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Isolable CO_2 Adducts of Polarized Alkenes: High Thermal Stability and Catalytic Activity for CO_2 Chemical Transformation

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Abstract. Various CO_2 adducts of tetra-hydropyrimidin-2-ylidene (THPE) derived from the commercially available 1, 5-diazabicyclo[4.3.0]non-5-ene (DBN) were firstly synthesized. X-ray single crystal analysis revealed the bent geometry of the binding CO_2 having an O−C−O angle of 127.50~129.51° for THPE-CO_2 adducts. In situ FTIR experiments demonstrated that THPE-CO_2 had unprecedented thermal stability in DMSO, even at 100 °C without decomposition. It was found that the THPE-CO_2 adducts were highly active in catalyzing the carboxylative cyclization of CO_2 with propargylic alcohols under mild conditions, significantly higher than the previously reported organocatalysts. Various internal and terminal functionalized propargylic alcohols were tolerated in these processes to afford the corresponding *α*-alkylidene cyclic carbonates in moderate to good yields with complete (*Z*)-stereoselectivity. Isotope labeling, in combination with in-situ FTIR and stoichiometric experiments, revealed that the catalytic reaction tends to proceed *via* the THPE-CO_2-mediated basic ionic pair mechanism.

Keywords: CO_2 adducts; Organocatalysis; Polarized Alkenes; CO_2 transformation; Cyclic carbonates

Introduction

The development of efficient catalytic processes for carbon dioxide (CO_2) transformation into valuable organic chemicals/materials has been a longstanding goal for chemists, since CO_2 represents a nontoxic, abundant, and renewable C1 building block for chemical synthesis and industrial applications as an alternative to the common feedstocks based on natural gas, petroleum oil or coal.[1,2] The biggest obstacle is lack of effective catalysts to facilitate its activation and subsequent transformation, since CO_2 is such a thermodynamically and kinetically inert molecule. [3] Although CO_2 is a linear nonpolar molecule in the ground state, its two carbon–oxygen double bonds are polar. A net partial charge is present on carbon and oxygen atoms, in which the carbon atom plays the role of a Lewis acid center, while the oxygen atoms show a Lewis base character. As a result, electron-rich nucleophiles tend to interact with CO_2 by binding to the carbon atom, while electrophiles will attack one or two of the oxygen atoms. In 1975, Aresta *et al*. reported the isolation of the first CO_2-based complex, $Ni(PCy_3)_2(CO_2)$, in which the CO_2 ligand was coordinated in η^2 mode through the carbon atom and one of the oxygen atoms, possessing a bent geometry with an O−C−O angle of 133°.[4] More recently, Bourissou and coworkers described a rare example of η^1-CO_2 adduct of a group 10 metal (Pt), stabilized by O→Al interaction. The binding CO_2 molecule is also bent [O−C−O 122.9°(9)]. [5]

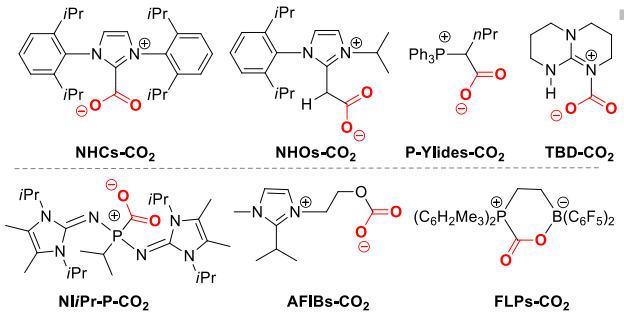


Figure 1. Representative CO_2 adducts employing organic molecules

Generally, CO_2 is a better acceptor than donor of electron density, due to the higher electrophilicity of carbon atom than the nucleophilicity of the oxygen atoms. It has been reported that strong Lewis bases such as the amidines and guanidines containing nitrogen heterocycles to react with CO_2, expectantly affording zwitterionic adducts.[6] The representative example is the *N*-heterocyclic carbene (NHC)-CO_2 adduct, in which a bent geometry with an O−C−O angle of 129~131° was revealed by X-ray single-crystal analysis.[7] Following this study, various organic base systems including 1,5,7-

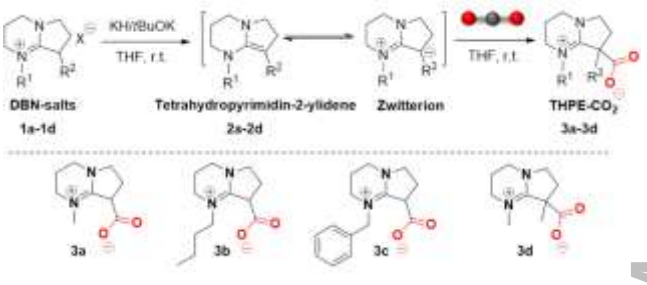
triazabicyclo[4.4.0]dec-5-ene (TBD),[8] *N*-heterocyclic olefins (NHOs),[9] alkoxide-functionalized imidazolium betaines (AFIBs),[10] phosphorus ylides (P-ylides),[11] 1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidenamino substituted phosphines (NI^{i}Pr-P)[12] and frustrated Lewis pairs (FLPs),[13] have been systematically studied for CO_2 sequestration, and the corresponding CO_2 adducts were successfully isolated (Figure 1). Moreover, these CO_2 adducts of superbases were found to be active in catalyzing the coupling of CO_2 with epoxides or aziridines to afford cyclic carbonates or oxazolidinones,[7c,14] the carboxylation with propargylic alcohols to α-alkylidene cyclic carbonates,[7f,9,10b] and the reduction of CO_2 to methanol, formamides and methylamines.[15] Noting that the structures of CO_2 adducts significantly affect their catalytic activities in CO_2 transformation. For example, the carboxylative cyclization of CO_2 with propargylic alcohols is one of the atom-economical routes to afford α-alkylidene cyclic carbonates.[16] In 2009, Ikariya *et al* reported the use of NHC-CO_2 adducts as organic catalysts for this process under a high CO_2 pressure of 4.5 MPa.[7f] Surprisingly, the significant increases in catalytic activity were observed in the application of NHO-CO_2 adducts as catalysts at the same conditions, in comparison with the corresponding NHC-CO_2 adducts.[9,17] Following this discovery, Lu *et al*. successively reported the AFIBs-CO_2 adducts[10b] and P-ylide CO_2 adducts[11b] catalyst systems for this process.

Indeed, both isotope labeling experiments and kinetic studies indicated that the above catalytic processes all concerned the decarboxylation of CO_2 adducts, in which the superbases could be really catalytic active species. In this process, the departure of the product from organic bases might be a possible rate-limiting step in the catalytic cycle. Although the decarboxylation of CO_2 adducts to free-superbases is beneficial for abstracting hydrogen of propargylic alcohol to form the intermediate, but has a negative effect on the departure of the product from organic bases. Therefore, from the comprehensive point, their CO_2 adducts rather than superbases themselves benefits for the final release of the product (the possible rate-limiting step), and thus probably significantly increasing the reaction rate.

In this paper, we firstly report the synthesis of various CO_2 adducts of tetra-hydropyrimidin-2-ylidene (THPE) derived from the commercially available 1, 5-diazabicyclo[4.3.0]non-5-ene (DBN) and unveil their geometries by X-ray single crystal analysis. Additionally, these adducts were also applied as effective organocatalysts for CO_2 transformation to useful chemicals under mild conditions, especially with a focus on the relevancy between the thermal stability and catalytic activity.

Results and Discussion

Synthesis and Characterization. THPE-CO_2 adducts (**3a-3d**) were synthesized in excellent yields using a procedure illustrated in Scheme 1. Firstly, in the presence of KH and a catalytic amount of *t*BuOK, the available DBN salts (**1a-1d**) were deprotonated in THF at ambient temperature, selectively affording THPEs **2a-2d**. Then, the resultant THPE solution was exposed to 1.0 atm CO_2 to afford THPE-CO_2 adducts as white solids. The characterizations including ^{1}H-NMR, ^{13}C-NMR data and FT-IR analysis for these THPE-CO_2 adducts **3a-3d** are given in the supporting information.



Scheme 1. Synthesis of THPE-CO_2 adducts **3a-3d**.

Single crystals of THPE-CO_2 adducts **3a**, **3c** and **3d** for the X-ray crystal structure analysis were obtained by slow diffusion of diethyl ether into CH_3CN solution at -35 °C. The selected bond lengths and bond angles are shown in Figure 2. The O–C–O angles of THPE-CO_2 adducts are in the range of 127.50~129.51°, which are nearly equivalent to those of the imidazo-functionalized NHO-CO_2 systems[9]. Interestingly, the two C–O bond distances regarding the binding CO_2 are different and the biggest discrepancy up to 0.033 Å was observed in the crystal data of compound **3d**. These data indicate that the negative charge of the THPE-CO_2 adducts is preferentially delocalized on O(2) atom, which is closer to N(2) atom.

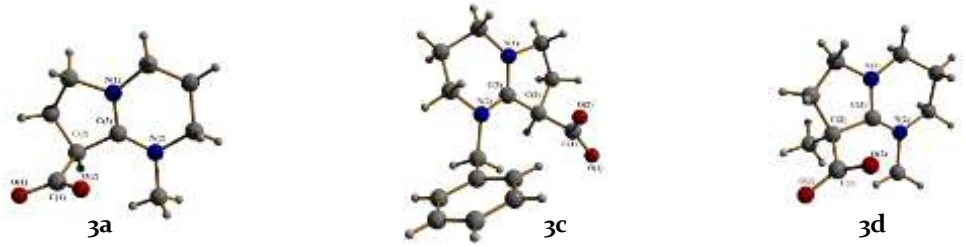


Figure 2. POV-Ray illustrations of the molecular structure of **3a**, **3c** and **3d**. Selected bond lengths (Å) and angles (°) for **3a**: C1–C2 1.566, O1–C1 1.245, O2–C1 1.249, O1–C1–O2 128.27; **3c**: C1–C2 1.544, O1–C1 1.231, O2–C1 1.251, O1–C1–O2 127.50; **3d**: C1–C2 1.548, O1–C1 1.210, O2–C1 1.243, O1–C1–O2 129.51.

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Thermostability Studies. Decarboxylation of CO_2 adducts of organic nucleophiles is normally observed at enhanced temperatures. Their thermal stabilities are significantly affected by the donating ability of organic nucleophiles and steric hindrance. In situ infrared spectroscopy was utilized to investigate the thermal stability of THPE-CO_2 adducts at different temperatures. As shown in Figure 3, the absorption peaks at 1679 cm^{-1} and 1604 cm^{-1} are attributable to the C=N and C=O band of **3a**, respectively. The C=O stretching frequency obviously red-shifted compared to the previously reported NHC-CO_2 or NHO-CO_2 adducts due to the inductive effect.[7b-d,7h,8-10,12b] In-situ FTIR study demonstrated that **3a** was very stable in DMSO at various temperatures. Even increasing the temperature to 100 °C still could not provoke the decarboxylation of **3a**, due to no obvious change in intensity both at 1679 cm^{-1} and 1604 cm^{-1} in 2 hours (Figure 3). It is worth mentioning that the previously reported NHC-CO_2 and NHO-CO_2 adducts are rapidly decarboxylated in DMSO solution at 40 °C (Figure 4). Meanwhile, in-situ FT-IR experiments by monitoring the C=O stretching frequency of **3b-3d** indicate that these CO_2 adducts are also very stable in DMSO solution at 100 °C (Figure S1-S7, see Supporting information for details).

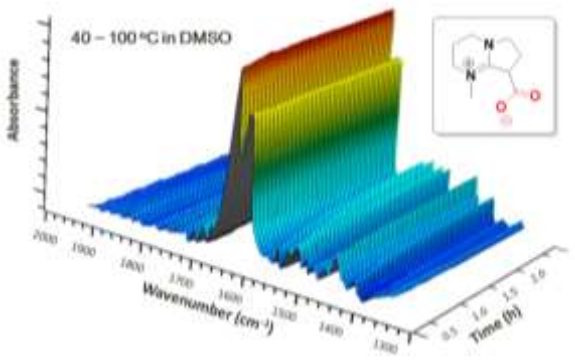


Figure 3. Thermal stability of **3a** in DMSO solution under different temperatures.

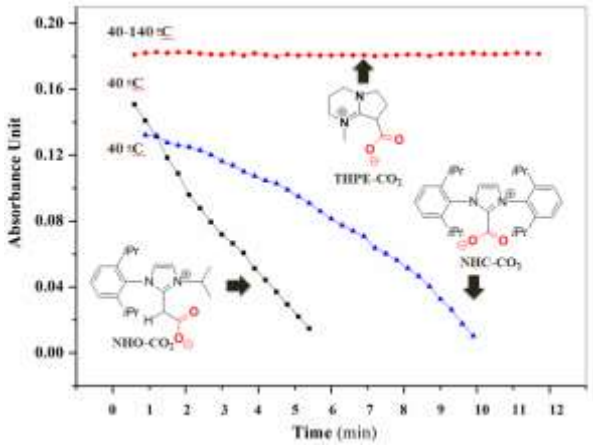
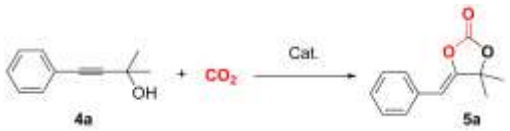


Figure 4. Difference in thermal stability of THPE-CO_2, NHC-CO_2 and NHO-CO_2 adducts in DMSO at different temperatures.

Catalytic Activities. The unique thermal stability of THPE-CO_2 adducts inspired us to further test their potential as organocatalysts for CO_2 transformation. We initially investigated these THPE-CO_2 adducts for catalyzing carboxylative cyclization of 2-methyl-4-phenylbut-3-yn-2-ol (**4a**) with CO_2 as model reaction. When using 5 mol % **3a**, the yield of **5a** was 92% under 60 °C and 2.0 MPa CO_2 pressure within 2 h (Table 1, entry 1). The catalytic activity of **3a** is obviously higher than that of imidazo-functionalized NHO-CO_2 adducts, which need 12 h to reach the similar yield under the same conditions.[9] **3b** and **3c** showed relatively lower activity, affording **5a** in 63% and 72% yields in 2 h, respectively (Table 1, entries 2, 3). **3d** is also an efficient catalyst, in which 90% yield was obtained (Table 1, entry 4). Notably, **3a** was found to be efficient even under room temperature, affording **5a** in good yield with a prolonged reaction time (Table 1, entry 5). Decreasing CO_2 pressure from 2.0 MPa to ambient pressure rapidly decreased the yield of **5a** (Table 2, entries 6-8). However, 20% yield of **5a** still could be obtained under ambient condition with 24 h. No reaction occurred without THPE-CO_2 adducts (Table 1, entry 9).

Table 1. Optimization of reaction conditions for the carboxylative cyclization of propargyl alcohol **4a** with CO_2. [a]



Entry	Cat.	T (°C)	P (MPa)	T (h)	Yield (%) [b]
1	**3a**	60	2.0	2	92
2	**3b**	60	2.0	2	63
3	**3c**	60	2.0	2	72
4	**3d**	60	2.0	2	90
5[c]	**3a**	25	2.0	24	86
6[c]	**3a**	25	1.0	24	80
7[c]	**3a**	25	0.5	24	66
8[c]	**3a**	25	0.1	24	20
9	-	60	2.0	24	NR [d]

[a] General conditions: neat, substrate **4a** (0.80 g, 5 mmol), THPE-CO_2 adduct (0.25 mmol, 5 mol%), CO_2 2.0 MPa. [b] Isolated yield. [c] CH_2Cl_2 (1.0 mL) was used as solvent. [d] No reaction.

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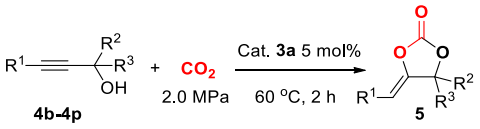
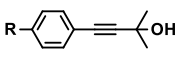
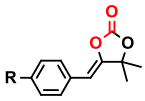
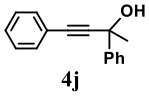
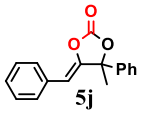
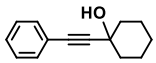
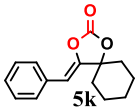
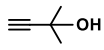
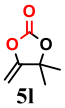
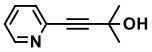
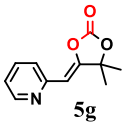
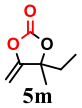
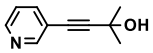
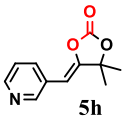
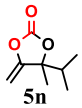
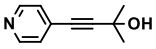
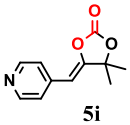
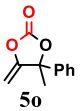
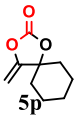
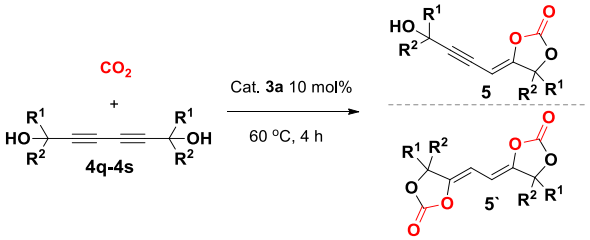
Table 2. THPE-CO_2 adduct **3a** catalyzed carboxylative cyclization of propargyl alcohol **4b-4p** with CO_2. [a]



Entry	Substrates **4**	Products **5**	Yield (%)[b]	Entry	Substrates **4**	Products **5**	Yield(%)[b]
1				5			92[c]
	4b: R = CH_3	**5b**	64		**4j**	**5j**	
	4c: R = OCH_3	**5c**	57	6			90[c]
	4d: R = Cl	**5d**	94		**4k**	**5k**	
	4e: R = CF_3	**5e**	94	7			91
	4f: R = $COCH_3$	**5f**	96		**4l**	**5l**	
2			94	8			95
	4g	**5g**			**4m**	**5m**	
3			96	9			86[c]
	4h	**5h**			**4n**	**5n**	
4			78	10			95[c]
	4i	**5i**			**4o**	**5o**	
				11			90[c]
					4p	**5p**	

[a] Reaction conditions: neat, substrate **4b-4p** (5 mmol), **3a** (5 mol%), 60 °C, 2 h, CO_2 2.0 MPa. [b] Isolated yield. [c] 4 h.

Table 3. THPE-CO_2 adduct **3a** catalyzed carboxylative cyclization of propargyl alcohol **4q-4s** with CO_2. [a]



Entry	Substrates **4**	Yield (%) [b] (5+5`)	Selectivity [c] (5/5`)
1	**4q**: $R^1 = R^2$ = -Me	94	19/81
2	**4r**: R^1 = -Me; R^2 = -Et	97	28/72
3	**4s**: $R^1 = R^2$ = -$(CH_2)_5$-	97	10/90

[a] Reaction conditions: neat, substrate **4q-4s** (5 mmol), **3a** (10 mol%), 60 °C, 4 h, CO_2 2.0 MPa. [b] Isolated yield. [c] The ratio of **5/5`** was determined by ^{1}H-NMR spectroscopy of the crude mixture.

Having established that THPE-CO_2 adduct **3a** is a highly active catalyst for the formation of α-alkylidene cyclic carbonate **5a** (Table 1), we further examined the scope of the carboxylative cyclization of CO_2 to a variety of highly functionalized propargylic alcohols, providing organic carbonates **5b-5s**, as shown in Tables 2 and 3. The reaction of 2-methyl-4-phenylbut-3-yn-2-ol bearing both electron-donating and electron-withdrawing groups on the aryl ring **4b-4f** gave the corresponding cyclic carbonates **5b-5f** in moderate to excellent yields (Table 2, entry 1). Alkynes bearing pyridine ring on the acetylenic carbon atoms **4g-4i** were also tolerated in this transformation to selectively generate **5g-5i** in high yields (Table 2, entries 2-4). Additionally, the high reactivities of various terminal propargylic alcohols **4l-4p** were discovered in the carboxylative cyclization with CO_2, providing excellent yield with a prolonged reaction time of 4 h (Table 2, entries 7-11). When 1,4-bis(1-hydroxyisopropyl)-1,3-butadiyne **4q** employed as the substrate, the carbonate **5q** and biscarbonate **5q'** were afforded in 18% and 76% yields, respectively (Table 3, entry 1). Both **5q** and **5q'** were easily isolated by silica gel column chromatography. It is noteworthy that the previously reported NHC-CO_2 or NHO-CO_2 adducts showed

very low activity at the same conditions (Supporting information, Table S5). Moreover, 1,4-bis(2-hydroxyisopentyl)-1,3-butadiyne **4r** and 1,4-bis(1-hydroxycyclohexyl)-1,3-butadiyne **4s** were also tolerated in this process (Table 3, entries 2 and 3). The molecular structure of **5s'** was further elucidated by single-crystal X-ray diffraction (Figure 5), which demonstrated that the two-step consecutive carboxylative cyclization of **4s** smoothly proceeded with complete (*Z*)-stereoselectivity to afford the double carboxylated product.

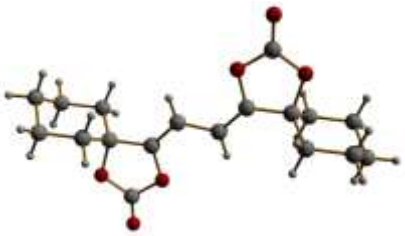


Figure 5. X-ray crystallographic structure of **5s'**.

Proposed Mechanism. Indeed, the reaction mechanism of carboxylative cyclization of CO_2 and propargyic alcohols using Lewis base-CO_2 adducts is still ambiguous. Earlier studies suggest that a dynamic equilibrium exists between organic nucleophiles and the corresponding CO_2 adducts under high temperature and high CO_2 pressure. Both of them could act as the nucleophiles to trigger the reaction on the basis of the nucleophilic addition mechanism or the basic ionic pair mechanism.[18]

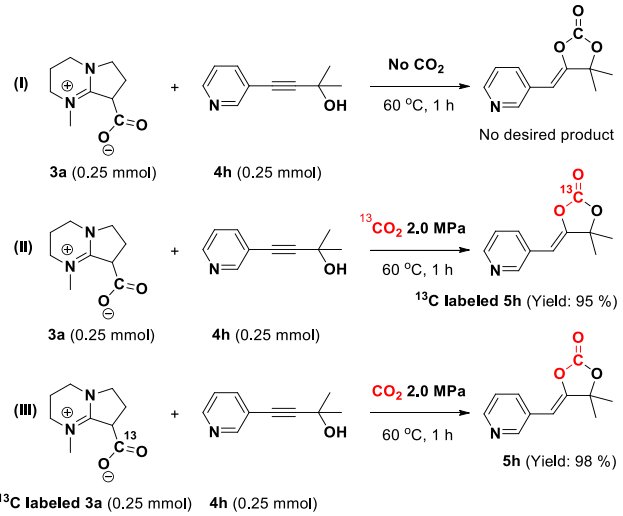


Figure 6. Preliminary mechanistic studies.

In order to better understand the reaction mechanism of THPE-CO_2 adducts for the carboxylic cyclization, several control experiments were carried out (Figure 6). Firstly, a stoichiometric reaction involving equivalent THPE-CO_2 adducts **3a** and propargylic alcohol **4h** was run in the absence of free CO_2 (Figure 6, **I**). No desired product **5h** was generated, and only the starting materials were retained in the reaction mixture according to ^{1}H NMR and HRMS spectra. When the above reaction proceeded in the presence of $^{13}CO_2$ atmosphere, ^{13}C labeled **5h** was generated as the sole product (Figure 6, **II**). Moreover, only **5h** was detected by employing THPE-$^{13}CO_2$ adducts **3a** in the presence of CO_2 atmosphere (Figure 6, **III**). These results indicate that the nucleophilic addition mechanism for THPE-CO_2 system could be excluded and the stable THPE-CO_2 adducts themselves act as organic bases for this process. This is different with that of the previously reported NHC-CO_2[7f] or NHO-CO_2 adducts[9,18].

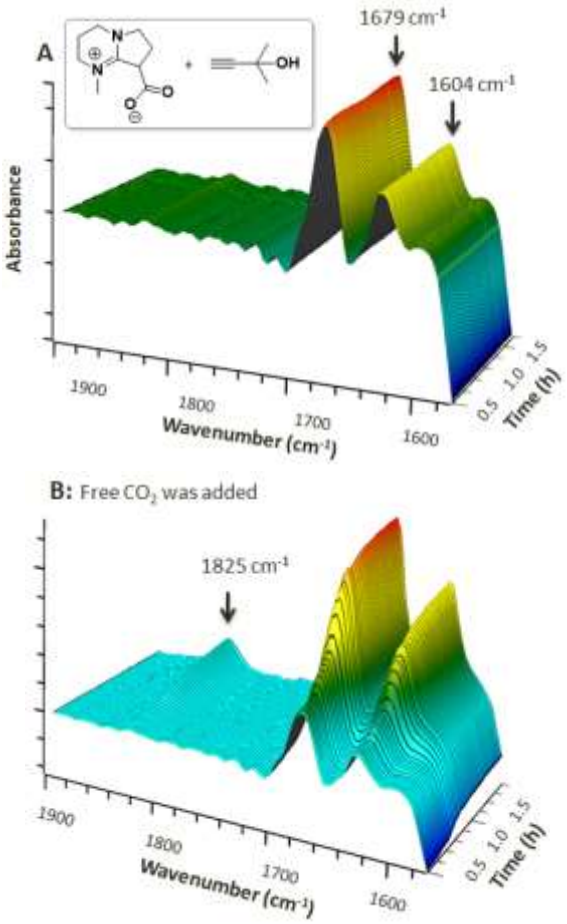


Figure 7. Three-dimensional stack plots of IR spectra collected every 15 s. Reaction conditions: (**A**) 2.0 mmol of **3a**, 10.0 mmol of propargylic alcohol, 60 °C, 1.5 h; (**B**) CO_2 balloon, 1.5 h. The absorption peaks at 1825, 1679 and 1604 cm^{-1} are attributable to the **5l** and **3a**, respectively.

Furthermore, in situ FTIR experiments showed that THPE-CO_2 **3a** is very stable in the presence of propargylic alcohol at 60 °C, and no product **5l** was observed (Figure 7**A**), which is in well agreement with NMR analysis. When introduced free CO_2, the carbonyl peak of **5l** at 1825 cm^{-1} gradually increased (Figure 7**B**). These results further demonstrate that CO_2 moiety of cyclic carbonates comes from free CO_2, rather than CO_2 moiety in THPE-CO_2 adducts (Further support for the assignment analysis of IR absorption peaks generated in Figure 7B, see Supporting Information).

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Based on the above experimental observations and previous publications, [7f, 9, 11b, 19] a mechanism in which THPE-CO_2 adducts themselves primarily acted as organic nucleophile to initiate the carboxylative cyclization of propargylic alcohols with CO_2 is proposed (Figure 8), leading to the formation of $[THPE\text{-}CO_2H]^+[carbonate]^-$ ion pair intermediate **A**. The $[carbonate]^-$ anion could be stabilized by the $[THPE\text{-}CO_2H]^+$ cation, which allows the carbonate anion to attack the triple bond of propargylic alcohol to generate an intermediate **B**. Then, the protonation of the alkenyl carbon anion allows the production of α-alkylidene cyclic carbonates, and meanwhile the release of THPE-CO_2 for the next catalytic cycle.

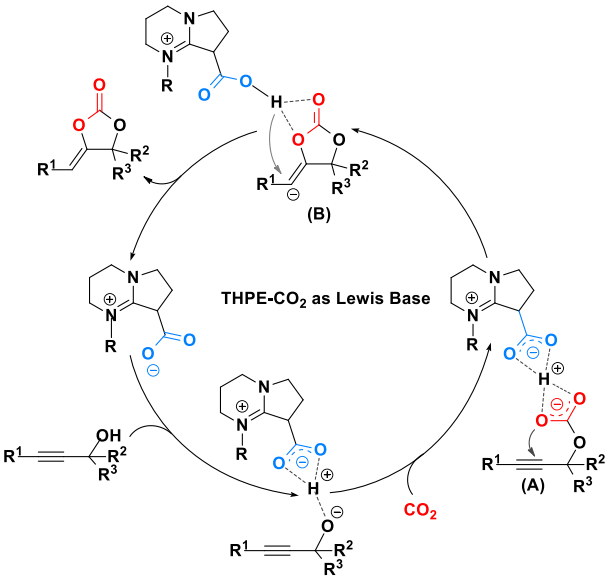
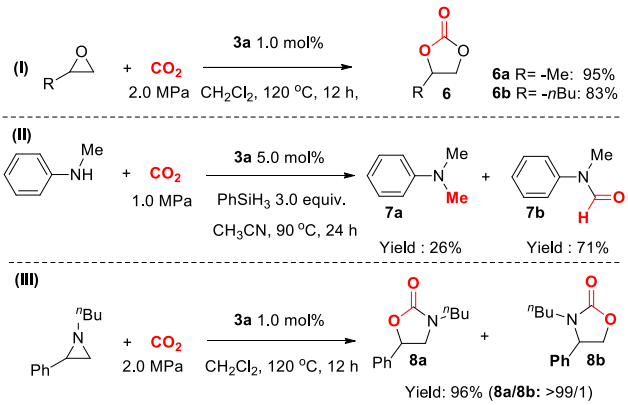


Figure 8. Proposed mechanism for synthesis of cyclic carbonates catalyzed by THPE-CO_2 adducts.

Application of THPE-CO_2 for other CO_2 transformations. The high activity profile for THPE-CO_2 adducts **3a** as organocatalyst for the carboxylative cyclization of propargylic alcohols with CO_2 inspires us to further investigate the new potential of this organocatalytic system for other related CO_2 conversion, and the preliminary results are presented in Figure 9.



Figuer 9. THPE-CO_2 adducts as organocatalysts for other related CO_2 transformations.

Firstly, the cycloaddition of CO_2 with terminal epoxides was carried out under optimized conditions (1.0 mol% Cat. **3a** 120 °C, CO_2 2.0 MPa, 12 h), and the desired cyclic carbonates **6a** and **6b** were successfully obtained in 95% and 83% yield, respectively (Figure 9. **I**). Then, in the presence of $PhSiH_3$ as the reducing agent, **3a** also could effectively catalyze the reductive functionalization of CO_2 with *N*-methylaniline as functionalizing reagent to form methylated **7a** and formylated **7b** at 90 °C under 2.0 MPa of CO_2 (Figure 9. **II**). Finally, **3a** catalyzed cycloaddition of 1-butyl-2-phenylaziridine with CO_2 proceeded smoothly to selectively synthesize *N*-butyl-5-phenyl oxazolidinone **8a** with high yield (Figure 9. **III**).

Conclusion

In summary, we have successfully synthesized a series of structurally simple THPE-CO_2 adducts derived from the readily available DBN. The single-crystal X-ray crystallographic analysis clearly shows the molecular structures of **3a**, **3c** and **3d** with the O–C–O angles of 126.13 ~ 129.51°. In situ FTIR experiments reveal that THPE-CO_2 adducts have exceptional thermal stability. Further catalytic application of THPE-CO_2 adducts as organocatalysts were undertaken to selectively synthesize the *cis* α-alkylidene cyclic carbonates by the cyclization of CO_2 with propargylic alcohols in moderate to high yields under mild conditions. To the best of our knowledge, THPE-CO_2 adducts are the most efficient among the reported organocatalysts for the carboxylative cyclization of CO_2 and propargylic alcohols. The reaction is tolerant to a wide range of internal and terminal functionalized propargylic alcohols with high stereoselectivity. Isotope labeling experiments, stoichiometric experiments and in situ FTIR data provide a proposed basic ionic pair mechanism for this process.

Moreover, THPE-CO_2 adducts systems exhibit considerable catalytic diversity in other CO_2 related transformations to selectively synthesize cyclic carbonates, methylamines, formamides and 5-substituted oxazolidinones.

Experimental Section

Representative experimental procedure for the synthesis of THPE-CO_2 adducts.

In a glove box, KH (0.12 g, 3.0 mmol) and KO*t*Bu (22.4 mg, 0.2 mmol) were added to a suspension of **1a** (0.53 g, 2.0 mmol) in THF (10 mL) respectively, and the mixture was stirred at room temperature for 48 h in the absence of light. After filtration, the filtrate was collected and exposed to 1.0 atm of CO_2 at ambient temperature for 2 h. The resulting white precipitate was collected via filtration, washed with *n*-hexane (3×20 mL) and then dried under high vacuum to afford desired product **3a** (0.32 g, 88% yield). **^{1}H NMR** (400 MHz, d_6-DMSO): δ 3.65 (q, *J* = 9.6 Hz, 1H), 3.58 (d, *J* = 8.8 Hz, 1H), 3.51 (dt, *J* = 1.9, 9.6 Hz, 1H), 3.31-3.36 (m, 4H), 3.16, (s, 3H), 2.06-2.23 (m, 2H), 1.87-1.99 (m, 2H). **^{13}C NMR** (100 MHz, d_6-DMSO): δ

166.70, 164.75, 52.99, 52.28, 46.17, 41.42, 39.69, 25.23, 18.80. **IR** $\nu_{C=O}$: 1604 cm^{-1} (vs). **HRMS (ESI)**: [M-CO_2+H]$^+$ calcd for $C_8H_{15}N_2$: 139.1230; Found: 139.1226.

3b. White solid (0.38 g, 85% yield). **^{1}H NMR** (400 MHz, d_6-DMSO): δ 3.64-3.73 (m, 2H), 3.49-3.56 (m, 2H), 3.31-3.36 (m, 5H), 2.13-2.18 (m, 2H), 1.88-1.96 (m 2H), 1.52-1.61 (m, 2H), 1.21-1.29 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, d_6-DMSO): δ 167.48, 164.83, 53.58, 52.84, 52.51, 44.26, 42.23, 29.29, 25.92, 19.69, 19.32, 14.11. **IR** $\nu_{C=O}$: 1608 cm^{-1} (vs). **HRMS (ESI)**: [M-CO_2+H]$^+$ calcd for $C_{11}H_{21}N_2$: 181.1699; Found: 181.1700.

3c White solid (0.44 g, 86% yield). **^{1}H NMR** (400 MHz, d_6-DMSO): δ 7.33-7.39 (m, 5H), 4.93 (d, *J* = 15.4 Hz, 1H), 4.69 (d, *J* = 15.4 Hz, 1H), 3.75 (q, *J* = 9.2 Hz, 1H), 3.68 (d, *J* = 8.4 Hz, 1H), 3.57 (dt, *J* = 2.1, 9.2 Hz, 1H), 3.34-3.42 (m. 2H), 3.13-3.18 (m, 1H), 2.16-2.28 (m, 2H), 1.83-1.96 (m, 2H). **^{13}C NMR** (100 MHz, d_6-DMSO): δ 167.06, 164.83, 134.90, 128.64, 128.12, 127.92, 55.29, 53.46, 52.83, 43.69, 41.84, 25.39, 18.76. **IR** $\nu_{C=O}$: 1611 cm^{-1} (vs). **HRMS (ESI)**: [M-CO_2+H]$^+$ calcd for $C_{14}H_{19}N_2$: 215.1543 . Found: 215.1541.

3d White solid (0.34 g, 87% yield). **^{1}H NMR** (400 MHz, d_6-DMSO): δ 3.57 (t, *J* = 7.2 Hz, 2H), 3.34 (t, *J* = 5.4 Hz, 2H), 3.05 (s, 3H), 2.34 (dt, *J* = 7.7, 12.2 Hz, 1H), 1.94-1.95 (m, 2H), 1.76-1.82 (m, 1H), 1.29 (s, 3H). **^{13}C NMR** (100 MHz, d_6-DMSO): δ 170.35, 167.97, 56.24, 51.58, 47.17, 41.84, 34.62, 21.34, 18.71. **IR** $\nu_{C=O}$: 1600 cm^{-1} (vs). **HRMS (ESI)**: [M-CO_2+H]$^+$ calcd for $C_9H_{17}N_2$: 153.1386. Found: 153.1387.

Representative experimental procedure for the carboxylative cyclization of CO_2 with functionalized propargylic alcohols to α-alkylidene cyclic carbonates

In a glove box, a 10 ml autoclave containing a stir bar was charged with propargylic alcohol **4a** (0.80 g, 5 mmol), and catalyst THPE-CO_2 **3a** (45.5 mg, 0.25 mmol, 5 mol%). After purging the autoclave with CO_2 three times, the sealed autoclave was pressurized to the appropriate pressure with CO_2. The reaction was carried out at 60 °C for 2 h with continuous stirring. Then, the autoclave was cooled, and the excess CO_2 was vented. The residue was purified by column chromatography (eluent: petroleum ether/EtOAc=10:1) to give the corresponding *α*-alkylidene cyclic carbonate **5a** (0.94 g, 92 %) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.51-7.53 (m, 2H), 7.23-7.35 (m, 3H), 5.47 (s, 1H), 1.66 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 151.2, 150.5, 132.4, 128.7, 128.8, 127.5, 101.3, 85.5, 27.4. All the resonances in ^{1}H and ^{13}C NMR spectra were in good agreement with literature values.[8]

X-Ray structure: Supplementary crystallographic data was deposited at the Cambridge Crystallographic Data Centre (CCDC) under the numbers CCDC 1455223 (**3a**), CCDC 1455222 (**3c**), CCDC 1401873 (**3d**), CCDC 1455756 (**5s'**) and can be obtained free of charge from via www.ccdc.cam.ac.uk/data_request.cif.

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FULL PAPER

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Adv. Synth. Catal. **Year**, *Volume*, Page – Page

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