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# Fast $CO_2$ Sequestration, Activation, and Catalytic Transformation Using *N*-Heterocyclic Olefins

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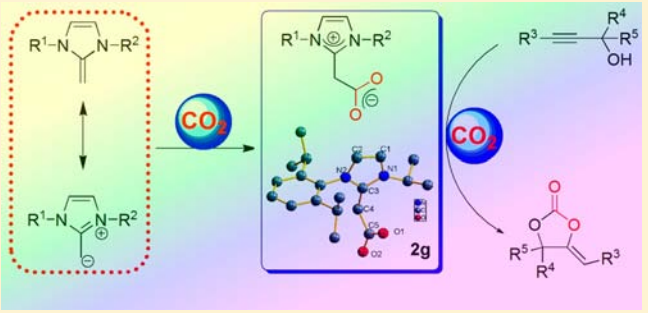
Supporting Information

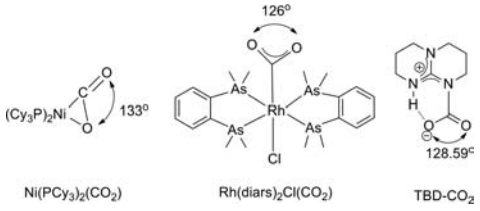
**ABSTRACT:** *N*-Heterocyclic Olefin (NHO) with high electronegativity at the terminal carbon atom was found to show a strong tendency for $CO_2$ sequestration, affording a $CO_2$ adduct (NHO−$CO_2$). X-ray single crystal analysis revealed the bent geometry of the binding $CO_2$ in the NHO−$CO_2$ adducts with an O−C−O angle of 127.7−129.9°, dependent on the substitute groups of *N*-heterocyclic ring. The length of the $C_{carboxylate}$−$C_{NHO}$ bond is in the range of 1.55−1.57 Å, significantly longer than that of the $C_{carboxylate}$−$C_{NHC}$ bond (1.52−1.53 Å) of the previously reported NHC−$CO_2$ adducts. The FTIR study by monitoring the $\nu(CO_2)$ region of transmittance change demonstrated that the decarboxylation of NHO−$CO_2$ adducts is easier than that of the corresponding NHC−$CO_2$ adducts. Notably, the NHO−$CO_2$ adducts were found to be highly active in catalyzing the carboxylative cyclization of $CO_2$ and propargylic alcohols at mild conditions (even at ambient temperature and 0.1 MPa $CO_2$ pressure), selectively giving $\alpha$-alkylidene cyclic carbonates in good yields. The catalytic activity is about 10−200 times that of the corresponding NHC−$CO_2$ adducts at the same conditions. Two reaction paths regarding the hydrogen at the alkenyl position of cyclic carbonates coming from substrate (path A) or both substrate and catalyst (path B) were proposed on the basis of deuterium labeling experiments. The high activity of NHO−$CO_2$ adduct was tentatively ascribed to its low stability for easily releasing the $CO_2$ moiety and/or the desired product, a possible rate-limiting step in the catalytic cycle.




## INTRODUCTION

The utilization of carbon dioxide as a C1 source for the production of organic chemicals can contribute to a more sustainable chemical industry.[1,2] The key issue is the lack of effective catalysts to facilitate its activation and subsequent transformation, since $CO_2$ is such a thermodynamically and kinetically stable molecule. In 1975, Aresta and co-worker reported the isolation of the first $CO_2$-based complex, $Ni(PCy_3)_2(CO_2)$.[3a,b] The X-ray single-crystal analysis revealed that the $CO_2$ ligand was coordinated through the carbon atom and one of the oxygen atoms and thus possessed bent geometry with a O−C−O angle of 133° (Scheme 1), being distinct from the nonpolar linear structure of free $CO_2$ at ground state. A similar bent structure with a O−C−O angle of 132° was also observed in [Co(I)($^n$Pr-salen)K($CO_2$)(THF)], in which $CO_2$ is anchored to the nucleophilic cobalt(I) ion through a Co−C $\sigma$ bond, while the oxygen atoms interact with the alkali cation in a polymeric structure.[3c] Soon after, Herskovitz and co-workers revealed the structure of $Rh(diars)_2Cl(CO_2)$, in which $CO_2$ trans to the chloride is formally $\eta^1$-bound toward Rh(I) (Scheme 1).[3d] Nevertheless, $CO_2$ prevalently behaves as an electrophile, since the electrophilicity of the carbon atom is higher than the nucleophilicity of each of the oxygen atoms. For example, strong nucleophiles such as the amidines and guanidines containing nitrogen heterocyclic have been reported to react with $CO_2$, expectantly affording zwitterionic adducts. Unfortunately, much effort to isolate and characterize a zwitterionic adduct between $CO_2$ and a nitrogen base was unsuccessful, and in most cases bicarbonate salts were unexpectedly produced owing to the presence of adventitious water.[4] Until recently, the TBD-$CO_2$ adduct from the reaction of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) with $CO_2$ was isolated under strictly anhydrous conditions and clearly characterized by the X-ray diffraction. The stability of TBD-$CO_2$ can be ascribed to the H-bond effect between N−H of TBD and O-atom of the carboxylate anion (Scheme 1).[5]

**Scheme 1**

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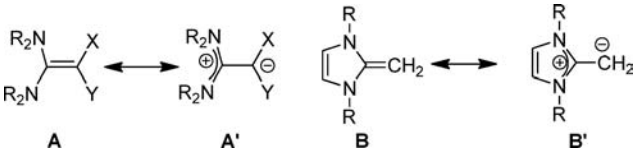
*N*-heterocyclic carbene (NHC), a stronger nucleophile, was also found to easily react with $CO_2$ to form NHC−$CO_2$ adduct, in which a bent geometry with a O−C−O angle of 129−131° was observed by X-ray single-crystal study.[6] Notably, the NHC−$CO_2$ adduct was shown to be an efficient organocatalyst for chemical fixation of $CO_2$ to organic compounds.[7] Recently, superbase-based protic ionic liquids were demonstrated to efficiently capture an equivalent $CO_2$.[8] It is noteworthy that the new metal-free systems of "frustrated Lewis pairs" first unveiled by Stephan et al.,[9] were found to straightforwardly sequester $CO_2$ binding into frustrated Lewis acid and Lewis base centers.[2d,e,10]

It is generally known that ene-1,1-diamines (ketene aminals) as a kind of ylidic olefins possess a strongly polarized C=C double bond and thus made the charge of olefin separation which can be described through their resonance structure A′) (Scheme 2).[11] Particularly, the incorporation of the nitrogen

**Scheme 2. Resonance Structures of Ene-1,2-diamine and *N,N′*-Disubstituents-2-Methylene Imidazoline**

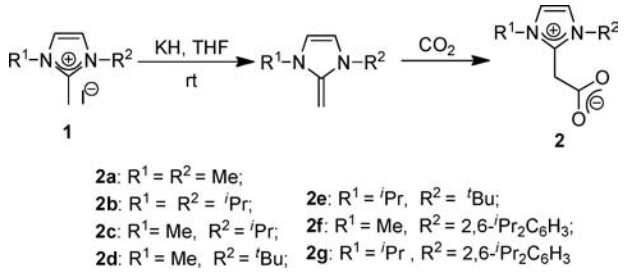



atoms into a five-membered ring, named *N*-heterocyclic olefin (NHO) shown in Scheme 2, will be advantageous to stabilize a positive charge, due to the aromatization of the heterocyclic ring, making the terminal carbon atom of the olefins more electronegative (resonance structure **B** ↔ **B′**). With respect to their special structures, NHOs were considered as potent nucleophiles and strong donor ligands.[12] A kind of *N*-heterocyclic olefin, IPr=$CH_2$ [IPr = 1,3-bis(2,6-diiso-propyl-phenyl) imidazol-2-ylidene], has been demonstrated by Rivard et al. as a nucleophile to stabilize $GeH_2$ and $SnH_2$ complexes.[13] Mayr and co-workers reported the exocyclic olefinic carbon atoms of the *N*-heterocyclic olefins attacked a benzhydrylium ion to give azolium salts.[14] More recently, treatment of the *N*-heterocyclic olefins with $B(C_6F_5)_3$ was described by Tamm et al. to afford classical or abnormal Lewis acid/base adducts.[15] The strong nucleophilicity grants NHO to possess great potential in the application of $CO_2$ capture, activation, and further transformation. Herein, we for the first time report the synthesis of various NHO−$CO_2$ adducts and unveil their geometries by X-ray single crystal analysis. Additionally, these $CO_2$ adducts were also applied as effective organocatalysts for $CO_2$ transformation to useful chemicals.

## RESULTS AND DISCUSSION

A series of NHO−$CO_2$ adducts **2a**−**2g** were prepared in good yields using a procedure shown in Scheme 3, utilizing the corresponding *N,N′*-disubstituted derivatives of 2-methyl imidazolium iodide **1** as starting material. Compound **1** was first treated with KH in tetrahydrofuran solvent at room temperature in the absence of light, affording the intermediate, *N,N′*-disubstituent-2-methyleneimidazoline, which was further transformed into the corresponding NHO−$CO_2$ adduct by diffusion of $CO_2$ into its tetrahydrofuran solution under strictly anhydrous conditions. Obvious differences in chemical shift were observed in the $^1$H and $^{13}$C NMR spectra of compounds **1** and **2**. In comparison with the 2-methyl of **1a**−**1g**, a chemical

**Scheme 3. Synthesis of NHO−$CO_2$ Adducts 2a−2g**




shift of methylene H at the same position in **2a**−**2g** clearly moves downfield. Meanwhile, $^{13}$C NMR data of **2a**−**2g** show strong carboxylate carbon signals at 162.3−164.3 ppm. The C=O stretching frequency of the carboxylate in **2a**−**2g** at FTIR spectra changes from 1615 $cm^{-1}$ to 1642 $cm^{-1}$, obviously lower than that of NHC−$CO_2$ adducts (1645−1695 $cm^{-1}$), dependent on the substitute groups in the imidazolium ring.[6f,7a]

Furthermore, the structures of compounds **2b**, **2c**, **2d**, **2f**, and **2g** were solved using single crystal X-ray crystallography (Figure 1). Selected bond lengths and bond angles are shown in Table 1. The O−C−O angles of NHO−$CO_2$ adducts are in the range of 127.7(2)° and 129.9(5)°, indicating the bent geometry of the binding $CO_2$. The C3−C4 bond length (1.470(3)∼1.491(5) Å), is significantly longer than that of the C=C bond in 1,3,4,5-tetramethyl-2-methyleneimidazoline (1.357(3) Å).[12b] This should be ascribed to the extreme polarization of the exocyclic double bond of imidazoline ring, since the polarization process allows for the most resonance stabilization of the zwitterionic structure consisting of an imidazolium cation and a carboxylic anion. Correspondingly, both N1−C3 and N2−C3 bond lengths become shorter in comparison with the N−C bond in 1,3,4,5-tetramethyl-2-methyleneimidazoline. Far different from the NHC−$CO_2$ adducts, the dissymmetrical *N*-alkyl substituent has little effect on the discrepancy between C5−O1 and C5−O2 bond lengths of the carboxylate. The distances of C5−O1(2) bonds for the carboxylate are nearly equivalent for asymmetrical NHO−$CO_2$ adducts, while the biggest discrepancy of only 0.009 Å was found in the crystal data of compound **2b** possessing a symmetrical substituent at the heterocyclic ring. This result indicates that the negative charge is uniformly distributed between the central carbon and the two oxygens. The lengths of C4−C5 bond in the NHO−$CO_2$ adducts are between 1.549(3) Å and 1.598(6) Å, which are significantly longer than that of the $C_{carboxylate}$−$C_{NHC}$ bond (1.520−1.530 Å) in the NHC−$CO_2$ adducts previously reported by Rogers[6a] and Louie.[6b,f] This might mean that the decarboxylation of NHO−$CO_2$ adducts are easier than that of NHC−$CO_2$ adducts. Note that the atoms C4, C5, O1, and O2 are nearly coplanar for all NHO−$CO_2$ adducts. Similarly, the atoms N1, N2, C3, and C4 are also nearly coplanar. The dihedral angle of two planes is 93.8°, 81.7°, 99.6°, 108.8°, and 109.6° for **2b**, **2c**, **2d**, **2f**, and **2g**, respectively.

Generally, the structural data reflects the physical and chemical properties of organic compounds. With those crystal data in hand, we then explored the thermal stability of NHO−$CO_2$ adducts. The thermal stability was studied by means of in situ FTIR method with monitoring the $\nu(CO_2)$ region of infrared spectra using a temperature-controlled high pressure liquid cell (HPL-TC).[7a] Because of its better solubility in $CH_2Cl_2$, the NHO−$CO_2$ adduct **2g** was first selected to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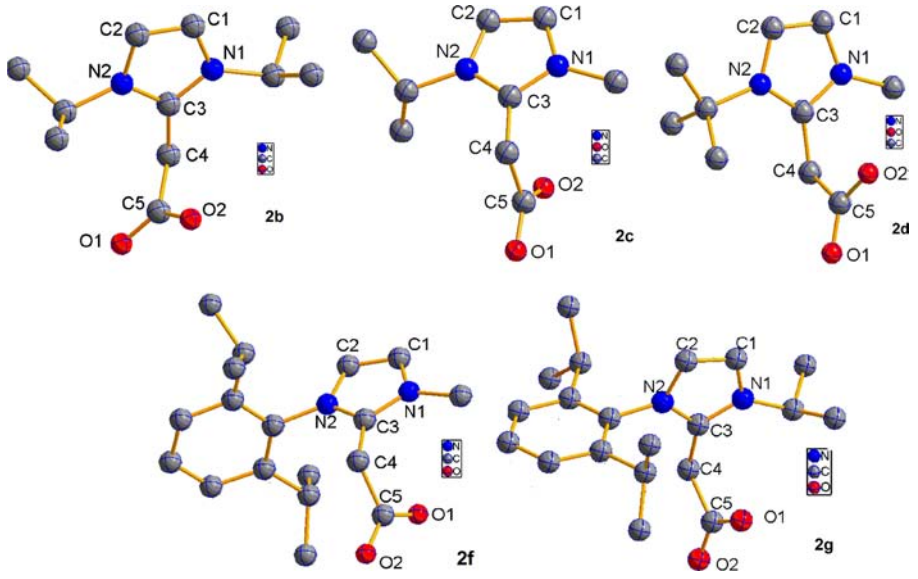


**Figure 1.** Molecular structures of **2b**, **2c**, **2d**, **2f**, and **2g** with thermal ellipsoids drawn at 30% probability. Hydrogen atoms have been omitted for clarity.

**Table 1. Selected Bond Lengths (Å) and Angles (deg) in Complexes 2b, 2c, 2d, 2f, and 2g**

| complex | C3−N1 (Å) | C3−N2 (Å) | C3−C4 (Å) | C4−C5 (Å) | C5−O1 (Å) | C5−O2 (Å) | N1−C3−N2 (deg) | O1−C5−O2 (deg) |
|---|---|---|---|---|---|---|---|---|
| **2b** | 1.337 (2) | 1.346 (2) | 1.480 (2) | 1.551 (2) | 1.234 (2) | 1.243 (2) | 107.2 (1) | 128.5 (2) |
| **2c** | 1.333 (2) | 1.343 (2) | 1.479 (2) | 1.549 (3) | 1.242 (2) | 1.242 (2) | 107.5 (2) | 127.7 (2) |
| **2d** | 1.344 (5) | 1.346 (5) | 1.491 (5) | 1.598 (6) | 1.226 (5) | 1.230 (5) | 107.6 (3) | 129.9 (5) |
| **2f** | 1.341 (3) | 1.340 (3) | 1.470 (3) | 1.557 (3) | 1.241 (3) | 1.241 (3) | 106.6 (2) | 128.3 (2) |
| **2g** | 1.340 (2) | 1.349 (2) | 1.476 (2) | 1.568 (2) | 1.230 (2) | 1.237 (2) | 106.7 (1) | 129.1 (2) |

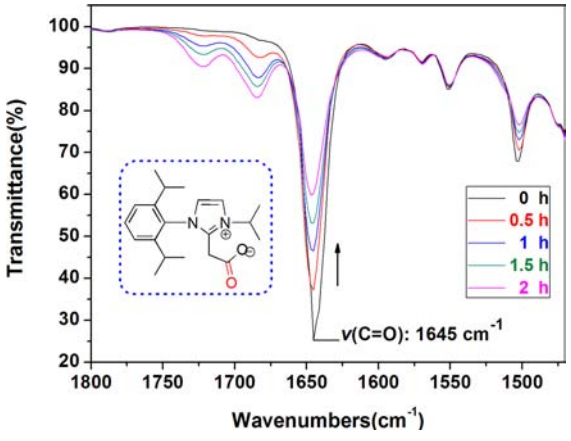


**Figure 2.** FTIR spectra of **2g** in $CH_2Cl_2$ at various times at 40 °C.

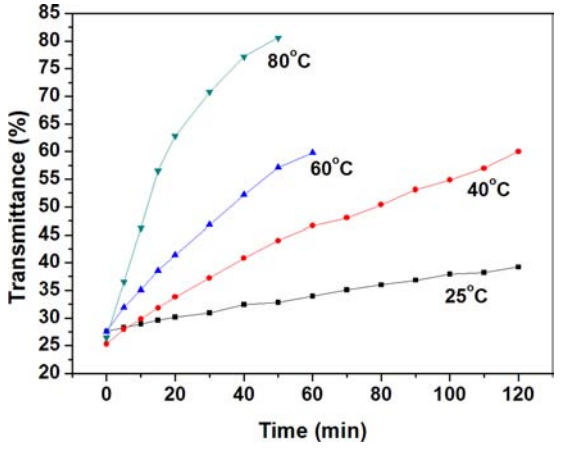


**Figure 3.** Plots of transmittance (%) at 1645 $cm^{-1}$ versus time for the decomposition of NHO−$CO_2$ adduct **2g** at various temperatures.

conduct the thermal stability study. Figure 2 shows the absorption intensity of asymmetric $\nu(CO_2)$ vibrations of **2g** at 1645 $cm^{-1}$ gradually decreases with the extension of time in $CH_2Cl_2$ at 40 °C, which clearly indicates the decarboxylation of **2g**. Meanwhile in situ infrared monitoring of **2g** in $CH_2Cl_2$ solution was conducted at various temperatures to further investigate the effect of temperature on thermal stability of NHO−$CO_2$ adducts. At 25 °C, **2g** is relatively stable in $CH_2Cl_2$. On the contrary, the decarboxylation of most **2g** molecules appeared within 40 min at 80 °C (Figure 3). Then the stability difference of NHO−$CO_2$ adducts **2b**, **2c**, **2d**, **2f**, and **2g** in $CH_2Cl_2$ at 40 °C was investigated (Figure 4). The result indicates that the decomposition rate was related to the C4−C5 bond length of NHO−$CO_2$ adduct. Generally, the longer the C4−C5 bond length is, the less stable the NHO−$CO_2$ adduct is, except **2d** out of the rule.

For a comparison purpose, a typically dissymmetric NHC−$CO_2$ adduct **3** (1-(2,6-diisopropylphenyl)-3-isopropyl-imidazolium-2-carboxylate) with the same imidazoline structure of compound **2g** was also prepared and its solid structure is shown in Figure 5. A decarboxylation experiment of in situ infrared monitoring of **3** in $CH_2Cl_2$ solution at 1683 $cm^{-1}$ was performed with time at 40 °C (Figure 6). Contrast to the decarboxylation of most **2g** molecules occurred within 2 h, only small amounts of compound **3** decomposed at the same condition. These results demonstrate that the decarboxylation


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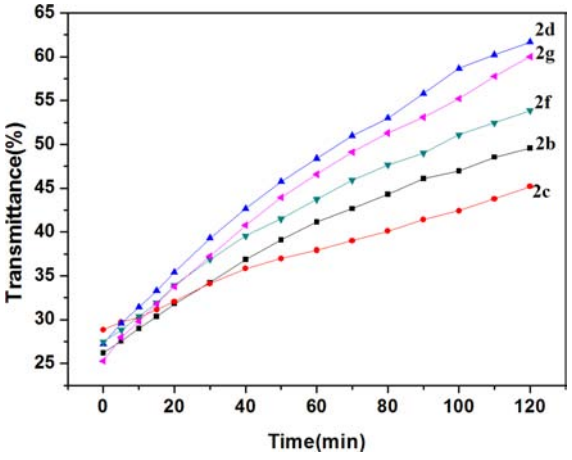



**Figure 4.** Comparison plots of transmittance for NHO−$CO_2$ adducts **2b**, **2c**, **2d**, **2f** and **2g** versus time for decomposition in $CH_2Cl_2$ at 40 °C.

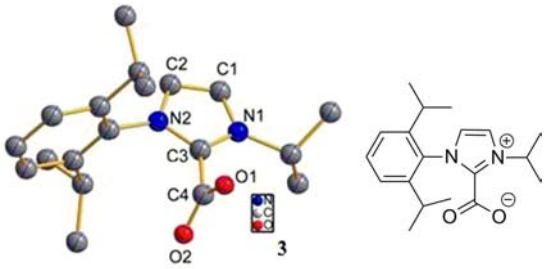



**Figure 5.** Molecular structure of the NHC−$CO_2$ adduct **3** with thermal ellipsoids drawn at 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): C3−C4 1.528(2), C4−O1 1.204(2), C4−O2 1.207(2), C3−N1 1.331 (2), C3−N2 1.342(2), N1−C3−N2 107.7(1), and O1−C4−O2 129.2(2).

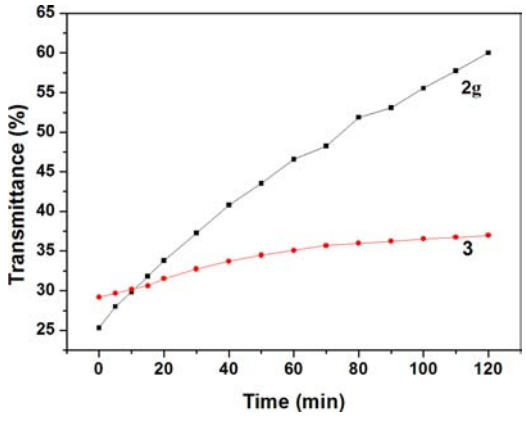
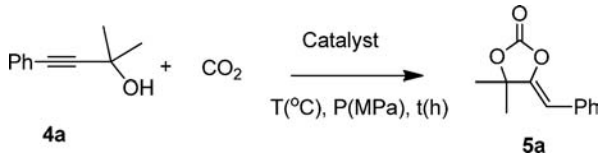



**Figure 6.** Comparison plots of transmittance at 1645 $cm^{-1}$ for NHO−$CO_2$ adduct **2g** and at 1683 $cm^{-1}$ for NHC−$CO_2$ adduct **3** versus time for decomposition in $CH_2Cl_2$ at 40 °C.

of NHO−$CO_2$ adduct is significantly easier than that of NHC−$CO_2$ adduct, which is agreement with the discrepancy in bond length: 1.568(2) Å of the C4−C5 bond of NHO−$CO_2$ adduct **2g** versus 1.528(2) Å of the C3−C4 bond of NHC−$CO_2$ adduct **3**. The relatively poor thermal stability of NHO−$CO_2$ adducts probably offers an important chance to serve as a highly active catalyst for $CO_2$ transformation. Therefore, the exploration of $CO_2$ transformation using NHO−$CO_2$ as potential catalyst become a primary goal of our research.

Chemical fixation of carbon dioxide into useful organic chemicals is of great interest and has been a long-standing goal for chemists,[16] since $CO_2$ is an abundant, inexpensive, and renewable C1 feedstock. Previously, NHC−$CO_2$ adducts were reported as an effective organocatalyst for $CO_2$ transformation. Because the carboxylate in NHO−$CO_2$ adduct shows lower stability than that of the corresponding NHC−$CO_2$ adduct, it perhaps exhibits more excellent reactivity toward some substrates, especially the nucleophile-promoted reaction. With kinds of NHO−$CO_2$ adducts in hand, we are of great interest to explore the transformation of the binding $CO_2$ and further application of these adducts as potential catalyst for $CO_2$ chemical fixation. We initially studied the carboxylative cyclization of propargylic alcohols with $CO_2$ to give $\alpha$-alkylidene cyclic carbonates, which are versatile intermediates in organic synthesis and polymer chemistry.[17] Usually, the use of a metallic species[18]including Ru, Co, Cu, Pd, or Ag as catalyst is necessary to make this reaction run smoothly. Although phosphine,[19] guanidine,[20] or *N*-heterocyclic carbenes[21] were found to be active in catalyzing this coupling reaction, the activities were not satisfactory. To our delight, we initially attempted this coupling reaction of 2-methyl-4-phenylbut-3-yn-2-ol (**4a**) with $CO_2$ using 2 mol % **2a** to give a yield of 51% under 60 °C and 2 MPa $CO_2$ pressure (Table 2, entry 1). Driven by this result, the carboxylative cyclization of **4a** with $CO_2$ as model reaction was chose to optimize reaction conditions. The results from Table 2 revealed that the substituents on the nitrogen atoms of the NHO framework have an obvious influence on the catalyst activity (Table 2, entries 1−7), the isopropyl-substituted NHO−$CO_2$ adducts showed higher catalytic activity than those methyl-substitued adducts, probably due to its higher solubility. The lower catalyst

**Table 2. Optimization of Reaction Conditions for the Carboxylative Cyclization of 2-methyl-4-phenylbut-3-yn-2-ol (4a) with $CO_2$[a]**




| entry | catalyst (mol %) | $T$ (°C) | $P$ (MPa) | $t$ (h) | yield (%)[b] |
|---|---|---|---|---|---|
| 1 | **2a** (2) | 60 | 2 | 12 | 51 |
| 2 | **2b** (2) | 60 | 2 | 12 | 72 |
| 3 | **2c** (2) | 60 | 2 | 12 | 64 |
| 4 | **2d** (2) | 60 | 2 | 12 | 68 |
| 5 | **2e** (2) | 60 | 2 | 12 | 84 |
| 6 | **2f** (2) | 60 | 2 | 12 | 70 |
| 7 | **2g** (2) | 60 | 2 | 12 | 88 |
| 8 | **2g** (5) | 60 | 2 | 12 | 93 |
| 9 | **2g** (1) | 60 | 2 | 12 | 70 |
| 10 | **2g** (5) | 50 | 2 | 12 | 76 |
| 11 | **2g** (5) | 70 | 2 | 12 | 85 |
| 12 | **2g** (5) | 60 | 2 | 6 | 72 |
| 13 | **2g** (5) | 60 | 2 | 24 | 94 |
| 14 | **2g** (5) | 60 | 1 | 12 | 88 |
| 15 | **2g** (5) | 60 | 4 | 12 | 94 |

[a]Reaction conditions: substrate **4** (3 mmol). [b]Isolated yield.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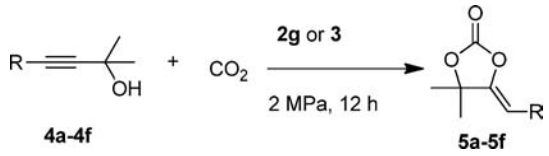
loading and the reduced temperature have negative effects on the yield (Table 2, entries 9–11). Interestingly, $CO_2$ pressure had very limited impact on the yield of the cyclic carbonate (Table 2, entries 8, 14, and 15).

The formation of carboxylative cyclization product **5a** from 2-methyl-4-phenylbut-3-yn-2-ol (**4a**) was once realized by MTBD-catalyzed reaction in supercritical carbon dioxide to give 55% yield.[20] The same reaction was reported by Ikariya and co-workers using 1,3-*ditert*-butyl-imidazolium-2-carboxylate as catalyst at an enhanced temperature of 80 °C and a 4.5 MPa $CO_2$ pressure to obtain **5a** in 84% yield.[21b] For a comparison purpose of the discrepancy in catalytic activity of NHO–$CO_2$ and NHC–$CO_2$ adducts, the reaction was conducted using compounds **2g** and **3** as catalyst, respectively, since they have the same substituents in the *N* atom of imidazole ring. The results are shown in Table 3. It was found that NHO–$CO_2$ adduct **2g** was superior to NHC–$CO_2$ adduct **3** in catalyzing the carboxylative cyclization of $CO_2$ with various propargyl alcohols. Furthermore, taking the carboxylative cyclization of **4f** and $CO_2$ as an example, simple kinetic studies of the two catalyst systems by monitoring the reaction at various time points using $^1$H NMR spectroscopy revealed that the rate using **2g** as catalyst was obviously higher than that with NHC–$CO_2$ adduct **3** system whether at 25 or 60 °C (Figure 7). It is worthy of mention that with **4e** or **4f** as substrate, the carboxylative cyclization with $CO_2$ performed smoothly at ambient temperature (Table 3, entries 10–15), a rare example of organocatalyzed $CO_2$ fixation at 25 °C. Notably, **5e** and **5f** were obtained in moderate yields under 1 atm $CO_2$. In comparison with NHC–$CO_2$ adduct, the instability of NHO–$CO_2$ adducts from the above crystal data and decarboxylation experiment should make a contribution to their higher activity in catalyzing this carboxylative cyclization. Furthermore, a relationship ($\rho$ = 1.876) between the rate constant $k$ of the 4-aryl substituted propargylic alcohol and the Hammett parameters was established. The result shows that the carboxylative cyclization was accelerated by the nucleophilic attack according to the hammett plot (see Supporting Information, SI, Figure S2).

Otherwise, the scope with respect to other propargylic alcohols substrates was then explored under the optimized reaction conditions. As shown in Table 4, various terminal and internal propargylic alcohols smoothly underwent the carboxylation cyclization reaction and were converted into the corresponding alkylidene cyclic carbonates in moderate to excellent yields.

We are greatly interested to note that only a slight difference in structure between NHO–$CO_2$ adduct **2g** and NHC–$CO_2$ adduct **3** resulted in the significant discrepancy of catalytic activity for the carboxylative cyclization reaction. The higher reactivity associated with NHO–$CO_2$ adduct was tentatively ascribed to the low stability of the $C_{carboxylate}$–$C_{NHO}$ bond, demonstrated by X-ray single crystal analysis and FTIR study. In NHC–$CO_2$ adduct catalyzed carboxylative cyclization of

**Table 3. Catalytic Activity Comparison for NHO–$CO_2$ Adduct 2g and NHC–$CO_2$ Adduct 3 toward Carboxylative Cyclization of Propargylic Alcohols with $CO_2$[a]**




4a-4f 5a-5f

| entry | R | catalyst | yield (%)[b] |
|---|---|---|---|
| 1 | $C_6H_5$(**4a**) | 2g | 93 (**5a**) |
| 2 | | 3 | 43 (**5a**) |
| 3 | 4-$MeOC_6H_4$(**4b**) | 2g | 56 (**5b**) |
| 4 | | 3 | 12 (**5b**) |
| 5 | 4-$MeC_6H_4$(**4c**) | 2g | 78 (**5c**) |
| 6 | | 3 | trace (**5c**) |
| 7 | 3-pyridyl(**4d**) | 2g | 90 (**5d**) |
| 8[c] | | 2g | 42 (**5d**) |
| 9 | | 3 | 40 (**5d**) |
| 10[d] | 4-$CF_3C_6H_4$(**4e**) | 2g | 93 (**5e**) |
| 11[c] | | 2g | 63 (**5e**) |
| 12[d] | | 3 | trace (**5e**) |
| 13[d] | 4-$CH_3COC_6H_4$(**4f**) | 2g | 94 (**5f**) |
| 14[c] | | 2g | 65 (**5f**) |
| 15[d] | | 3 | trace (**5f**) |

[a]Reaction conditions: **2g** or **3** (0.15 mmol), substrate **4** (3 mmol), 60 °C, 12 h, 2 MPa $CO_2$. [b]Isolated yield. [c]Reaction conditions: **2g** (0.15 mmol), substrate **4** (3 mmol), rt, 0.5 mL $CH_2Cl_2$, 1 atm $CO_2$. [d]Reaction conditions: **2g** or **3** (0.15 mmol), substrate **4** (3 mmol), rt, 0.5 mL $CH_2Cl_2$, 2 MPa $CO_2$.

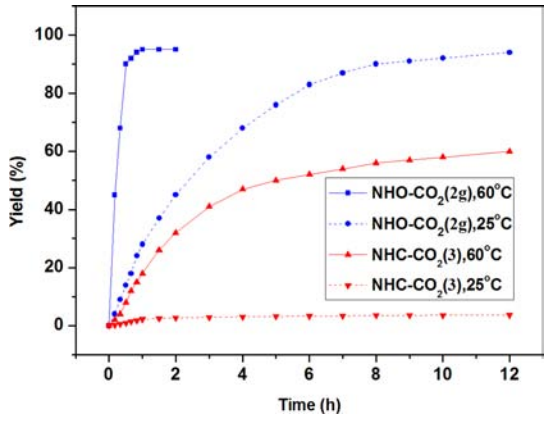
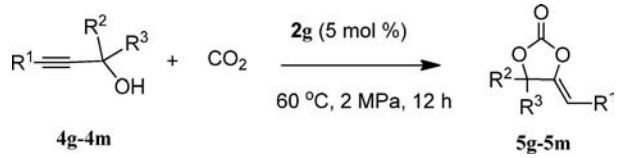



**Figure 7.** Plot of yield versus time for the carboxylative cyclization of **4f** and $CO_2$ catalyzed by **2g** and **3** at *various* temperature. Yields were determined by $^1$H NMR.

**Table 4. Carboxylative Cyclization of Various Propargylic Alcohols with $CO_2$ to Give $\alpha$-alkylidene Cyclic Carbonates by 2g[a]**




4g-4m 5g-5m

| entry | substrate | $R^1$ | $R^2$ | $R^3$ | yield (%)[b] |
|---|---|---|---|---|---|
| 1 | **4g** | H | Me | Me | >98[c] |
| 2 | **4h** | H | Me | Ph | 87 |
| 3 | **4i** | H | $-(CH_2)_5-$ | | 83 |
| 4 | **4j** | Ph | $-(CH_2)_5-$ | | 66 |
| 5 | **4k** | Ph | Me | Ph | 50 |
| 6 | **4l** | 2-pyridyl | Me | Me | 83 |
| 7 | **4m** | 4-$ClC_6H_4$ | Me | Me | 84 |

[a]Reaction conditions: **2g** (0.15 mmol), substrate **4** (3 mmol), 60 °C, 12 h, 2 MPa $CO_2$. [b]Isolated yield. [c]Yield determined by GC spectroscopy.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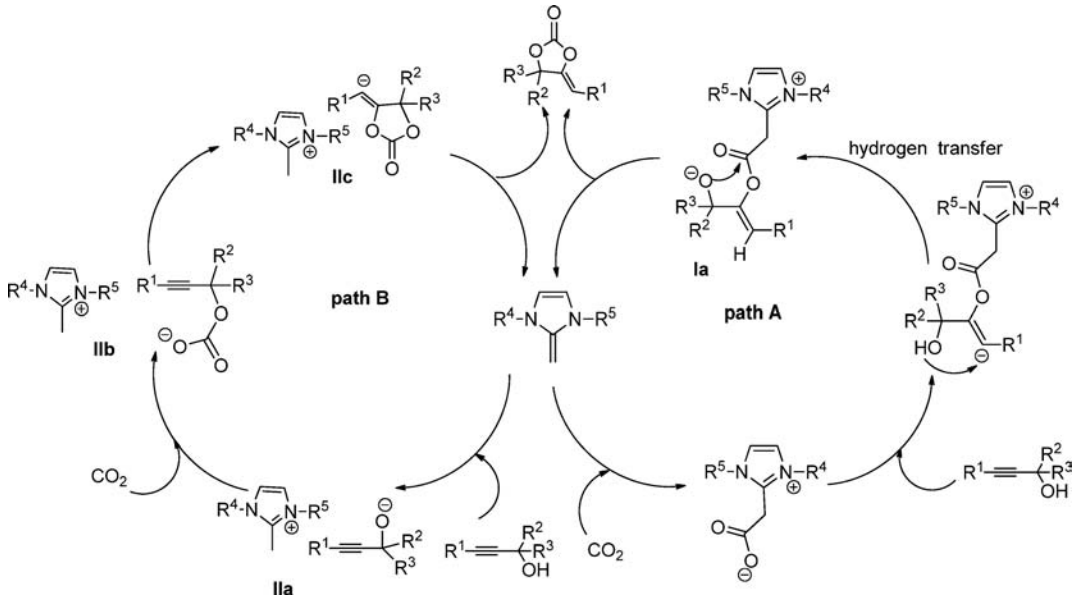
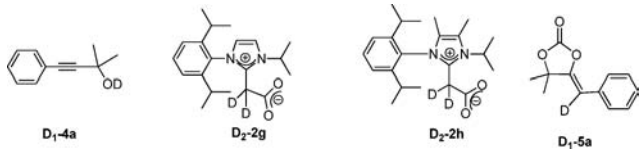
**Scheme 4. Plausible Mechanisms for Carboxylative Cyclization of Propargyl Alcohols with $CO_2$ Catalyzed by NHO−$CO_2$**



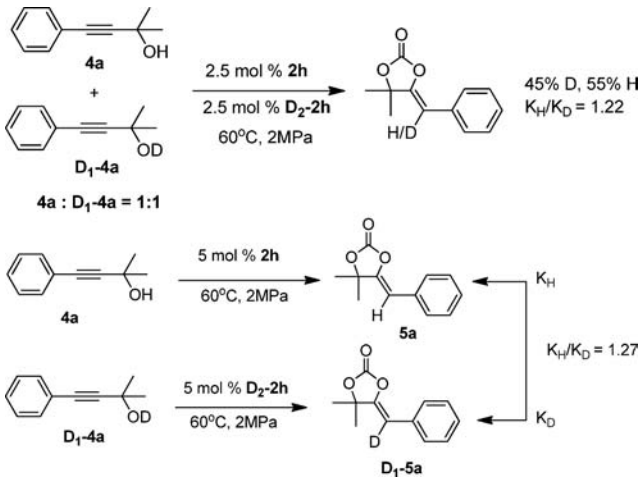

propargylic alcohols with $CO_2$, Ikariya et al. proposed a mechanism regarding the nucleophilic attack of the $CO_2$ moiety bound to the NHC onto the substrates. First, the zwitterionic compound NHO−$CO_2$ could add to triple bond of propargylic alcohol by nucleophilic attack. Meanwhile, hydrogen transfer of alcohol generates the new zwitterions (**Ia**) (Scheme 4), alkoxide anion of which attacked the carbonyl carbon to release the desired product and NHO, which rapidly captures free $CO_2$ to form the compound NHO−$CO_2$ for finishing a catalyst cycle. However, because of the instability of NHO−$CO_2$ adduct, it is possible to release the free NHO from the decomposition of the adduct, and thus a kinetic equilibrium exists in the catalytic system, dependent on $CO_2$ pressure and reaction temperature. NHO with high electronegativity at the terminal carbon atom could abstract hydrogen of propargylic alcohol to form the intermediate **IIa**, which reacts with $CO_2$ to give the intermediate **IIb**. Subsequently, the intermediate **IIc** can be obtained by an intramolecular ring-closing reaction of the intermediate **IIb**, which snatchs the hydrogen of 2-methyl imidazolium to release the desired product. The obvious difference of two paths is the hydrogen at the alkenyl position of cyclic carbonates coming from substrate (see Scheme 4, path A) or both substrate and catalyst (path B). In our study, deuterium labeling experiments were carried out to gain insight into the reaction course (see Scheme 5 and the SI). Due to the strong H/D exchange between the hydrogen atom of C4, C5 in the imidazoline ring and −$CD_2CO_2$ (see SI Figure S6), the systhesis of deuterated NHO−$CO_2$ adducted **$D_2$-2g** was unsuccessful. **$D_2$-2h** was obtained by replacing the H atom of C4, C5 in the imidazoline ring with methyl. Unfortunately, the

**Scheme 5. Deuterium Labelling Substrate, Catalyst, and Product**




H/D exchange between the hydrogen atom of propargylic alcohols and −$CD_2CO_2$ was observed (see SI Figure S10). Since the mechanism of path B involves the cleavage of a C−H bond of the intermediate **IIc**, the measurement of kinetic isotope effects (KIEs)[22] was performed. As shown in Scheme 6,

**Scheme 6. KIE Measurement from Intermolecular and Intramolecular Reactions**




whether an intramolecular or intermolecular labeled substrate and catalyst, the value of KIE reveals a small, perhaps secondary isotope effect, indicating that path B makes a lower contribution to the carboxylative cyclization. Otherwise, when **4f** reacted with $^{13}C$-labeled **2g** under 1 atm $CO_2$, $^{13}C_{carbonyl}$-labeled **5f** was detected (see SI Figure S11), which may imply that NHO−$CO_2$ adduct was involved in the catalytic reaction. Compared with NHC−$CO_2$ adduct, the decreased stability of the NHO−$CO_2$ adduct benefits the departure of the product from NHO, which might be a possible rate-limiting step in the catalytic cycle.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## CONCLUSIONS

In summary, we have established a simple procedure for the synthesis of various NHO−$CO_2$ adducts from *N*-heterocyclic olefins. The X-ray single crystal study revealed that the binding $CO_2$ moiety possesses a bent geometry with an O−C−O angle of 127.7−129.9°, dependent on the substitute groups of *N*-heterocyclic ring. The length of the $C_{carboxylate}$−$C_{NHO}$ bond is in the range of 1.55−1.57 Å, significantly longer than that of the $C_{carboxylate}$−$C_{NHC}$ bond of the corresponding NHC−$CO_2$ adducts.

Moreover, the NHO−$CO_2$ adduct was demonstrated to be an efficient organocatalyst for the carboxylative cyclization of $CO_2$ and propargylic alcohols at mild temperature and pressure, selectively giving $\alpha$-alkylidene cyclic carbonates in good yields. The catalytic activity is about 10−200 times that of the corresponding NHC−$CO_2$ adducts at the same conditions. The plausible mechanism of the carboxylative cyclization was suggested, with regard to the hydrogen at the alkenyl position of cyclic carbonates coming from substrate (path A) or both substrate and catalyst (path B) on the basis of deuterated labeling experiments.

## EXPERIMENTAL SECTION

**General Procedure for the Synthesis of NHO−$CO_2$ Adducts.** Taking the synthesis of **2a** as example: *N*,*N*′-dimethyl-2-methyl imidazolium iodide (2 mmol, 0.48g) was added to a suspension of KH (0.16 g, 4 mmol) in THF (10 mL) and the mixture was stirred at ambient temperature for 48 h in the absence of light. After filtration to remove the salt, the filtrate filled in antipressure Schlenk flask was transferred to the Schlenk line equipped with a $CO_2$ and the flask was degassed at −78 °C in vacuo, filled with 1 atm $CO_2$. The solution was stirred to room temperature for 2 h. The precipitate was formed and collected via filtration. Subsequent the solid was washed with $Et_2O$ (10 mL) to afforded the corresponding NHO−$CO_2$ adduct **2a** and then pumped to dryness in 85% yield as white power. 2a: $^1$H NMR(400 MHz, DMSO-$d_6$): $\delta$ = 7.52 (s, 2H, C*H*═C*H*), 3.71 (s, 2H, $CH_2CO_2$), 3.60 (s, 6H, $NCH_3$). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ = 164.0, 146.9, 121.7, 34.9, 34.5. IR (KBr) 1616 $cm^{-1}$ (vs).

**Representative Experimental Procedure for the Carboxylative Cyclization.** Taking the carboxylative cyclization of 2-methyl-4-phenylbut-3-yn-2-ol (**4a**) with $CO_2$ as example: A 10 mL oven-dried autoclave containing a stir bar was charged the 4a (480.6 mg, 3 mmol), 2g (49.2 mg, 0.15 mmol) after purging the autoclave with $CO_2$ three times. The sealed autoclave was pressurized to appropriate pressure with $CO_2$. The reaction mixture was stirred at 60 °C for 12 h, then the autoclave was cooled to room temperature and the remaining $CO_2$ was vented slowly. The crude reaction mixture was purified by column chromatography on silica gel (PE/EtOAc = 10:1) to give **5a** in 93% yield. **5a**: $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.53−7.55 (m, 2H, $C_6H_5$), 7.23−7.37 (m, 3H, $C_6H_5$), 5.50 (s, 1H, C═C*H*), 1.68 (s, 6H, $CH_3$). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 151.4, 150.8, 132.5, 128.7, 128.6, 127.7, 101.6, 85.7, 27.8. IR ($cm^{-1}$) (neat) 1835, 1814, 1701. HRMS (ESI, *m*/*z*) calcd. for $C_{12}H_{12}O_3Na$ $[M + Na]^+$: 227.0684, found: 227.0676.

## ASSOCIATED CONTENT

### Supporting Information

General experimental procedures for the synthesis of various $CO_2$ complexes, as well as their characterizations. X-ray crystallographic file in CIF format for the structure determination of NHO−$CO_2$ adducts **2b**, **2c**, **2d**, **2f** and **2g**, and NHC−$CO_2$ adduct **3**. Synthetic procedures of various $\alpha$-alkylidene cyclic carbonates and labeling experiments. 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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