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# Reversible carboxylation of N-heterocyclic carbenes†

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***Received (in Cambridge, UK) 17th September 2003, Accepted 28th October 2003***
***First published as an Advance Article on the web 10th November 2003***

DOI: 10.1039/b311350g

**Spectroscopic analysis, thermogravimetric analysis, and cross-over experiments performed on a series of imidazolium carboxylates revealed carboxylation was reversible with *N*-aryl substituted adducts.**

Since their isolation by Arduengo in 1991,[1] N-heterocyclic carbenes (NHCs) have been widely used compounds in several areas in chemistry. For example, when used as ligands for transition metals, they often enhance performance and selectivity.[2] Independently, they have been shown to function as nucleophilic organic catalysts for transesterifications,[3,4] acylations,[5] and ring-opening polymerizations.[6] Although NHCs are typically air and moisture sensitive, Waymouth demonstrated how a biphasic system that generates catalytic amounts of NHCs from imidazolylidene-based ionic liquids can be used to circumvent the need to use Schlenk techniques.[7] Similar biphasic systems have been recently integrated with supercritical $CO_2$ to create environmentally friendly separation systems.[8–10] While studying the use of NHCs as ligands for metal-mediated cycloadditions,[11] we discovered that NHCs freely add $CO_2$ to form the corresponding imidazolium carboxylates. Herein, we report the synthesis of a series of imidazolium carboxylates and present evidence which indicates that their formation is reversible. These results should be of prime importance to the aforementioned programs.

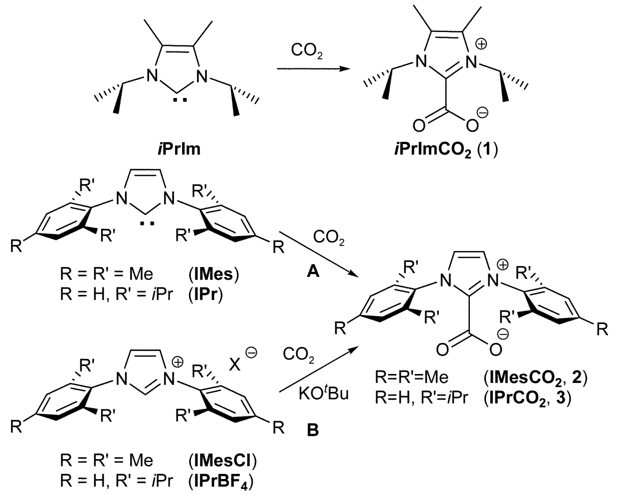
There are very few examples in the chemical literature of synthesizing and studying imidazolium carboxylates. Although Kuhn demonstrated that the direct addition of $CO_2$ to 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (*i*PrIm) cleanly afforded the corresponding carboxylate,[12] mechanistic details were not provided. The only other known example was reported by Holbrey in their “unexpected synthesis” of 1,3-dimethylimidazolium-2-carboxylate from the reaction between 1-methylimidazole and dimethyl carbonate.[13,14]

We discovered that the addition of $CO_2$ (1 atm) to *i*PrIm, 1,3-dimesitylimidazol-2-ylidene (IMes), or 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) afforded the corresponding zwitterionic imidazolium carboxylate quantitatively (Scheme 1, Pathway A).‡ However, carboxylates **2** (IMes $CO_2$) and **3** (IPr$CO_2$) were also prepared using a more convenient protocol. Simply deprotonating the corresponding salts with potassium *tert*-butoxide under an atmosphere of $CO_2$ (Pathway B) afforded the products in high yields (75–95%). All carboxylates were sparingly soluble in THF, aromatic solvents, and water. However, carboxylates **2** and **3** displayed enhanced solubilities in methanol, DMSO, and chlorinated solvents. Although air-stable as solids, solutions of **2** and **3** decomposed readily in aerated solutions.

The X-ray crystal structure of carboxylate **3** was determined[15] and is shown in Fig. 1.§ The near equivalent C–O bond distances (1.221(4) and 1.225(4) Å) indicated that the negative charge was equally distributed between the central carbon (C6) and the two oxygens (O1 and O2). In contrast, the two C–N bond distances are substantially different (1.334(4) Å *vs.* 1.376(4) Å) which suggested some delocalization of the positive charge between a single N atom and the aryl ring. There appeared to be no delocalization of the carboxylate charge into the imidazole ring as its plane was perpendicular to the plane of the $CO_2$ group. The crystal structure also indicated that the methine protons on the isopropyl groups were twisted inward toward the imidazolylidene plane. This was also observed in solution as two doublets for the isopropyl methyls were observed in the $^1H$ NMR spectrum of compound **3**. Combined, this suggested that their rotation was restricted.

Using $^{13}C$ NMR analysis, signals attributable to the carboxylate carbon were observed in all complexes. In addition, no free IPr or $CO_2$ was observed in solution, even after prolonged periods of time, which indicated a high coordination constant between the two species.[16] Furthermore, the addition of $^{13}CO_2$ (1 atm) to a solution of IPr$CO_2$ led to an enhancement in the carbonyl peak of the IPr$CO_2$ and suggested that the bound $CO_2$ was equilibrating with free $^{13}CO_2$. As expected, reintroduction of $CO_2$ (1 atm) attenuated the signal.

Thermogravimetric analysis provided further evidence for decarboxylation in **2** and **3**. Clean loss of 10.6% of the weight of



**Scheme 1** Synthesis of imidazolium carboxylates **1, 2** and **3**.

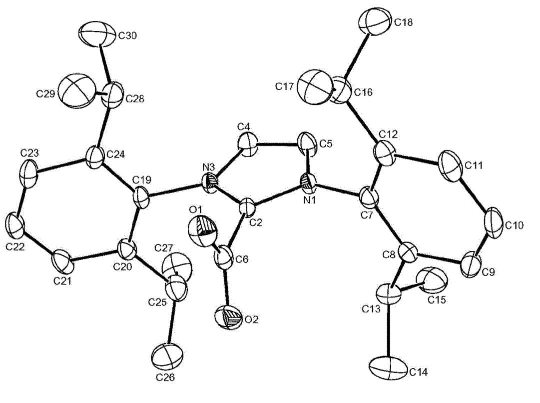


**Fig. 1** Molecular structure of IPr$CO_2$ (**3**). Selected bond lengths (Å) and angles (°): C(6)–O(1) 1.225(4), C(6)–O(2) 1.221(4), C(2)–N(1) 1.334(4), C(2)–N(3) 1.332(4), O(1)–C(6)–O(2) 129.9(3), N(1)–C(2)–N(3) 107.1(2).

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† Electronic supplementary information (ESI) available: crystal structure data and ORTEP for 1,3-bis(2,6-diisopropylphenyl)imidazolylium-2-carboxylate (**3**). See http://www.rsc.org/suppdata/cc/b3/b311350g/

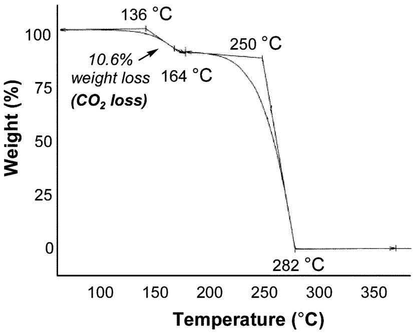

**Fig. 2** TGA of $IPrCO_2$ (**3**) under $N_2$ atmosphere. Ramp rate = 5 °C $min^{-1}$.

$IPrCO_2$ **3** (corresponding to the mass of $CO_2$) was observed between 136 and 164 °C (Fig. 2). Decomposition occurred at 250 °C. $IMesCO_2$ **2** appeared to have a higher stability toward decarboxylation as weight loss began at 187 °C and continued until decomposition ensued (203 °C). No decarboxylation was observed for *i*$PrImCO_2$ (**1**) which decomposed at 160 °C.

Crossover experiments between free imidazolylidenes and their carboxylates revealed a trend in their relative stabilities (Equations 1–5). The addition of *i*PrIm to either $IMesCO_2$ (**2**) or $IPrCO_2$ (**3**) led to quantitative formation of *i*$PrImCO_2$ (**1**) and IMes or IPr, respectively. The reverse addition of IMes or IPr to *i*$PrImCO_2$ (**1**) gave no reaction. Similarly, the addition of IMes to $IPrCO_2$ (**3**) led to the quantitative formation of free IPr and $IMesCO_2$ (**2**), but the reverse reaction was not observed. Thus, the relative order of adduct stability appeared to be: *i*$PrImCO_2$ (**1**) > $IMesCO_2$ (**2**) > $IPrCO_2$ (**3**).[17] The same trend in relative stabilities was extracted from our TGA data.

$$\mathrm{IMesCO_2}\ (\mathbf{2}) + i\mathrm{PrIm} \rightarrow \mathrm{IMes} + i\mathrm{PrImCO_2}\ (\mathbf{1}) \qquad (1)$$

$$\mathrm{IPrCO_2}\ (\mathbf{3}) + i\mathrm{PrIm} \rightarrow \mathrm{IPr} + i\mathrm{PrImCO_2}\ (\mathbf{1}) \qquad (2)$$

$$\left.\begin{array}{l}\mathrm{IMes} + i\mathrm{PrImCO_2}\ (\mathbf{1}) \\ \mathrm{IPr} + i\mathrm{PrImCO_2}\ (\mathbf{1})\end{array}\right\} \rightarrow \text{no reaction} \qquad (3)$$

$$\mathrm{IPrCO_2}\ (\mathbf{3}) + \mathrm{IMes} \rightarrow \mathrm{IMesCO_2}\ (\mathbf{2}) + \mathrm{IPr} \qquad (4)$$

$$\mathrm{IMesCO_2}\ (\mathbf{2}) + \mathrm{IPr} \rightarrow \text{no reaction} \qquad (5)$$

In conclusion, free N-heterocyclic carbenes were converted to their respective imidazolylidene carboxylates by introducing them to $CO_2$. The adducts were found to readily exchange their carboxylate groups with free $CO_2$ in solution and with relatively less stable imidazolium carboxylates. Likewise, adduct stability also affected the onset temperature of a thermally induced decarboxylation. Collectively, our data indicate that the formation of imidazolium carboxylates may be reversible under certain conditions. These results should be considered when working with imidazolylidene or NHC-based ligands or ionic liquids in the presence of $CO_2$.

We gratefully acknowledge the University of Utah and the Petroleum Research Fund (Type G) for support of this research.

## Notes and references

‡ *i*PrIm, IMes, and IPr were prepared using literature procedures.[1,18] *General procedure for the synthesis of* **1**, **2** *and* **3** *through direct carboxylation of the carbenes*: In a Schlenk flask, a solution of N-heterocyclic carbene in ether was cooled to −78 °C and $CO_2$ (1 atm) was added *via* condensation. The solution was warmed to room temperature and a white precipitate formed. The precipitate was collected by filtration and washed with ether to afford the imidazolylidene carboxylate in 85, 95, and 90% yields for **1, 2** and **3**, respectively.

**2**: $\delta_H$(500 MHz, DMSO-$d_6$) 2.09 (s, 12H, ArC$H_3$), 2.31 (s, 6H, ArC$H_3$), 7.08 (s, 4H, Ar*H*), 7.87 (s, 2H, NC*H*C*H*N). $\delta_C$(126 MHz, DMSO-$d_6$): 17.0, 20.8, 125.0, 129.5, 131.1, 134.5, 138.6, 140.8, 149.2. IR (KBr): 1675 $cm^{-1}$ (vs). mp: 315 °C (dec). Anal. Calc. for $C_{22}H_{24}N_2O_2$: C, 75.83; H, 6.94; N, 8.04. Found: C, 75.57; H, 6.98; N, 7.89%.

**3**: $\delta_H$(300 MHz, $CD_2Cl_2$) 1.22 (d, 12H, $^3J_{H-H}$ = 6.9 Hz, CH(C$H_3$)$_2$), 1.28 (d, 12H, $^3J_{H-H}$ = 6.6 Hz, CH(C$H_3$)$_2$), 2.53 (sept., 2H, C*H*), 7.19 (s, 2H, NC*H*C*H*N), 7.35 (d, 4H, $^3J_{H-H}$ = 7.8 Hz, Ar*H*), 7.55 (t, 2*H*, $^3J_{H-H}$ = 7.8 Hz, ArH). $\delta_C$(75.6 MHz, $CD_2Cl_2$): 23.4, 24.3, 29.4, 122.9, 124.3, 130.8, 132.8, 145.1, 147.6, 152.3. IR (KBr): 1678 $cm^{-1}$ (vs). mp: 216 °C (dec). Anal. Calc. for $C_{28}H_{36}N_2O_2$: C, 77.74; H, 8.39; N, 6.48. Found: C, 77.71; H, 8.34; N, 6.42%.

*General procedure for the synthesis of* **2** *and* **3** *through carboxylation of the imidazolium salts*: An oven-dried two-neck round-bottomed flask equipped with a magnetic stir bar, septum, gas adapter and balloon was evacuated and filled with $CO_2$. A solution of the imidazolylidene salt and potassium *tert*-butoxide (1.2 equiv.) was then added and the reaction was stirred at room temperature for 2–6 hours. For the synthesis of **2**, the solvent was removed and the residue was extracted with $CH_2Cl_2$. The solution was filtered through Celite and concentrated *in vacuo*. Subsequent washing with $Et_2O$ afforded the imidazolium carboxylate as a white solid in 95% yield. For the synthesis of **3**, hexane was added to induce precipitation. The precipitate was collected *via* filtration and dissolved in $CH_2Cl_2$. The solution was then filtered through Celite and concentrated *in vacuo*. Subsequent washing with $Et_2O$ afforded the imidazolium carboxylate as a white solid in 75% yield.

§ *Crystal data for* $C_{28}H_{36}N_2O_2$ **3**: *M* = 432.59, monoclinic, *a* = 12.6385(7), *b* = 12.5779(8), *c* = 16.6868(12) Å, $\beta$ = 92.993(2)°, *U* = 2649.0(3) Å$^3$, *T* = 150 K, space group $P2_1/n$, *Z* = 4, $\mu$(Mo-K) = 0.71073 Å, 9106 reflections collected, 4822 unique ($R_{int}$ = 0.0721) which were used in all calculations. The *R*1 was 0.1638 and the final $wR(F^2)$ was 0.2314 (all data). Single crystals of **3** were grown from slow diffusion of $CO_2$ into a solution of IPr in THF at room temperature. The crystals were mounted in inert oil and transferred to a cold gas stream in the diffractometer. The structure was solved by a combination of direct methods and heavy atoms using SIR 97 and refined by full-matrix least-squares on $F^2$. CCDC 219086. See http://www.rsc.org/suppdata/cc/b3/b311350g/ for crystallographic data in .cif or other electronic format.

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