ChemPubSoc Europe

DOI: 10.1002/cssc.201402921

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Bifunctional Silver(I) Complex-Catalyzed CO_2 Conversion at Ambient Conditions: Synthesis of α-Methylene Cyclic Carbonates and Derivatives

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The chemical conversion of CO_2 at atmospheric pressure and room temperature remains a great challenge. The triphenylphosphine complex of silver(I) carbonate was proved to be a robust bifunctional catalyst for the carboxylative cyclization of propargylic alcohols and CO_2 at ambient conditions leading to the formation of α-methylene cyclic carbonates in excellent yields. The unprecedented performance of $[(PPh_3)_2Ag]_2CO_3$ is presumably attributed to the simultaneous activation of CO_2 and propargylic alcohol. Moreover, the highly compatible basicity of the catalytic species allows propargylic alcohol to react with CO_2 leading to key silver alkylcarbonate intermediates: the bulkier $[(Ph_3P)_2Ag^I]^+$ effectively activates the carbon–carbon triple bond and enhances O-nucleophilicity of the alkylcarbonic anion, thereby greatly promoting the intramolecular nucleophilic cyclization. Notably, this catalytic protocol also worked well for the reaction of propargylic alcohols, secondary amines, and CO_2 (at atmospheric pressure) to afford β-oxopropylcarbamates.

Introduction

With increasing awareness of ever-growing CO_2 levels in the atmosphere, great efforts have been made to develop strategies and technologies towards the reduction of carbon emissions.[1] Indeed, CO_2 fixation and conversion hold great promise for recycling CO_2 into value-added products due to the great potential of CO_2 as an abundant, nontoxic, easily accessible, and sustainable C_1 feedstock.[2] However, only a small proportion of the total abundance of CO_2 is currently being consumed in industry; the main reason is that establishing catalytic and economical carbon neutral processes (with a high turnover number of a million) is challenging due to the thermodynamic stability and kinetic inertness of CO_2. In general, a highly reactive metal reagent or catalyst, and/or nucleophile and high pressure/temperature are required to activate and further incorporate CO_2 into organic compounds.[3] The chemical transformation of CO_2 at atmospheric pressure and room temperature remains a great challenge, though great progress has been made. In this context, the development of efficacious processes using CO_2 as chemical feedstock under mild conditions (particularly low CO_2 pressure, ideally at 1 bar) could be still highly desirable.[4]

The catalytic carboxylative cyclization of propargylic alcohols with CO_2 shows great promise for the direct incorporation of CO_2 into high-value-added chemicals; namely α-alkylidene cyclic carbonates, which are compounds incorporating a framework that is important in natural products with potential bioactivity,[5] and have a broad range of applications as intermediates in organic synthesis.[6] To date, several metal-free catalytic systems, such as tertiary phosphine,[7] the *N*-heterocyclic carbene (NHC)/CO_2 adduct,[8] bicyclic guanidine,[9] and the *N*-heterocyclic olefin/CO_2 adduct[10] have been developed for the preparation of α-alkylidene cyclic carbonates. However, high CO_2 pressure and high reaction temperatures are usually required for an efficient reaction. In this regard, further enhanced reactivity and selectivity could depend on transition-metal catalysts (containing Pd,[11] Co,[12] Cu,[13] and Ag)[14] capable of activating the carbon–carbon triple bond of propargylic alcohols. Unfortunately, higher CO_2 pressure or additional energy is eventually inevitable for practical syntheses, despite the fact that, according to the literature, relatively high selectivities have been attained with metal catalysts so far. In 2007, Yamada et al. reported on the silver-catalyzed procedure for the carboxylative ring-closing reaction of internal propargylic alcohols under low CO_2 pressure in the presence of an organic base, such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), which presumably acts as a promoter for the formation of alkylcarbonic intermediate **I** (Scheme 1).[14a] However, relatively large amounts of AgOAc and stoichiometric amounts of the organic base were still required for a smooth reaction. Notably, Yamada et al. achieved the enantioselective incorporation of CO_2 into chiral internal propargylic alcohols catalyzed by

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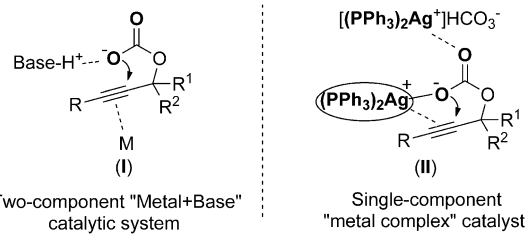
Supporting Information for this article is available on the WWW under http://dx.doi.org/10.1002/cssc.201402921.



Scheme 1. Dual activation mode by the two-component catalyst system (Base: tertiary amine) in the literature (**I**) and well-defined robust metal complex used herein (**II**).

a AgOAc/chiral Schiff base system.[14b] Recently, Mizuno et al.[4b] reported that ammonium tungstate (able to activate CO_2) allowed the reaction of propargylic alcohols with CO_2 to proceed smoothly under mild conditions. Yet, higher temperatures and longer reaction times were indispensable to reach satisfactory yields.

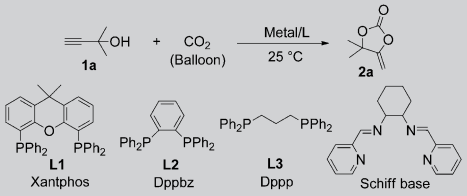
Scheme 1 shows **I** participating in the two-component metal–base-catalyzed reaction of propargylic alcohols and CO_2.[12,14] A tertiary amine was used as a sacrificial promoter to abstract protons from hydroxyl groups. Higher CO_2 pressure and reaction temperatures were still unavoidable probably because the strong interaction between base–H^+ and $HC{\equiv}CC(R^1R^2)OCO_2^-$ hindered the O-nucleophilicity of **I**. Fortunately, the presence of bulky cations enhanced the O-nucleophilicity and basicity of oxo-anions.[4b,15] In this context, we successfully developed the two-component catalyst system comprising Ag_2WO_4 and Ph_3P for this kind of carboxylative cyclization under low pressure.[16] We envisioned that the triphenylphosphine complex of silver(I) carbonate, that is $[(PPh_3)_2Ag]_2CO_3$, prepared from Ag_2CO_3 and PPh_3,[17] would serve as a well-defined single-component bifunctional catalyst capable of activating both the C≡C bond[18] as well as CO_2, and thus enable the reaction to efficiently proceed at low pressure and temperature presumably going through intermediate **II** (Scheme 1). Furthermore, the bulkier cation, that is $[(Ph_3P)_2Ag^I]^+$, could stabilize the carbonic anion and enhance its O-nucleophilicity relative to base–H^+ (**I**, Scheme 1), and thus promote the subsequent intramolecular nucleophilic cyclization of **II** resulting in the formation of α-methylene cyclic carbonates.

Herein, we describe the use of $[(PPh_3)_2Ag]_2CO_3$ (in situ formed from Ag_2CO_3 and PPh_3) as a robust and highly efficient single-component bifunctional catalyst for the reaction of propargylic alcohols with CO_2 at room temperature and atmospheric pressure; comparisons with the present state-of-the-art two-component metal–base catalyst system were also drawn. Notably, the catalyst worked well for the three-component reaction of propargylic alcohols, secondary amines, and CO_2 (1 bar) affording β-oxopropylcarbamates.

Results and Discussion

Several metal compounds were initially investigated for the reaction of 2-methylbut-3-yn-2-ol (**1a**) as the model substrate under a CO_2 balloon without any solvent at 25 °C for 12 h (Table 1). Without catalyst or additive, the reaction did not occur and the starting material was quantitatively recovered (Table 1, entry 1). DBU and Ph_3P were ineffective under the given conditions (Table 1, entries 2 and 3). Then, CuCl and various silver salts capable of activating carbon–carbon triple bonds were screened in combination with Ph_3P as an additive. Unfortunately, CuCl, $AgNO_3$, AgOAc, and $AgSO_3CF_3$ showed no activity (Table 1, entries 4–7). Gratifyingly, α-alkylidene cyclic carbonates (**2a**) were obtained in a yield of 41% by employing Ag_2WO_4 (1 mol%) in conjunction with Ph_3P (2 mol%) at 25 °C for 2 h (Table 1, entry 8). Notably, silver(I) compounds, such as Ag_2O, Ag_3PO_4, and Ag_2CO_3 displayed higher activity than Ag_2WO_4 under identical conditions (Table 1, entries 9–11 versus 8). Particularly the Ag_2CO_3/PPh_3 (1:2 molar ratio) system gave the best result with a quantitative yield of **2a** (Table 1, entry 11).

Table 1. Carboxylic cyclization of propargylic alcohols with CO_2.[a]



Entry	Catalyst [1 mol%]	L/Additive [2 mol%]	*t* [h]	Yield[b] [%]
1	–	–	12	–[c]
2	DBU	–	12	–[c]
3	PPh_3	–	12	–[c]
4	CuCl	PPh_3	12	–[c]
5	$AgNO_3$	PPh_3	12	–[c]
6	AgOAc	PPh_3	12	–[c]
7	$AgSO_3CF_3$	PPh_3	12	–[c]
8	Ag_2WO_4	PPh_3	2	41
9	Ag_2O	PPh_3	2	86
10	Ag_3PO_4	PPh_3	2	81
11	Ag_2CO_3	PPh_3	2	97
12	Ag_2CO_3	–	2	–[c]
13	Ag_2CO_3	Et_3N	2	<1
14	Ag_2CO_3	2,2′-bipyridine	2	–[c]
15	Ag_2CO_3	DBU	2	4
16[d]	Ag_2CO_3	**L1**	2	74
17[d]	Ag_2CO_3	**L2**	2	15
18[d]	Ag_2CO_3	**L3**	2	40
19[e]	Ag_2CO_3	$(p\text{-}MeOC_6H_4)_3P$	1	57
20[e]	Ag_2CO_3	PPh_3	1	55
21[e]	Ag_2CO_3	$(p\text{-}FC_6H_4)_3P$	1	17
22[e]	Ag_2CO_3	$(p\text{-}CF_3C_6H_4)_3P$	1	–[c]
23[f]	AgOAc	Schiff base	2	1
24[g]	$[(PPh_3)_2Ag]_2CO_3$	–	2	93

[a] Unless otherwise specified, all reactions were performed with **1a** (0.211 g, 2.5 mmol), CO_2 (1 bar), and catalyst (1 mol% relative to **1a**) at ambient conditions. [b] Determined by GC analysis with biphenyl as the internal standard. [c] No reaction with full recovery of the starting material. [d] Ligand (1.0 mol%). [e] Ag_2CO_3 (3.5 mg, 0.5 mol%), ligand (13.1 mg, 1.0 mol%). [f] The silver system of Yamada et al. with AgOAc (2 mol%) and a Schiff base (8 mol%). [g] Prior to use, $[(PPh_3)_2Ag]_2CO_3$ (34.0 mg, 1.0 mol%) was prepared according to Ref. [17].

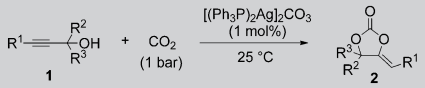
However, Ag_2CO_3 itself was ineffective (Table 1, entry 12), suggesting a crucial role of PPh_3 in promoting catalytic performance. Further screening of additives showed that Et_3N, 2,2′-bipyridine, and DBU had a negative effect on the reaction (Table 1, entries 13–15). On the other hand, bidentate phosphine ligands, such as Xantphos (**L1**) were more active than, for example, 1,2-bis(diphenylphosphanyl)benzene (Dppbz, **L2**) and 1,3-bis(diphenylphosphino)propane (Dppp, **L3**; Table 1, entry 16 versus 17–18). Subsequently, several monophosphines were investigated. The monophosphine outfitted with a methoxy group performed slightly better than PPh_3 (Table 1, entry 19 versus 20), whereas fluorinated groups retarded the reaction sharply (Table 1, entry 21). In addition, the reaction was completely suppressed once a strong withdrawing group was introduced (e.g., CF_3; Table 1, entry 22). Especially the silver system with the Schiff base[14b] showed almost total inactivity under ambient conditions (Table 1, entry 23).

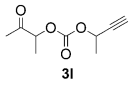
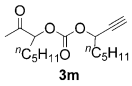
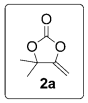
Furthermore, efforts were made to explore the appropriate ratio of $PPh_3/[Ag^+]$ (see the Supporting Information, Table S1). At a fixed Ag_2CO_3 loading (0.5 mol%), the **2a** yield increased from 21 to 92% with an increase in the $PPh_3/[Ag^+]$ molar ratio from 0.5 to 2 (see the Supporting Information, Table S1, entries 1–4), and then remained invariable with a further increase in PPh_3 concentration (see the Supporting Information, Table S1, entries 5–6). Accordingly, the optimal $PPh_3/[Ag^+]$ ratio was found to be 2, which was identical with the $PPh_3/[Ag^+]$ molar ratio in $[(PPh_3)_2Ag]_2CO_3$. Indeed, $[(Ph_3P)_2Ag]_2CO_3$ gave results that were comparable to the Ag_2CO_3/PPh_3 system (Table 1, entry 24 versus 11), presumably implying that $[(PPh_3)_2Ag]_2CO_3$ could be a real catalytic species. The formation of $[(Ph_3P)_2Ag]_2CO_3$ from Ag_2CO_3/PPh_3 during the reaction was also supported by ^1H NMR, ^{13}C NMR, and ^{31}P NMR analyses (see the Supporting Information, Figure S1). In addition, the precipitate recovered after the reaction was reused in a subsequent carboxylative cyclization to produce **2a** in 94% yield under CO_2 (1 bar) at room temperature for 2 h (see the Supporting Information, Figure S2).

Having established the $[(PPh_3)_2Ag]_2CO_3$-catalyzed carboxylative cyclization protocol, we then studied the reactivity of various propargylic alcohols to further explore the substrate scope (Table 2). Numerous terminal propargylic alcohols with a variety of alkyl and aryl substituents at the propargylic position (**1a**–**g**) underwent the reaction smoothly with a CO_2 balloon at room temperature to afford the corresponding α-alkylidene cyclic carbonates (**2a**–**g**) in 82–99% yield. Nonetheless, relatively high pressure (25 or 60 bar) and temperatures (80 °C) were required for the substrates with a small ring or bulky isopropyl group at the propargylic position (**1h**–**i**) to react, probably due to the steric hindrance effect on the formation of the silver(I) alkylcarbonic anion intermediate (**II**, Scheme 1). Interestingly, the electron-rich monodentate alkyl phosphine ligand, for example PCy_3 (Cy = cyclohexyl), greatly facilitated the reaction for the inert substrate **1h** under ambient conditions.

The introduction of a phenyl group at the terminal position also caused a decrease in reactivity. Up to that point, internal propargylic alcohols with a terminal aryl substituent had been generally unreactive with low-pressure CO_2 even at higher re-

Table 2. Carboxylative cyclization of various propargylic alcohols with CO_2.[a]



Product	Reaction conditions	Reaction time [h]	Yield [%]
 **2a**	neat	1	92
 **2b**	neat	3	99 (97)
 **2c**	neat	12	89
 **2d**	–	4	>99
 **2e**	–	6	96
 **2f**	–	4	99
 **2g**	– 10 bar, neat	2 1	82 99
 **2h**	25 bar	24	94[b], >99[c]
 **2i**	60 bar, neat	18	54[b]
 **2j**	10 bar	3	90[d]
 **2k**	10 bar	4	99[d]
 **3l**	neat	12	91[e]
 **3m**	neat	12	87[e]
 **2a**	neat	15	92[f]

[a] Unless otherwise specified, all reactions are run using **1** (2.5 mmol), fresh prepared $[(Ph_3P)_2Ag]_2CO_3$ (34 mg, 1 mol% relative to **1**) with 0.5 mL $CHCl_3$ under 1 bar CO_2 at 25 °C. GC yields are based on the propargylic alcohols. The isolated yields are given in parentheses. [b] 80 °C. [c] Ag_2CO_3 (2 mol%), PCy_3 (8 mol%), 1 bar CO_2, 25 °C, 24 h. [d] $[(Ph_3P)_2Ag]_2CO_3$ (85 mg, 2.5 mol%). [e] **3l**/**3m** were formed from secondary propargylic alcohols **1l** and **1m** through alcoholysis of the unstable cyclic carbonate **2l**/**2m** and subsequent tautomerization (see Figure S3). [f] On a 120 mmol scale; yield 14.14 g; Ag_2CO_3 (0.1 mol%), PPh_3 (0.4 mol%).

action temperatures.[14,15] Our protocol worked well for internal propargylic alcohols, such as **1j–k**, at a CO_2 pressure of 10 bar, leading to the formation of **2j–k** in 90 and 99% yield, respectively. On the other hand, secondary alcohols (**1l–m**) did not give the cyclization product, but subsequent alcoholysis products (**3l–m**) were isolated. That was understandable because **1l–m** initially reacted with CO_2 through the carboxylative cyclization pathway to in situ form **2l–m**, followed by alcoholysis and tautomerization[9] to afford **3l–m** (see the Supporting Information, Figure S3).

Using a catalyst at lower loads, excellent yields (up to 92%) were still attained in a scaled-up experiment (120 mmol, Table 2). Thus, the present protocol could potentially be applied in the large-scale chemical fixation of CO_2 at atmospheric pressure through a facile operating procedure.

The reactions of **1a/1j** with $^{13}CO_2$ were monitored by ^1H and ^{13}C NMR spectroscopy (Figure 1) to elucidate the catalytic role of $[(Ph_3P)_2Ag]_2CO_3$. The OH signal became broad and shifted from $\delta = 5.46$ to 5.77 ppm (Figure 1a and b) in ^1H NMR spectra, suggesting hydrogen bonding formation between $[(Ph_3P)_2Ag]_2CO_3$ and **1j**, and presumably leading to activation of propargylic alcohol by the silver complex and also enhancement of O-nucleophilicity. As seen in Figure 1c–d, changes in signals arising from the C1, C2, and C3 sites could be attributed to the interaction between soluble silver salts and the carbon–carbon triple bond, that is, resulting in activation of propargylic alcohol. The interaction of $[(Ph_3P)_2Ag]_2CO_3$ with $^{13}CO_2$ was examined by ^{13}C NMR spectroscopy (Figure 1e–f). In the case of $^{13}CO_2$ (1 bar), analyses were performed using a solution of $[(Ph_3P)_2Ag]_2CO_3$ in $CDCl_3$; a new signal centered at $\delta = 163.02$ ppm was deemed as evidence of the formation of the carbonate species (and thus $^{13}CO_2$ activation) because it resembled the signal found in ^{13}C NMR spectra of $[WO_4]^{2-}/CO_2$ adducts.[4b]

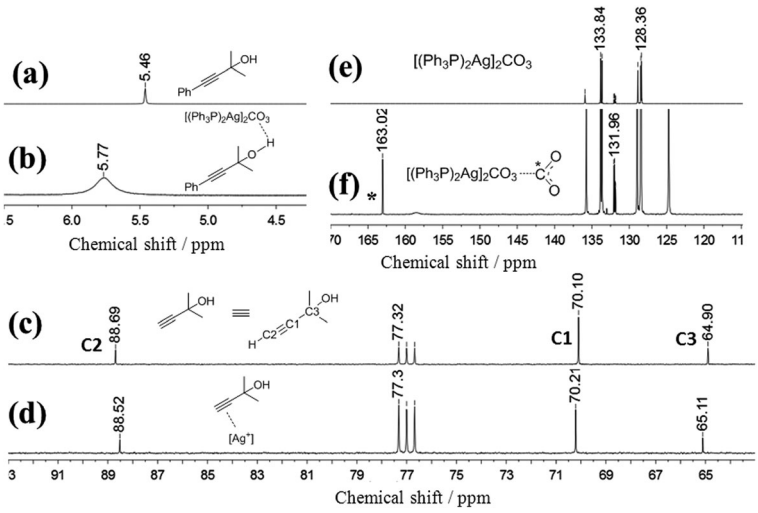


Figure 1. ^1H NMR (a, b) and ^{13}C NMR (c–f) investigation. (a, b) **1j** (8.0 mg), Ag_2CO_3 (2.8 mg) and Ph_3P (10.5 mg) ([D$_6$]DMSO 0.6 mL). (c, d) **1a** (20.2 mg), $AgNO_3$ (40.8 mg) ($CDCl_3$ 0.6 mL). (e) $[(Ph_3P)_2Ag]_2CO_3$ (158.6 mg) in 0.6 mL of $CDCl_3$. (f) $[(Ph_3P)_2Ag]_2CO_3$ (158.6 mg) in 0.6 mL of $CDCl_3$ in the presence of $^{13}CO_2$ (1 bar).

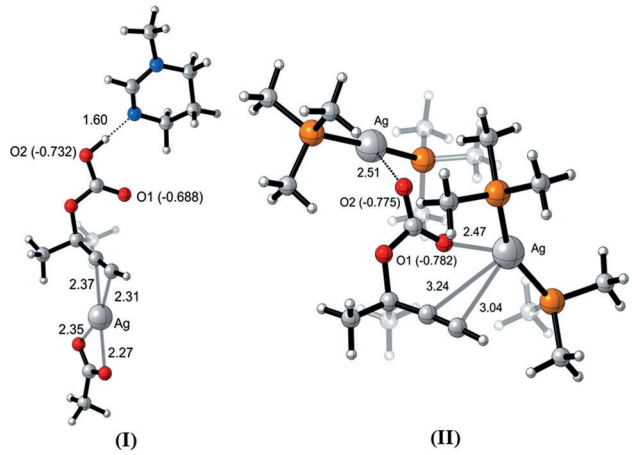


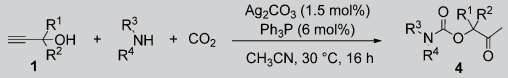
Figure 2. Models **I** and **II** with nature bond orbital (NBO) charge distribution, calculated by the M06/6-311++G(d,p)/LANL2DZ//B3LYP/6-31G(d)/LANL2DZ/SMD method. **I**: AgOAc-activated formation of propargyl carbonic ester with simplified DBU; **II**: dual $[(Me_3P)_2Ag]CO_3$-activated mode (presented herein). H: white, C: gray, N: blue, O: red, P: orange. Bond lengths and distances in Å.

DFT calculations were performed (Figure 2; also see the Supporting Information) to gain a deeper insight into activation modes **I** and **II** in Scheme 1. As demonstrated in Figure 2 (**I** and **II**), the higher electron charge at an oxygen atom of **II** (O1: −0.782, O2: −0.775) is connected with stronger O-nucleophilicity relative to that of **I** (O1: −0.688, O2: −0.732); the lower stabilization energy (SE) of **II** (−67.7 kcal mol^{-1}) than that of **I** (−32.4 kcal mol^{-1}) suggests that **II** is more active. On the other hand, the lower relative activation energy (RAE) of **II** (−20.47 kcal mol^{-1}) relative to that of **I** (−18.17 kcal mol^{-1}) corresponds to higher activation efficiency with the complex of silver(I) carbonate as model **II**. In addition, such hypotheses could also be in agreement with the effect of silver concentration on the yield in **2a** (see the Supporting Information).

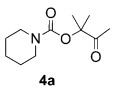
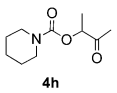
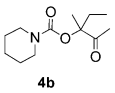
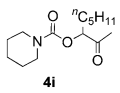
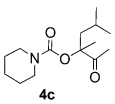
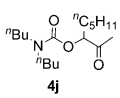
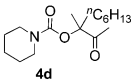
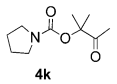
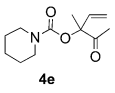
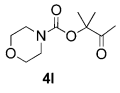
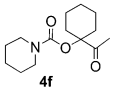
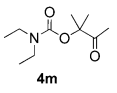
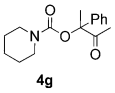
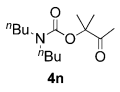
More importantly, the chemical utilization of CO_2 was applied to the production of an array of value-added products, such as oxazolidinones, quinazolines, carbamates, isocyanates, and polyurethanes, through C–N bond formation.[2e] However, the typical three-component reaction of propargylic alcohols, secondary amines, and CO_2 to access β-oxopropylcarbamates usually requires high pressure and temperature.[9,19] In this respect, effective methodologies using CO_2 as a feedstock to β-oxopropylcarbamates under atmospheric pressure and mild conditions are still challenging.

With an optimized catalytic system in hand, we explored the scope of the three-component reaction by employing a variety of terminal propargylic alcohols and secondary amines under CO_2 at atmospheric pressure (Table 3). Generally, reactions took place via the formation of α-methylene cyclic carbonates and a subsequent aminolysis sequence.[9] To our delight, a series of

Table 3. Three-component reaction of propargylic alcohols, secondary amines, and CO_2.[a]



1 4

Product	Yield[b]	Product	Yield[b]
 4a	98 (86[c])	 4h	98
 4b	96	 4i	96
 4c	87	 4j	76
 4d	98	 4k	93
 4e	83	 4l	82
 4f	90	 4m	91
 4g	68	 4n	96

[a] **1** (2 mmol), amines (2 mmol, 1 equiv.), Ag_2CO_3 (8.3 mg, 1.5 mol%), Ph_3P (31.5 mg, 6 mol%), CO_2 balloon, CH_3CN (1 mL). [b] Isolated yield. [c] On a 10 mmol scale under neat conditions for 24 h.

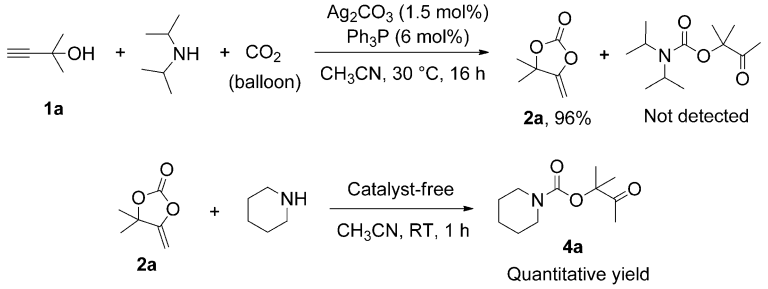
tertiary terminal propargylic alcohols (**1a–g**) reacted with CO_2 and piperidine leading to the formation of β-oxopropylcarbamates (**4a–g**) in 68–98% yields. Notably, the present protocol was also fruitful on a 10 mmol scale (**4a**, Table 3).

In addition, our protocol was also suitable for secondary propargylic alcohols combined with a variety of secondary amines to afford the corresponding β-oxopropylcarbamates (**4h–j**) in high to excellent yields (76–98%) under optimal conditions. The secondary aliphatic amines also gave **4k–n** in high yields (82–96%).

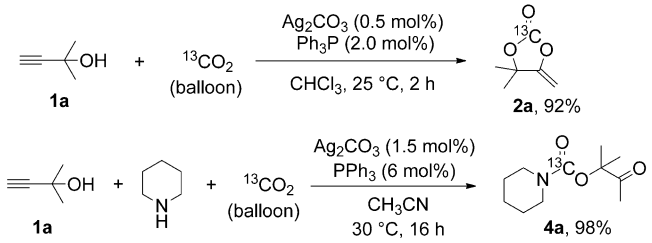
To further confirm the catalytic conversion of CO_2 to cyclic carbonates we performed the reaction in the presence of $^{13}CO_2$. As shown in Scheme 2, the presence of $^{13}C_{carbonyl}$-labelled **2a** and **4a** verified successful conversion (see the Supporting Information, Figure S4–S7).

To get more information about the $[(Ph_3P)_2Ag]_2CO_3$-catalyzed three-component reaction of propargylic alcohols, secondary amines, and CO_2, we also performed additional control experiments (Scheme 3). As shown in Table 3, the reaction of **1a**, piperidine, and CO_2 gave **4a**; whereas the reaction with a bulkier amine (e.g., diisopropylamine) stopped at the formation of **2a**. In addition, **2a** reacted with piperidine to afford **4a** smoothly in the absence of any silver catalyst. Accordingly, this kind of three-component reaction is assumed to go through the cyclic carbonate pathway.

On the basis of experimental results, NMR analyses, and DFT calculations, a tentative mechanism for the $[(Ph_3P)_2Ag]_2CO_3$-promoted fixation of CO_2 at atmospheric pressure with propargylic alcohols is illustrated in Scheme 4. Propargylic alcohol initially activated by $[(Ph_3P)_2Ag]_2CO_3$, which can be in situ formed from Ag_2CO_3 and Ph_3P, reacts with activated CO_2 to generate the silver propargylic carbonate intermediate (**A**) along with $(Ph_3P)_2AgHCO_3$ (Scheme 4a); $(Ph_3P)_2AgHCO_3$ was inactive in carboxylative cyclizations (see the Supporting Information). Subsequently, an intramolecular nucleophilic cyclization occurs at the silver(I)-activated C≡C bond. Finally, the corresponding cyclic carbonate is formed via intermediates **B** and **C**, followed by proto-demetallation (with the aid of HCO_3^-) and by the regeneration of $[(Ph_3P)_2Ag]_2CO_3$.



Scheme 3. Control experiments.

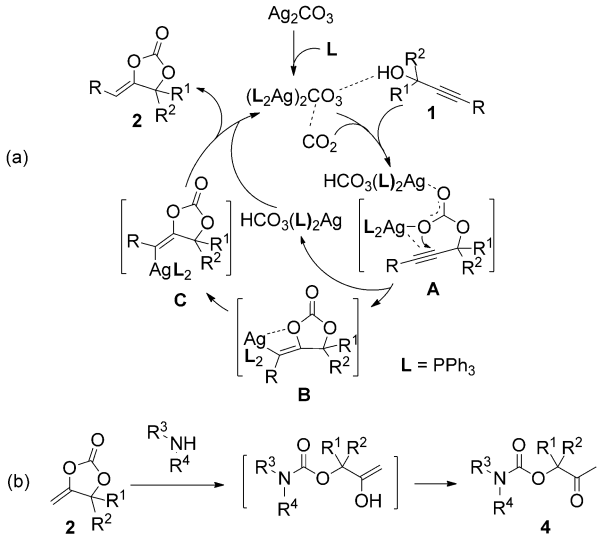


Scheme 2. Isotope labeling experiments.

In the case of the three-component reaction, α-alkylidene cyclic carbonates (**2**), formed according to Scheme 4a, further undergo a nucleophilic ring-opening with a secondary amine to generate the carbamate species (Scheme 4b). Finally, the corresponding β-oxopropylcarbamates (**4**) are obtained through tautomerization.

Conclusions

An elegant protocol was established for the expeditious chemical fixation of CO_2 at atmospheric pressure to prepare α-alkyli-



Scheme 4. Plausible mechanism for the $[(Ph_3P)_2Ag]_2CO_3$-catalyzed carboxylic reaction of propargylic alcohols, secondary amines, and CO_2: (a) formation of of alkylidene cyclic carbonates and (b) formation of β-oxopropylcarbamates through the alkylidene cyclic carbonate intermediate.

dene cyclic carbonates in good to excellent yields at room temperature. Such an efficient strategy relies on the ingenious design of the relatively stable $[(Ph_3P)_2Ag]_2CO_3$ (which could also be in situ generated from Ag_2CO_3 and PPh_3) as a robust bifunctional catalyst to spontaneously trap CO_2 at atmospheric pressure and simultaneously activate propargylic alcohol and CO_2. Notably, this interesting procedure could be easily scaled up for the fixation of CO_2 at atmospheric pressure. That catalytic protocol was also applied to the three-component reaction of terminal propargylic alcohols, secondary amines, and CO_2.

Experimental Section

General procedure for the synthesis of α-alkylidene cyclic carbonates: Taking the carboxylative cyclization of 2-methylbut-3-yn-2-ol (**1a**) with CO_2 as an example: a 10 mL Schlenk tube equipped with a stir bar was charged with $[(PPh_3)_2Ag]_2CO_3$ (34.0 mg, 1.0 mol%) and **1a** (210.3 mg, 2.5 mmol) with the addition of solvent ($CHCl_3$, 0.5 mL) or under solvent-free conditions. Subsequently, the Schlenk tube was attached to a balloon filled with CO_2 (99.99%). Then, the reaction mixture was stirred at 25 °C for the desired time. Carefully releasing excessive CO_2 after the reaction, the mixture was extracted with Et_2O (3×5 mL). The combined organic phases were analyzed by GC or concentrated in vacuo and purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1–20:1) to give the product **2a** as a colorless oil (312 mg, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.75–4.31 (dd, J = 4.0 Hz, J = 4.0 Hz, 2H, CH_2), 1.59 ppm (s, 6H, $2CH_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 158.6, 151.2 (C=O), 85.2, 84.6, 27.5 ppm; IR (neat): $\tilde{\nu}$ = 1825, 1687, 1271, 1086, 1032, 856 cm^{-1}; MS (EI, 70 eV): m/z (%): 128.10 (2.81), 85.10 (6.49), 84.10 (100), 83.10 (3.54), 69.10 (48.16).

General procedure for the synthesis of β-oxopropylcarbamates: Taking the three-component reaction of 2-methylbut-3-yn-2-ol (**1a**), piperidine, and CO_2 as an example: a 10 mL Schlenk tube equipped with a stir bar was charged with Ag_2CO_3 (8.3 mg, 1.5 mol%), Ph_3P (31.5 mg, 6 mol%), **1a** (168 mg, 2 mmol), piperidine (170 mg, 2 mmol), and CH_3CN (1 mL). Next, the Schlenk tube was attached to a balloon filled with CO_2 (99.99) and sealed; the mixture was left to react at 30 °C for 16 h. Excessive CO_2 was carefully released after the reaction. The residue was flushed with CH_2Cl_2 (3×5 mL) and removed under vacuum. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1–10:1) to give **4a** as a light brown oil (421 mg, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.39 (m, 4H, 2N-CH_2), 2.11 (s, 3H, $COCH_3$), 1.59–1.49 (m, 6H, $-CH_2CH_2CH_2-$), 1.43 ppm (s, 6H, $2CH_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 207.5 (C=O), 154.0 (N–C=O), 82.7, 44.6, 25.6, 24.0, 23.4, 23.2 ppm; IR (neat): $\tilde{\nu}$ = 1827, 1685, 1271, 1172, 1085, 1031 cm^{-1}; GC-MS (EI, 70 eV): m/z (%): 213.15 (0.33), 171.15 (1.66), 170.20 (15.03), 129.15 (1.20), 128.15 (12.49), 114.15 (1.02), 113.15 (8.01), 112.15 (100), 69.10 (45.97).

Acknowledgements

We are grateful to the National Natural Sciences Foundation of China (grant number 21421001, 21121002, 21472103), Specialized Research Fund for the Doctoral Program of Higher Education (project 20130031110013), MOE Innovation Team (IRT13022) of China for financial support.

Keywords: carbon dioxide fixation · catalysis · density functional calculations · silver · synthetic methods

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Received: August 29, 2014
Revised: October 22, 2014
Published online on ■■ ▮▮, 0000

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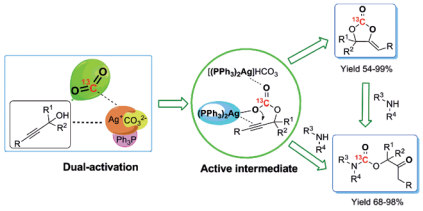
Bifunctional Silver(I) Complex-Catalyzed CO_2 Conversion at Ambient Conditions: Synthesis of α-Methylene Cyclic Carbonates and Derivatives



Catalytic fixation of CO_2: $[(PPh_3)_2Ag]_2CO_3$ is proven to be a robust bifunctional catalyst for the chemical upgrading of CO_2 at atmospheric pressure to produce valuable compounds at ambient conditions. $[(PPh_3)_2Ag]_2CO_3$ can activate both CO_2 and propargylic alcohol, and promote the subsequent intramolecular nucleophilic cyclization.