperatures. For example, decarboxylation began at 182 °C for $IMe_{Me}CO_2$ ($\mathbf{2a_{Me}}$) and at 139 °C for $IiPr_{Me}CO_2$ ($\mathbf{2c_{Me}}$).

An interesting effect caused by the methylation of the backbone of the NHC-CO_2's was also observed. The TGAs of $\mathbf{2a_{Me}}$ displayed a 20 °C increase in the decarboxylation/decomposition temperatures over **2a** (i.e., 182 and 162 °C, respectively). In contrast, $\mathbf{2c_{Me}}$ and **2c**, both of which possess isopropyl *N*-substituents, have almost identical decarboxylation/decomposition temperatures (i.e., a difference of only 1 °C, entries 4 and 5, Table 2).

Computations performed by Yates et al. have shown that methylation of the backbone increases the basicity of a carbene relative to that of the unsaturated parent carbene (Table 2).[18] As electron density of a particular carbene increases, the NHC-CO_2 would most likely possess a stronger $C_{carbene}$–CO_2 bond, which would result in an elevated decarboxylation temperature. Thus, the higher decarboxylation temperature and inferred increased C–CO_2 bond strength of $\mathbf{2a_{Me}}$ (182 °C) relative to that of **2a** (162 °C) may be attributed to the higher pK_a of the parent carbene (i.e., $\mathbf{1a_{Me}}$ versus **1a**). Although $\mathbf{1c_{Me}}$ has a higher pK_a than **1c**, their corresponding carboxylates, **2c** and $\mathbf{2c_{Me}}$, decarboxylate at almost identical temperatures. Thus, as the *N*-substituents become larger, the steric bulk of the highly branched *N*-substituents overrides the enhanced

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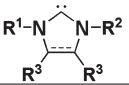
TABLE 2. Calculated pK_a's of Carboxylate Precursor Carbenes with Decarboxylation Temperatures of the Corresponding NHC-CO_2

Entry		pK_a	-CO_2 of NHC·CO_2 (°C)
1	R^1=R^2=Me; R^3=H (**1a**)	27.4±0.4	162
2	R^1=R^2=Me; R^3=Me ($\mathbf{1a_{Me}}$)	29.5±0.3	182
3	R^1=R^2=Me, R^3=saturated	28.5±0.4	-
4	R^1=R^2=^{i}Pr; R^3=H (**1c**)	28.2 0.3	140
5	R^1=R^2=^{i}Pr; R^3=Me ($\mathbf{1c_{Me}}$)	30.4 0.3	139
6	R^1=R^2=^{t}Bu; R^3=H (**1d**)	28.3±0.1	71

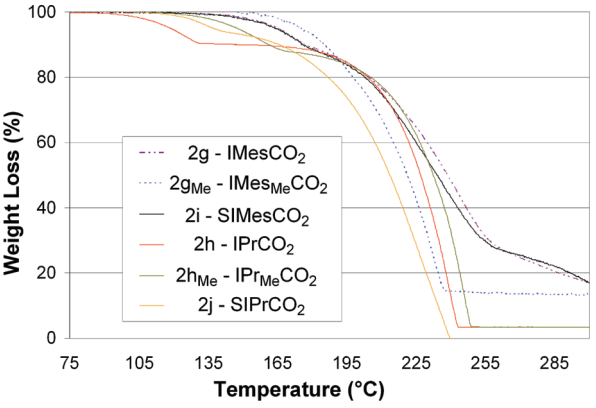


FIGURE 3. TGA analysis of aryl NHC-CO_2's **2g**–**2j**, $\mathbf{2g_{Me}}$, and $\mathbf{2h_{Me}}$.

stability of the $C_{carbene}$–CO_2 bond provided by the extra electron density at the carbene.

TGA of *N*-Aryl Imidazolium Carboxylates (2g–2j, $\mathbf{2g_{Me}}$–$\mathbf{2h_{Me}}$). With NHC-CO_2's **2g**–**2j**, $\mathbf{2g_{Me}}$, and $\mathbf{2h_{Me}}$ in hand, the TGAs of structurally similar, but electronically different, aryl NHC-CO_2's could be compared (Figure 3). As noted above, methylation of the backbone on the imidazole ring results in an increased pK_a. In the computational study by Yates, saturation of the backbone purportedly leads to a loss in aromaticity in the imidazole ring thereby also resulting in a higher pK_a. The NHC-CO_2 series (**2h**, $\mathbf{2h_{Me}}$, and **2j**) possessing *N*-(2,6-diisopropyl)phenyl substituents (i.e., IPr) displays decarboxylation temperatures that correlate directly to the increased electron density in the imidazole ring. For example, both $SIPrCO_2$ (**2j**) and $IPr_{Me}CO_2$ ($\mathbf{2h_{Me}}$) possess higher decarboxylation temperatures than $IPrCO_2$ (**2h**). $SIPrCO_2$ (**2j**) decarboxylates at 136 °C and $IPr_{Me}CO_2$ ($\mathbf{2h_{Me}}$) decarboxylates at 120 °C, while $IPrCO_2$ (**2h**) decarboxylates at 108 °C. Biphasic decomposition was observed in all cases, similar to what was observed in the TGA analysis of I^tBuCO_2 (**2d**). The biphasic decomposition suggests that a stable intermediate is formed after decarboxylation. Indeed, when the TGA of $IPrCO_2$ (**2h**) was interrupted at 108 °C, the ^{1}H NMR analysis of the residual solid displayed a spectrum identical to an authentic sample of the parent NHC, IPr. Thus, in some cases, decarboxylation occurs at a lower temperature than the decomposition of the parent carbenes.

When the *N*-substituent is replaced with (2,4,6-trimethyl)-phenyl groups (i.e., IMes), the decarboxylation temperature for $IMes_{Me}CO_2$ ($\mathbf{2h_{Me}}$), which possesses a methylated backbone, is once again higher than for $IMesCO_2$ (**2h**) (193

TABLE 3. IR, Decarboxylation Temperature and C−CO_2 Bond Lengths of the NHC-CO_2's

entry	carboxylate	ν_{COasym} (cm^{-1})	$-CO_2$ temp (°C)	C−CO_2 length bond (Å)
1	**2a**	1653	162	1.523
2	**32**	1654	128	NA
3	**2c**	1666	140	NA
4	**2d**	1629	71	NA
5	**2e**	1647	117	NA
6	**$2a_{Me}$**	1669	182	1.521
7	**$2b_{Me}$**	1657	144	1.535
8	**$2c_{Me}$**	1662	139	1.536
9	**2f**	1675	129	1.525−1.544
10	**2g**	1675	155	NA
11	**$2g_{Me}$**	1674	193	NA
12	**2h**	1678	108	1.536
13	**$2h_{Me}$**	1683	136	1.542
45	**2i**	1680	156	NA
15	**2j**	1683	120	1.535

and 155 °C, respectively). However, the saturated analogue $SIMesCO_2$ (**2j**) decarboxylates at 156 °C, a temperature that is not markedly different than the decarboxylation temperature of $IMesCO_2$ (**2h**). Thus, simple pK_a effects may not be the only factor that determines the decarboxylation ability of the NHC-CO_2 complexes. Alternatively, the difference in electron density of saturated and unsaturated NHCs may not be significant. Indeed, Nolan et al. reported the CO stretching frequencies of various saturated and unsatured NHC-ligated metal carbonyl were almost identical suggesting similar σ-donor capabilities of saturated and unsaturated NHCs.[19] Furthermore, conflicting reports regarding the effect of saturation on the electron density of the NHC exist.[20]

TGA of Asymmetric Imidazolium Carboxylates 2e and 2f. The TGA of asymmetric imidazolium carboxylates IMeI^{t}BuCO$_2$ (**2e**) and I^{t}BuIPrCO$_2$ (**2f**) were also evaluated (Figure 4). Not surprisingly, decarboxylation/decomposition of IMeI^{t}BuCO$_2$ (**2e**) occurred at 117 °C, a temperature in between the decarboxylation temperatures of $IMeCO_2$ (**2a**) and I^{t}BuCO$_2$ (**2d**). In addition, a one-step decarboxylation/decomposition was observed for **2e**. However, the low decomposition temperature of **2e** relative to other *N*-alkyl imidazolium carboxylates **2a**−**2c** suggests that the one *tert*-butyl group plays a significant role in the lowering the decarboxylation temperature of **2e**. Despite the increased bulkiness of the ^{t}Bu group relative to the 2,6-diisopropylphenyl group,[19] the decarboxylation temperature of **2f** was strikingly similar to that of $IPrCO_2$ (**2h**). However, no prolonged carbene intermediate was observed.

Single Crystal X-ray Analysis. The structures of **$2a_{Me}$**, **$2b_{Me}$**, **$2i_{Me}$**, and **2f** were solved using single crystal X-ray crystallography. Selected bond lengths, bond angles, dihedral angles, and structures of all solved NHC-CO_2's are listed in Table 4.[5a,c,11] For comparison, a summary of all of the decarboxylation temperatures, IR stretching frequencies, and C−CO_2 lengths are listed in Table 3.

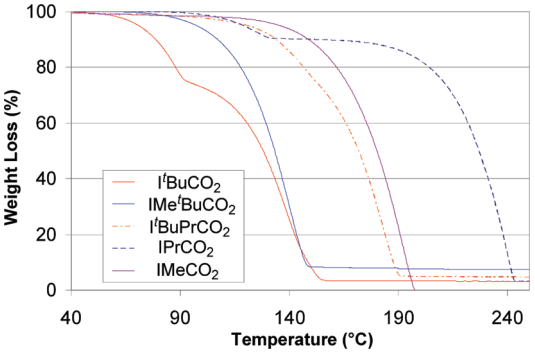


FIGURE 4. TGA analysis of asymmetric NHC-CO_2's **2e** and **2f**.

An increase in the size of the *N*-alkyl substituent causes the N−C_2 bond length to decrease. Specifically, this bond length decreases from 1.359 to 1.341 to 1.336 Å in $IMe_{Me}CO_2$ (**$2a_{Me}$**), $IEt_{Me}CO_2$ (**$2b_{Me}$**), and $I^iPr_{Me}CO_2$ (**$2c_{Me}$**), respectively. In contrast, the N_1−C_2−N_2 bond angle steadily increases from 105.32° in **$2a_{Me}$** to 108.02° in **$2c_{Me}$**. Less of an effect is observed on the C_6−O bond lengths. For example, $IEt_{Me}CO_2$ (**$2b_{Me}$**) and $I^iPr_{Me}CO_2$ (**$2c_{Me}$**) both possess a C_6−O bond length of 1.244 Å, although this bond length is significantly longer than the C_6−O bond length of **$2a_{Me}$** (1.230 Å). A similar phenomenom is observed with the C_2−C_6 bond lengths. that is, the C_2−C_6 bond lengths of $IEt_{Me}CO_2$ (**$2b_{Me}$**) and $I^iPr_{Me}CO_2$ (**$2c_{Me}$**) do not greatly differ (1.535 Å and 1.536 Å, respectively) but are significantly larger than the C_2−C_6 bond length of **$2a_{Me}$** (1.521 Å). A direct correlation exists between the C_2−C_6 bond lengths and decarboxylation/decomposition temperature. **$2a_{Me}$** has both a significantly smaller bond length and a higher decarboxylation temperature than **$2b_{Me}$** and **$2c_{Me}$** (Table 4). However, the differences in C_2−C_6 bond lengths as well as decarboxylation temperatures are small between **$2b_{Me}$** and **$2c_{Me}$**.

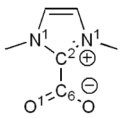
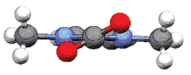
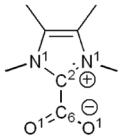
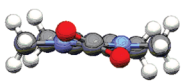
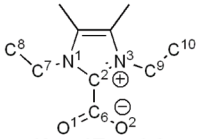
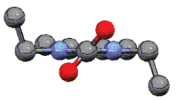
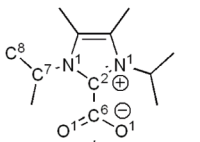
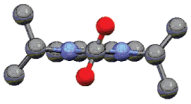
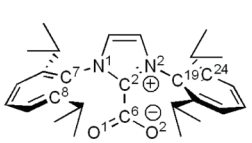
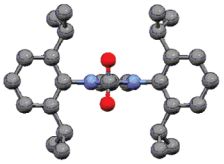
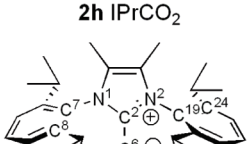
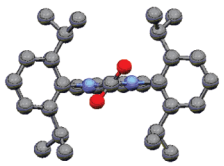
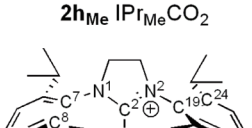
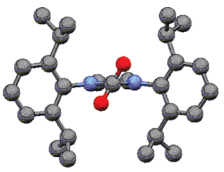
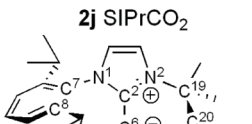
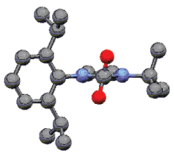
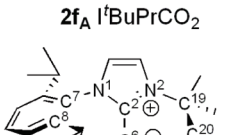
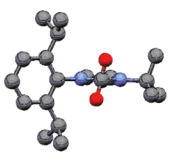
Methylation of the backbone appears to cause predictable changes to the structure. Both N−C_2 bond lengths of $IMe_{Me}CO_2$ (**$2a_{Me}$**) and $IPr_{Me}CO_2$ (**$2h_{Me}$**) are longer by 0.014 Å than their unmethylated counterparts $IMeCO_2$ (**2a**) and $IPrCO_2$ (**2h**). In addition, both C_6−O bond lengths of $IMe_{Me}CO_2$ (**$2a_{Me}$**) and $IPr_{Me}CO_2$ (**$2h_{Me}$**) are shorter by 0.010 Å. Interestingly, less of a difference is observed between the C_2−C_6 bond lengths (i.e., 0.002 and 0.006 Å differences, respectively).

Saturation of the backbone also appears to cause changes to the structure. For example, the N−C_2 bond lengths of $SIPrCO_2$ (**2j**) is 0.009 Å shorter than that of $IPrCO_2$ (**2h**). The C_6−O bond lengths of $SIPrCO_2$ (**2j**) is 0.015 Å longer than that of $IPrCO_2$ (**2h**). However, no distinct difference is observed in the C_2−C_6 bond length of $SIPrCO_2$ (**2j**) and $IPrCO_2$ (**2h**). Thus, saturation appears to have the opposite effect on the structures of the imidazolium carboxylates than methylation of the backbone.

As steric bulk is introduced into the *N*-substituents of an NHC-CO_2, the cant of the CO_2 moiety becomes more pronounced with regard to the imidazole ring. The carboxylate torsional angles for NHC-CO_2's **$2a_{Me}$**, **$2b_{Me}$**, and **$2c_{Me}$** are 22.40°, 49.16°, and 68.96°, respectively. As the torsional angle of the carboxylate moiety of the

(19) Dorta, R.; Stevens, E. D.; Scott, N. M.; Costabile, C.; Cavallo, L.; Hoff, C. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2005**, *127*, 2485–2495.
(20) (a) Khramov, D. M.; Rosen, E. L.; Er, J. A. V.; Vu, P. D.; Lynch, V. M.; Bielawski, C. W. *Tetrahedron* **2008**, *64*, 6853. (b) Khramov, D. M.; Lynch, V. M.; Bielawski, C. W. *Organometallics* **2007**, *26*, 6042.

TABLE 4. Structural Features of 2a, $2a_{Me}$, $2b_{Me}$, $2c_{Me}$, 2i, $2i_{Me}$, 2g, and the Rotamer of 2g

NHC·CO_2	Bond Lengths (Å)		Bond/Dihedral Angles (°)		Structure
 **2a** $IMeCO_2$	N_1-C_2	1.345	N_1-C_2-N_2	107.15	
	N_3-C_2	-	O_1-C_1-O_2	129.78	
	C_6-O_1	1.240	N_1-C_2-C_6-O_1	29.03	
	C_6-O_2	-	C_2-N_1-C_7-H_c	61.49	
	C_2-C_6	1.523			
 **$2a_{Me}$** $IMe_{Me}CO_2$	N_1-C_2	1.359	N_1-C_2-N_2	105.32	
	N_3-C_2	-	O_1-C_1-O_2	129.52	
	C_6-O_1	1.230	N_1-C_2-C_6-O_1	22.40	
	C_6-O_2	-	C_2-N_1-C_7-H_c	7.18	
	C_2-C_6	1.521			
 **$2b_{Me}$** $IEt_{Me}CO_2$	N_1-C_2	1.341	N_1-C_2-N_2	107.49	
	N_3-C_2	1.338	O_1-C_1-O_2	130.69	
	C_6-O_1	1.244	N_1-C_2-C_6-O_1	47.54	
	C_6-O_2	1.239	N_3-C_2-C_6-O_2	50.78	
	C_2-C_6	1.535	C_2-N_1-C_7-C_8	78.50	
			C_2-N_1-C_9-C_{10}	79.94	
 **$2c_{Me}$** $I^iPr_{Me}CO_2$	N_1-C_2	1.336	N_1-C_2-N_2	108.02	
	N_3-C_2	-	O_1-C_1-O_2	131.25	
	C_6-O_1	1.244	N_1-C_2-C_6-O_1	68.96	
	C_6-O_2	-	N_3-C_2-C_6-O_2	-	
	C_2-C_6	1.536	C_2-N_1-C_7-C_8	100.99	
			C_2-N_1-C_9-C_{10}	-	
 **2h** $IPrCO_2$	N_1-C_2	1.335	N_1-C_2-N_2	107.09	
	N_3-C_2	1.332	O_1-C_1-O_2	129.88	
	C_6-O_1	1.222	N_1-C_2-C_6-O_1	88.14	
	C_6-O_2	1.225	N_3-C_2-C_6-O_2	89.75	
	C_2-C_6	1.536	C_2-N_1-C_7-C_8	90.64	
			C_2-N_1-C_{19}-C_{24}	88.75	
 **$2h_{Me}$** $IPr_{Me}CO_2$	N_1-C_2	1.341	N_1-C_2-N_2	107.22	
	N_3-C_2	1.338	O_1-C_1-O_2	131.31	
	C_6-O_1	1.232	N_1-C_2-C_6-O_1	46.72	
	C_6-O_2	1.233	N_3-C_2-C_6-O_2	49.46	
	C_2-C_6	1.542	C_2-N_1-C_7-C_8	84.16	
			C_2-N_1-C_{19}-C_{24}	81.69	
 **2j** $SIPrCO_2$	N_1-C_2	1.326	N_1-C_2-N_2	111.94	
	N_3-C_2	1.317	O_1-C_1-O_2	131.78	
	C_6-O_1	1.237	N_1-C_2-C_6-O_1	57.99	
	C_6-O_2	1.234	N_3-C_2-C_6-O_2	59.85	
	C_2-C_6	1.535	C_2-N_1-C_7-C_8	80.28	
			C_2-N_1-C_{19}-C_{24}	91.50	
 **$2f_A$** $I^tBuPrCO_2$	N_1-C_2	1.341	N_1-C_2-N_2	107.14	
	N_3-C_2	1.348	O_1-C_1-O_2	130.43	
	C_6-O_1	1.243	N_1-C_2-C_6-O_1	79.50	
	C_6-O_2	1.222	N_3-C_2-C_6-O_2	76.72	
	C_2-C_6	1.525	C_2-N_1-C_7-C_8	86.87	
			C_2-N_1-C_{19}-C_{20}	27.92	
 **2f** $I^tBuPrCO_2$	N_1-C_2	1.348	N_1-C_2-N_2	107.82	
	N_3-C_2	1.334	O_1-C_1-O_2	130.73	
	C_6-O_1	1.238	N_1-C_2-C_6-O_1	79.01	
	C_6-O_2	1.226	N_3-C_2-C_6-O_2	79.18	
	C_2-C_6	1.544	C_2-N_1-C_7-C_8	91.10	
			C_2-N_1-C_{19}-C_{20}	26.45	

$NHC\text{-}CO_2$ becomes larger. The decarboxylation temperature of the $NHC\text{-}CO_2$ decreases. The decarboxylation temperatures for $\mathbf{2a_{Me}}$, $\mathbf{2b_{Me}}$, and $\mathbf{2c_{Me}}$ are 182, 144, and 139 °C, respectively. This is further exemplified with $IPrCO_2$ (**2h**), where the CO_2 group is rotated even more than $\mathbf{2c_{Me}}$ (i.e., 88°) and possesses a lower decarboxylation temperature of 108 °C.

Although $IPr_{Me}CO_2$ ($\mathbf{2h_{Me}}$) and $SIPrCO_2$ (**2j**) possess very large *N*-substitutents, methylation and saturation of the imidazole backbone decrease the cant of the CO_2 with

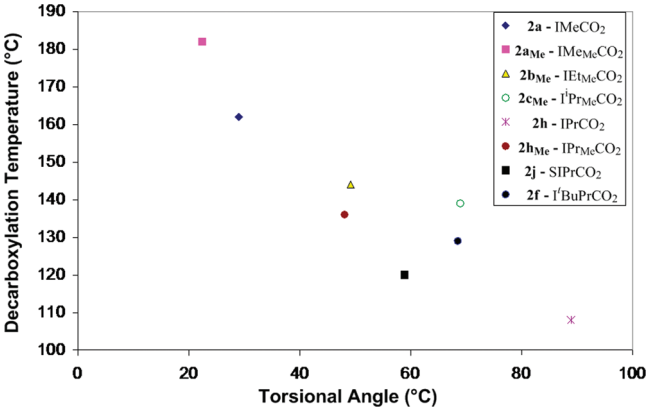


FIGURE 5. Graph of decarboxylation temperatures versus the torsional angle of imidazolium carboxylates (i.e., the N_1-C_2-C_6-O_1 angle).

respect to the imidazole ring. That is, the carboxylate torsional angles for $IPr_{Me}CO_2$ (**2h$_{Me}$**) and $SIPrCO_2$ (**2j**) are 46.72° and 57.99°, significantly lower than the 88.14° observed in $IPrCO_2$ (**2h**). The decreased carboxylate torsional angles are exemplified in the decarboxylation temperatures. Indeed, $IPr_{Me}CO_2$ (**2h$_{Me}$**) and $SIPrCO_2$ (**2j**) decarboxylate at higher temperatures (i.e., 120° for **2j** and136° for **2h$_{Me}$**) than $IPrCO_2$ (**2h**) (108°).

Imidazolium carboxylates are more stable when the carboxylates lie in the same plane as the imidazolium ring since this geometry allows for the most resonance stabilization. Not surprisingly, our data suggest that decarboxylation temperatures are directly related to the carboxylate torsional angles (Figure 5). Specifically, an increase in torsional angle leads to a decrease in decarboxylate temperature. Steric interactions can lead to an increase in the torsional angle and subsequently lead to a decrease in decarboxylation temperature. Although electronic effects can counteract some of the steric effects (i.e., $IPrCO_2$ (**2h**) versus $IPr_{Me}CO_2$ (**2h$_{Me}$**) versus $SIPrCO_2$ (**2j**)), the relationship between the decarboxylation temperature and the torsional angle remains.

Conclusion

The synthesis of a series of NHC-CO_2's from the reaction of *N*-heterocyclic carbene and carbon dioxide allowed for a thorough study decarboxylating ability of this class of molecules. Thermogravimetric analysis, single crystal X-ray crystallography, and IR analysis were used to study potential variables involved in a particular NHC-CO_2's ability to decarboxylate. TGA analysis of the NHC-CO_2's clearly shows that the decarboxylating ability of an NHC-CO_2 is largely dependent on the steric bulk of the *N*-subsituent. The TGA analysis of **2a**−**2d** and **2a$_{Me}$**−**2c$_{Me}$** also shows that electronics in this system can be overridden by steric bulk. Single crystal X-ray of a series of NHC-CO_2's indicates that the carbon−carbon bond-breaking event may be mechanical in nature.

Experimental Section

General Procedures. All listed procedures were performed under a N_2 atmosphere unless otherwise stated. ^{1}H and ^{13}C NMR spectra of pure compounds were acquired at 300 and 75 MHz, respectively, unless otherwise noted and were referenced to residual protiated solvent. IR spectra were collected on a Bruker Tensor 27 instrument. TGA was performed on a TA Instruments TGA2050. The TGA data was recorded using Therma Advantage, ver. 1.14. All TGA analyses were performed in a N_2 atmosphere at a heating rate of 5 °C/min. All glassware was dried in an oven at 130 °C for 24 h prior to use. Elemental analyses were performed by Midwest Microlabs, LLC.

Materials. Solvents were purified and deoxygenated by passing through packed silica columns. All oil from NaH was removed by thorough washing with hexanes. KO^{t}Bu (98%) was purchased from Sigma-Aldrich and used without further purification. KHMDS (95%) was purchased from Sigma-Aldrich and used without further purification. All other reagents were purchased from standard chemical providers without further purification, unless specified. All NMR solvents were thoroughly dried using standard procedures prior to use. The NHC-CO_2 **2a** was synthesized using a literature procedure.[7a] Imidazolium salts **3h** and **3i** were synthesized using a literature procedure.[21]

General Synthesis A for NHC-CO_2's 2b−2j, 2g$_{Me}$, and 2h$_{Me}$. The imidazolium salt[22] (1 equiv) and toluene were put into a 100-mL round-bottom flask equipped with a stir-bar. To this suspension was added KHMDS (1 equiv). The solution was allowed to stir for 2 h before being filtered through Celite. The carbene solution was then transferred to a 100-mL Schlenk flask, and CO_2 was introduced into the flask. The NHC-CO_2 precipitated as a white solid and was collected via filtration, washed with ether, and dried *in vacuo*.

2b: General Synthesis A was used with 1,3-diethylimidazolium iodide (0.28 g, 1.2 mmol), toluene (50 mL), and KHMDS (0.25 g, 1.2 mmol) to afford 1,3-diethylimidazolium-2-carboxylate **2b** as a white powder (0.06 g, 35%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.05 (s, 2H, *H*C-C=C-C*H*), 4.57 (quartet, 4H, J = 7.3 Hz, *N*-CH_2-CH$_3$), 1.491 (t, 6H, J = 7.3 Hz, N-CH$_2$-CH_3). ^{13}C NMR (75.6 MHz, CD_2Cl_2): δ 155.0, 143.4, 120.2, 45.6, 16.2. IR (KBr) 1654, 1507, 1385, 1350, 1216 cm^{-1}. Anal. Calcd for $C_8H_{12}N_2O_2$: C, 57.13; H, 7.19; N, 16.66; O, 19.03; Found: C, 56.79; H, 7.39; N, 16.77; O, 19.97.

2c: General Synthesis A was used with 1,3-diisopropylimidazolium iodide (0.72 g, 2.6 mmol), toluene (75 mL), and KHMDS (0.54 g, 2.6 mmol) to afford 1,3-diisopropylimidazolium-2-carboxylate **2c** as a white powder (0.17 g, 29%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.12 (s, 2H, *H*C-C=C-C*H*), 5.55 (septet, 2H, J = 6.6 Hz, *N*-C*H*-(CH$_3$)$_2$), 1.47 (d, 12H, J = 6.7 Hz, *N*-CH-(CH_3)$_2$). ^{13}C NMR (75.6 MHz, CD_2Cl_2): δ 155.4, 144.0, 116.6, 51.5, 23.3. IR (KBr) 1666, 1487, 1371, 1329, 1220 cm^{-1}. Anal. Calcd for $C_{10}H_{16}N_2O_2$: C, 61.20; H, 8.22; N, 14.27; O, 16.31; Found: C, 61.35; H, 8.16; N, 14.28; O, 16.51.

2e: General Synthesis A was used with 1-*tert*-butyl-3-methylimidazolium iodide (0.69 g, 2.6 mmol), toluene (75 mL), and KHMDS (0.54 g, 2.6 mmol) to afford 1-methyl-3-*tert*-butylimidazolium-2-carboxylate **2e** as a gray powder (0.30 g, 48%). ^{1}H NMR (300 MHz, CD_3CN): δ 7.24 (d, 1H, J_{H-H} = 2.0 Hz, (CH$_3$-N)(*H*)C=C(H)(N-C(CH$_3$)), 7.08 (d, 1H, J_{H-H} = 2.0 Hz, (CH$_3$-N)(H)C=C(*H*)(N-C(CH$_3$)), 3.754 (s, 3H, (CH_3-N)(H)-C=C(H)(N-C(CH$_3$)), 1.713 (s, 9H, (CH$_3$-N)(H)C=C(H)(N-C-(CH_3)). ^{13}C NMR (75.6 MHz, CD_3CN): δ.147.7, 119.6, 116.8, 61.7, 36.1, 29.8. IR (KBr) 1647, 1437, 1385, 1342, 12119 cm^{-1}. Anal. Calcd for $C_9H_{14}N_2O_2$: C, 59.32; H, 7.74; N, 15.37; O, 17.56; Found: C, 59.30; H, 7.62; N, 15.34; O, 17.30.

2f: General Synthesis A was used with 1-(2,6-diisopropylphenyl)-3-*tert*-butylimidazolium tetrefluoroborate (0.42 g, 1.1 mmol), toluene (75 mL), and KHMDS (0.24 g, 1.1 mmol) to afford 1-(2,6-diisopropylphenyl)-3-*tert*-butylimidazo-

(21) Nolan, S. P. U.S. Patent 653688, 2003.
(22) See Supporting Information for synthesis of imidazolium salts.

lium-2-carboxylate as a gray powder (0.32 g, 87%). ^{1}H NMR (300 MHz, CD_3CN): δ 7.50 (t, 1H, J = 7.8 Hz, *para*-Ar*H*), 7.28 (d, 4H, J = 7.8 Hz, *meta*-Ar*H*), 6.88 (s, 2H, *H*C=C*H*), 2.44 (sept, 1H, J = 6.6 Hz, C*H*(CH_3)$_2$), 1.81 (s, 9H, C(CH_3)$_3$), 1.28 (d, 6H, J = 6.6 Hz, CH(CH_3)$_2$), 1.09 (d, 6H, J = 6.9 Hz, CH(CH_3)$_2$). ^{13}C NMR (75.6 MHz, CD_3CN): δ 148.9, 146.9, 131.5, 124.7, 120.8, 116.9, 29.9, 29.3, 25.5, 23.2. IR (KBr) 1675, 1632, 1478, 1462, 1321, 1303, 1208 cm^{-1}. Anal. Calcd for $C_{20}H_{28}N_2O_2$: C, 73.14; H, 8.59; N, 8.53; O, 9.74; Found: C, 72.85; H, 8.54; N, 8.42; O, 9.91.

2g$_{Me}$: General Synthesis A was used with 1,3-bis(2,4,6-trimethylphenyl)-4,5-dimethyl-imidazolium chloride (0.50 g, 1.3 mmol), toluene (75 mL), and KHMDS (0.27 g, 1.3 mmol) to afford 1,3-bis(2,4,6-trimethylphenyl)-4,5-dimethyl-imidazolium-2-carboxylate as a white powder (0.38 g, 75%). ^{1}H NMR (300 MHz, CD_3CN): δ 7.09 (s, 4H, *m*-ArH), 2.35 (s, 6H, *p*-ArH), 2.10 (s, 12H, *o*-Ar-C*H*$_3$), 1.91 (s, 6H, C*H*$_3$-C=C-C*H*$_3$-N). ^{13}C NMR (75.6 MHz, CD_2Cl_2): 154.5, 145.9, 140.8, 135.6, 130.8, 129.8, 124.8, 21.5, 17.8, 8.9. IR (KBr): 1674, 1494, 1301 cm^{-1}. Anal. Calcd for $C_{24}H_{28}N_2O_2$: C, 76.56; H, 7.50; N, 7.44; O, 8.50. Found: C, 76.37; H, 7.42; N, 7.48; O, 8.63.

2h$_{Me}$: General Synthesis A was used with 1,3-bis(2,6-diisopropylphenyl)-4,5-methyl-3-imidazolium chloride (0.50 g, 1.1 mmol), toluene (75 mL), and KHMDS (0.22 g, 1.1 mmol) to afford1,3-bis(2,6-diisopropylphenyl)-4,5-methyl-3-imidazolium-2-carboxylate, (0.40 g, 75%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.540 (t, 2H, J = 6.8 Hz, 8.4 Hz, *para*-ArH), 7.31 (d, 4H, J = 7.8 Hz *meta*-ArH), 2.38 (septet, 4H, J = 7.05 Hz, IPr-C*H*-(CH_3)$_2$), 1.95 (s, 6H, C*H*$_3$-C=C-C*H*$_3$), 1.24 (d, 12H, J = 7.0 Hz IPr-CH-(C*H*$_3$)$_2$), 1.22 (d, 12H, J = 6.9 Hz IPr-CH-(C*H*$_3$)$_2$). ^{13}C NMR (75.6 MHz, CD_2Cl_2): 153.2, 146.6, 145.3, 135.5, 130.9, 126.9, 124.8, 29.7, 24.3, 23.9, 9.6. IR (KBr): 1683, 1549, 1467, 1298 cm^{-1}. Anal. Calcd for $C_{30}H_{40}N_2O_2$: C, 78.22; H, 8.75; N, 6.08; O, 6.95. Found: C, 77.95; H, 8.54; N, 6.05; O, 6.71.

General Synthesis B for NHC-CO$_2$'s 2a$_{Me}$−2c$_{Me}$. Carbenes **1a$_{Me}$**−**1c$_{Me}$** were synthesized via potassium reduction of the appropriate thiourea following a literature procedure.[15] The appropriate carbene (1 equiv) was dissolved in THF in an airless flask, and the N_2 atmosphere was removed and replaced with CO_2. The NHC-CO_2 precipitated out of solution upon CO_2 introduction. The reaction was allowed to stir for 2 h before filtering the white precipitate away.

2a$_{Me}$: General Synthesis B was used with 1,3,4,5-methyl-imidazolylid (1.16 g, 9.3 mmol) and THF (100 mL) to afford 1,3,4,5-methyl-imidazolium-2-carboxylate as a white solid (1.23 g, 78%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 3.89 (s, 6H, *N*-C*H*$_3$), 2.16 (s, 6H, *H*$_3$C-C=C-C*H*$_3$). ^{13}C NMR (75.6 MHz, CD_2Cl_2): 155.9, 142.8, 125.6, 33.5, 8.9. IR (KBr): 1669, 1510, 1440, 1423, 1315, 1230 cm^{-1}. Anal. Calcd for $C_8H_{12}N_2O_2$: C, 57.13; H, 7.19; N, 16.66; O, 19.03. Found: C, 56.85; H, 7.06; N, 16.76; O, 19.21.

2b$_{Me}$: General Synthesis B was used with 1,3-diethyl-4,5-methyl-imidazolylid (0.24 g, 1.5 mmol) and THF (50 mL) to afford 1,3-diethyl-4,5-methyl-imidazolium-2-carboxylate as a white solid (0.16 g, 52%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 4.45 (quart, J = 7.2 Hz, 4H, NC*H*$_2$,CH$_3$), 2.20 (s, 6H, C*H*$_3$C=C*H*$_3$), 1.38 (t, J = 7.22 Hz, 6H, *N*CH$_2$C*H*$_3$). ^{13}C NMR (75.6 MHz, CD_2Cl_2): 155.8, 142.5, 124.7, 41.9, 15.9, 8.7. IR (KBr): 1657, 1503, 1456, 1323, 1274, 1209 cm^{-1}. Anal. Calcd for $C_{10}H_{16}N_2O_2$: C, 61.20; H, 8.22; N, 14.27; O, 16.31. Found: C, 61.41; H, 8.27; N, 14.36; O, 16.41.

Reaction of IPrCO$_2$ with H$_2$O. A heterogeneous solution of NHC-CO_2 in CD_3CN was made, and a background spectrum was obtained. To the sample was added 25 equiv of H_2O and mixed thoroughly, forming a homogeneous solution. Another spectrum was obtained. The spectra indicate that there is a small interaction with H_2O as noted above. All of the liquid in the sample was then removed in vacuo, and another spectrum was obtained with CD_3CN, showing only NHC-CO_2 peaks.

Reactions of Carboxylates + MX with H$_2$O. Carboxylates (1 equiv) were mixed with any MX (M = Li, Na, or K; X = BPH_4, BF_4, Cl, or I) salt (1 equiv) in CD_3CN. A background spectrum was obtained prior to insertion of deoxygenated, deionized H_2O (10 equiv). ^{1}H NMR showed the acidic imidazolium proton at ~9 ppm.

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Supporting Information Available: Additional experimental procedures, X-ray, ^{1}H NMR, ^{13}C NMR, and IR data for all compounds and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.