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Synthesis of α-alkylidene cyclic carbonates *via* CO_2 fixation under ambient conditions promoted by an easily available silver carbamate†

Giulio Bresciani,[ab] Marco Bortoluzzi,[bc] Claudia Ghelarducci,[a] Fabio Marchetti[ab] and Guido Pampaloni*[ab]

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The simple and cost-effective compound $[Ag(O_2CNEt_2)]$, in combination with PPh_3, works as an effective catalytic precursor in the carboxylation of propargyl alcohols at ambient temperature and atmospheric CO_2 pressure, and in most cases under solventless conditions. The silver carbamate revealed a better performance than commercial silver oxide, Ag_2O, and allowed to obtain a series of α-alkylidene cyclic carbonates in high yields.

Introduction

The opportunity to use carbon dioxide as a convenient C_1 synthon in organic synthesis has fueled a research field of increasing interest, and many efforts have been devoted to develop synthetic strategies aimed to incorporate CO_2 into valuable fine chemicals.[1–4] In particular, five-membered cyclic carbonates are now available through a green approach from epoxides and CO_2, and a variety of efficient catalytic systems have been reported to promote this synthetic process.[5–7]

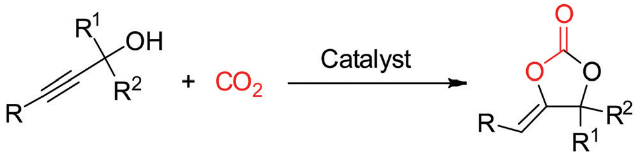
The carboxylation of propargyl alcohols is another attractive reaction providing access to α-alkylidene cyclic carbonates (Scheme 1),[8–11] which find important applications in the pharmaceutical industry[12,13] and as starting materials for the synthesis of polycarbonates and polyurethanes.[14–16]

A variety of metal-free catalytic systems has been proposed for the coupling between propargyl alcohols and CO_2.[17–21] Nevertheless, since the activation of the carbon–carbon triple bond is a key rate-limiting step, late transition metal compounds are potentially ideal catalysts, due to their propensity to coordinate and activate alkynes.[22,23] Several studies have been carried out,[17,24–28] and especially silver complexes[29–34] and silver-supported materials and nanoparticles[11,35–37] have been investigated, usually in association with a Lewis base. In this scenario, the development of simple and relatively cost-effective silver catalysts operating under solvent-free and ambient conditions is highly desirable due to sustainability issues. Moreover, the use of CO_2 at atmospheric pressure is an added value also in terms of safety, since it allows the synthesis by means of conventional laboratory glassware and a safe and cheap balloon technique, thus avoiding a pressurized equipment. In the actual state of the art, many of the proposed catalytic systems operating at ambient pressure of CO_2 require a solvent or high temperatures.[29,31,32,38] On the other hand, examples of catalytic systems working without needing a solvent, at room temperature and ambient pressure, are still rare.[33,39,40]

Metal *N*,*N*-dialkylcarbamates constitute a family of well available molecular compounds of general formula $[M(O_2CNR_2)_n]$, which are widely represented across the periodic table.[41–43] Their synthesis is usually straightforward, consisting of the reaction of the parent metal chlorides with secondary amines under an atmospheric pressure of CO_2 (eqn (1)).

$$MCl_n + nCO_2 + 2nNHR_2 \rightarrow [M(O_2CNR_2)_n] + n(NH_2R_2)Cl \quad (1)$$

The potential of transition metal carbamates in catalysis, although still limitedly explored, is intriguing on considering the versatility of the carbamato ligand, which easily adapts



Scheme 1 Coupling of propargyl alcohol with CO_2 affording α-alkylidene cyclic carbonate.

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[a] *Università di Pisa, Dipartimento di Chimica e Chimica Industriale, Via Moruzzi 13, I-56124 Pisa, Italy. E-mail: guido.pampaloni@unipi.it*

[b] *CIRCC, via Celso Ulpiani 27, I-70126 Bari, Italy*

[c] *Ca' Foscari Università di Venezia, Dipartimento di Scienze Molecolari e Nanosistemi, Via Torino 155, I-30170 Mestre (VE), Italy*

† Electronic supplementary information (ESI) available: ^1H NMR signals of propargyl alcohols and their corresponding α-alkylidene cyclic carbonates. ^1H NMR spectra of products. DFT structures. Cartesian coordinates of the DFT structures are collected in a separated. *xyz* file. See DOI: 10.1039/d0nj05657j

from bi- to monodentate coordination and *vice versa*, allowing the generation of vacant metal sites. Our group has recently reported that some transition metal carbamates are effective catalytic precursors in the carboxylation of epoxides[44,45] and terminal alkynes.[46] Apart from the above mentioned flexibility, the carbamato ligand contains a CO_2 fragment that can be dynamically exchanged with an external CO_2 molecule, resulting in an enhancement of the catalytic activity.[44] In other words, the carbamato moiety might act as an ''anteroom'' where carbon dioxide is pre-activated before entering the catalytic cycle.

On account of these facts, we decided to study $Ag(O_2CNEt_2)$ as a new catalyst (in combination with a Lewis base) for the carboxylation of a series of propargyl alcohol. Such silver(I) carbamate possesses a dimeric structure and, at variance to the general synthetic method (eqn (1)), is obtained from Ag_2O by treatment with diethylamine under atmospheric CO_2 pressure.[46,47] The optimization of the catalytic performance of commercial silver oxide has also been investigated,[33] and the results obtained with the two silver catalysts will be comparatively presented and discussed.

Experimental section

General experimental details

Carbon dioxide (99.99%) was purchased from Rivoira. Reactants were obtained from Merck, TCI Europe or Strem Chemicals, were of the highest purity available and stored under N_2 atmosphere as received. Solvents were purchased from Merck and distilled before use under N_2 from appropriate drying agents. $[Al(O_2CNEt_2)_3]$,[45] $[Ti(O_2CNEt_2)_4]$,[48] $[Fe(O_2CNEt_2)_3]$,[49] $[Ru(O_2CNEt_2)Cl(\eta^6\text{-}p\text{-cymene})]$,[50] $[Co(O_2CNEt_2)_2]$,[51] $[Cu(O_2CNEt_2)_2]$,[52] $[Ag(O_2CNEt_2)]$,[46] $[Ag(O_2CNEt_2)(PPh_3)_2]$[46] and $[Au(O_2CNEt_2)(PPh_3)]$[47] were prepared according to the respective literature procedures. NMR spectra were recorded at 298 K on a Bruker Avance II DRX400 instrument equipped with a BBFO broadband probe; chemical shifts (expressed in parts per million) have been referenced to the residual solvent peaks.[53]

Reaction between propargyl alcohols and carbon dioxide

The selected propargyl alcohol (1 mL) was introduced under CO_2 atmosphere into a Schlenk tube, containing the appropriate amounts of catalyst and Lewis base. A balloon filled with CO_2 was connected to the Schlenk tube and the mixture was left reacting at ambient temperature (*ca.* 21 °C). After 5 hours under vigorous stirring, a carefully controlled amount of 1,1,2,2-tetrachloroethane (*ca.* 0.2 mL) was added as an internal standard. An aliquot (*ca.* 0.1 mL) of the resulting solution was transferred into an NMR tube and added of $CDCl_3$ (0.5 mL). Selectivity and conversion values were determined by ^1H NMR (Table S1, ESI†), and are referred to 1,1,2,2-tetrachloroethane.

DFT calculations

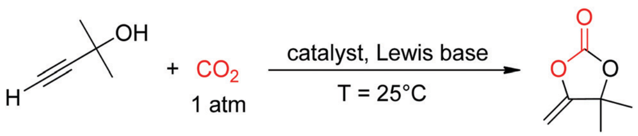
The computational geometry optimizations of the complexes were carried out without symmetry constraints, using the range-separated hybrid functional ωB97X[54–56] and the def2 split-valence polarized basis set of Ahlrichs and Weigend, with 28 core electrons of silver enclosed in pseudopotential.[57,58] The C-PCM solvation model was added considering acetonitrile as continuous medium.[59,60] The ''restricted'' formalism was always applied. The achievement of stationary points was confirmed by IR simulations (harmonic approximation), from which zero-point vibrational energies and thermal corrections (T = 298.15 K) were obtained.[61] The software used was Gaussian 09.[62] Cartesian coordinates of the DFT-optimized structures are collected in a separated ESI.†

Results and discussion

We started studying a model reaction, $HC{\equiv}CCMe_2OH + CO_2$, for which a range of late transition metal carbamates was evaluated as potential catalysts (Table 1); $[Al(O_2CNEt_2)_3]$ and Ag_2O were also examined. Triethylamine and triphenylphosphine were tested as possible auxiliary Lewis bases.[63] Fixed experimental conditions were adopted, *i.e.* ambient temperature, CO_2 atmospheric pressure, and absence of solvent. The results of this preliminary screening are compiled in Table 1.

All the metal species resulted substantially inactive during 24 hours except the two silver compounds, which worked in combination with PPh_3 (runs 13–15, 18–21). The optimal concentration values of catalyst and co-catalyst were revealed

Table 1 Synthesis of 4,4-dimethyl-5-methylene-1,3-dioxolan-2-one from 2-methyl-3-butyn-2-ol(dimethylpropargyl alcohol) and CO_2[a]



Run	Catalyst, mol%	Lewis base, mol%	Reaction time (h)	Yield[b] (%)
1	—	PPh_3, 1	24	0
2	$[Al(O_2CNEt_2)_3]$, 1	PPh_3, 1	24	0
3	$[Ti(O_2CNEt_2)_4]$, 1	NEt_3, 1	24	0
4	$[Fe(O_2CNEt_2)_3]$, 1	NEt_3, 1	24	0
5	$[RuCl(O_2CNEt_2)(\eta^6\text{-}p\text{-cymene})]$, 1	NEt_3, 1	24	0
6	$[RuCl(O_2CNEt_2)(\eta^6\text{-}p\text{-cymene})]$, 1	PPh_3, 1	24	Traces
7	$[Co(O_2CNEt_2)_2]$, 1	NEt_3, 1	24	Traces
8	$[Co(O_2CNEt_2)_2]$, 1	PPh_3, 1	24	0
9	$[RhCl(PPh_3)_3]$, 1	PPh_3, 1	24	0
10	CuCl, 1	PPh_3, 1	24	0
11	$[Cu(O_2CNEt_2)_2]$, 1	NEt_3, 1	24	5
12	$[Cu(O_2CNEt_2)_2]$, 1	PPh_3, 1	24	2
13	$[Ag(O_2CNEt_2)]$, 1	PPh_3, 1	24	>99
14	$[Ag(O_2CNEt_2)]$, 1	PPh_3, 1	5	93
15	$[Ag(O_2CNEt_2)]$, 1	PPh_3, 2	5	>99
16	$[Ag(O_2CNEt_2)]$, 1	NEt_3, 1	24	0
17	$[Ag(O_2CNEt_2)(PPh_3)_2]$, 1	—	5	65
18	Ag_2O, 1	PPh_3, 1	24	>99
19	Ag_2O, 1	PPh_3, 1	2.5	54
20	Ag_2O, 0.5	PPh_3, 1	2.5	85
21	Ag_2O, 0.5	PPh_3, 2	5	84
22	Ag_2O, 0.5	$NH_{3(aq)}$, 1	5	Traces
23	$[Au(O_2CNEt_2)(PPh_3)]$, 0.3	PPh_3, 1	24	Traces

[a] Reaction conditions: dimethylpropargyl alcohol 1.0 mL, 10.3 mmol; T = 25 °C; $p(CO_2)$ = 1 atm. [b] Determined by ^1H-NMR using 1,1,2,2-tetrachloroethane as internal standard (selectivity >99% in all cases).

to be those ones in runs 15 and 20, respectively. The mononuclear, tetrahedral complex $[Ag(O_2CNEt_2)(PPh_3)_2]$[47] performed worse than the 1 : 2 mixture $[Ag(O_2CNEt_2)]/PPh_3$ (compare runs 15 and 17), suggesting that the former does not correspond to the active catalytic species derived from $[Ag(O_2CNEt_2)]$ (*vide infra*). Probably, the presence of two bulky phosphines in the metal coordination sphere slows down the alkyne coordination, slowing down the reaction rate.

In order to examine more in detail the effect of the co-catalyst, some experiments were carried out with silver oxide (Table 2). It was found that PPh_3 is the only practicable option among a series of phosphines, probably the role of the phosphine is finely related to a combination of steric and electronic factors. Coherently, large variability in the yields of propargyl alcohol carboxylation on changing the phosphine co-catalyst was previously observed with Ag_2CO_3[33] and Ag_2WO_4.[40] Blank experiments confirm that the two components of the catalytic system (Ag_2O and PPh_3) are synergistically needed in order to obtain the product (runs 1 and 9).

Overall, the results in Tables 1 and 2 indicate that both $[Ag(O_2CNEt_2)]$ and Ag_2O, in combination with PPh_3, are effective to promote the carboxylation of dimethylpropargyl alcohol at ambient and solventless conditions. We extended the comparative evaluation of the two silver catalysts to the carboxylation of other commercial propargyl alcohols using the optimized reaction parameters (Table 1, runs 15 and 20). The reactions involving 1-ethynyl-1-cyclohexanol (melting point = 30–33 °C; runs 11 and 12) were conducted at *ca.* 40 °C in order to avoid viscosity; on the other hand, the use of a solvent became necessary in the cases of high melting-point substrates (Table 3, runs 13–18). Acetonitrile was chosen, being one of the most widely employed solvents for the present reaction.[17,36] The α-alkylidene cyclic carbonate derived from 1,1,3-triphenylprop-2-yn-1-ol (Table 3, runs 17–18) was selectively obtained as a Z stereoisomer according to ^{1}H NMR.

Using silver carbamate, eight products were synthesized in 87% to quantitative yields, and only 5-methylene-4,4-diphenyl-1,3-dioxolan-2-one was obtained in a moderate yield (Table 3, run 16). On comparing the results obtained with 1,1-diphenylprop-2-yn-1-ol and 1,1,3-triphenylprop-2-yn-1-ol (Table 3, runs 17 and 18), the relatively low yield with which the former is produced might be related to electronic rather than steric effects. In general, the silver carbamate exhibits superior performance with respect to silver oxide, and this is particularly evident in those reactions involving terminal alkynes with sterically hindered substituents (Table 3, runs 11–16). The bis-triphenylphosphine complex $[Ag(O_2CNEt_2)(PPh_3)_2]$ confirmed its lower activity compared to the $[Ag(O_2CNEt_2)]/PPh_3$ mixture also in the carboxylation reaction of 3-methyl-1-pentyn-3-ol (runs 3 and 6 in Table 3).

Table 2 Effect of the phosphine on the yield of the model reaction catalyzed by silver oxide[a]

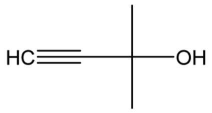
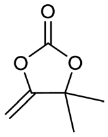
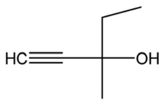
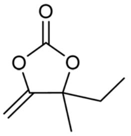
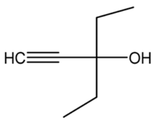
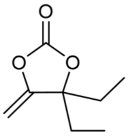
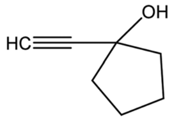
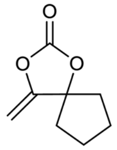
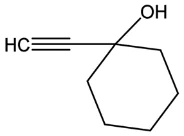
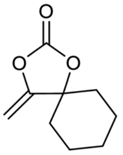
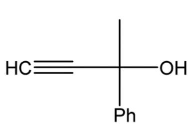
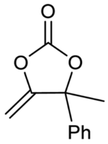
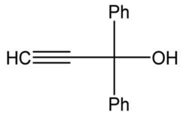
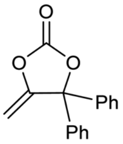
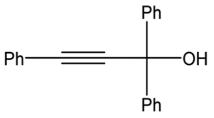
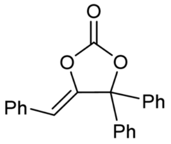
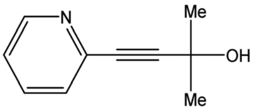
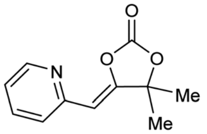
Run	Catalyst Ag_2O (mol%)	Lewis base, mol%	Yield[b] (%)
1	—	PPh_3, 1	0
2	0.2	PPh_3, 1	85
3	0.2	PCy_3, 1	0
4	0.2	DPPPh, 1	0
5	0.2	PCl_2Ph, 1	0
6	0.2	PCl_3, 1	0
7	0.2	DPPE, 0.5	0
8	0.2	DCyPE, 0.5	0
9	0.2	—	0

[a] Reaction conditions: dimethylpropargyl alcohol 1.0 mL, 10.3 mmol; DPPPh = (2-diphenylphosphino)phenol, DPPE = 1,2-bis(diphenylphosphino)ethane, DCyPE = 1,2-bis(dicyclohexylphosphino)ethane; T = 25 °C; $p(CO_2)$ = 1 atm; reaction time = 5 hours. [b] Determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as internal standard (selectivity $>$99% in all cases).

The presence of the carbamato ligand is likely to strongly address the catalytic activity of the silver complex, and in general mechanistic studies on the promising catalytic activity of metal carbamates are still in their infancy. We carried out a DFT study in order to shed some light on the role of the carbamato moiety and to detect plausible reaction intermediates (Scheme 2). Thus, we considered the model reaction between dimethylpropargyl alcohol and CO_2, and $[Ag(\kappa^2\text{-}O_2CNEt_2)(PPh_3)_2]$ was analyzed as the catalytic precursor due to its mononuclear nature,[47] with the aim of reducing the calculation effort. However, the release of one PPh_3 ligand from this complex is associated to a slightly positive Gibbs energy variation, 1.4 kcal mol^{-1}: based on this outcome and the experimental evidence that $[Ag(\kappa^2\text{-}O_2CNEt_2)(PPh_3)_2]$ is less efficient than the equivalent $[Ag(\kappa^2\text{-}O_2CNEt_2)]/PPh_3$ mixture (see above), we believe that the tri-coordinated complex $[Ag(\kappa^2\text{-}O_2CNEt_2)(PPh_3)]$ is the probable active species, which may be generated starting from both $[Ag(\kappa^2\text{-}O_2CNEt_2)(PPh_3)_2]$ and $[Ag(\kappa^2\text{-}O_2CNEt_2)]/PPh_3$. A view of the structure of $[Ag(\kappa^2\text{-}O_2CNEt_2)(PPh_3)]$ is shown in Fig. 1.

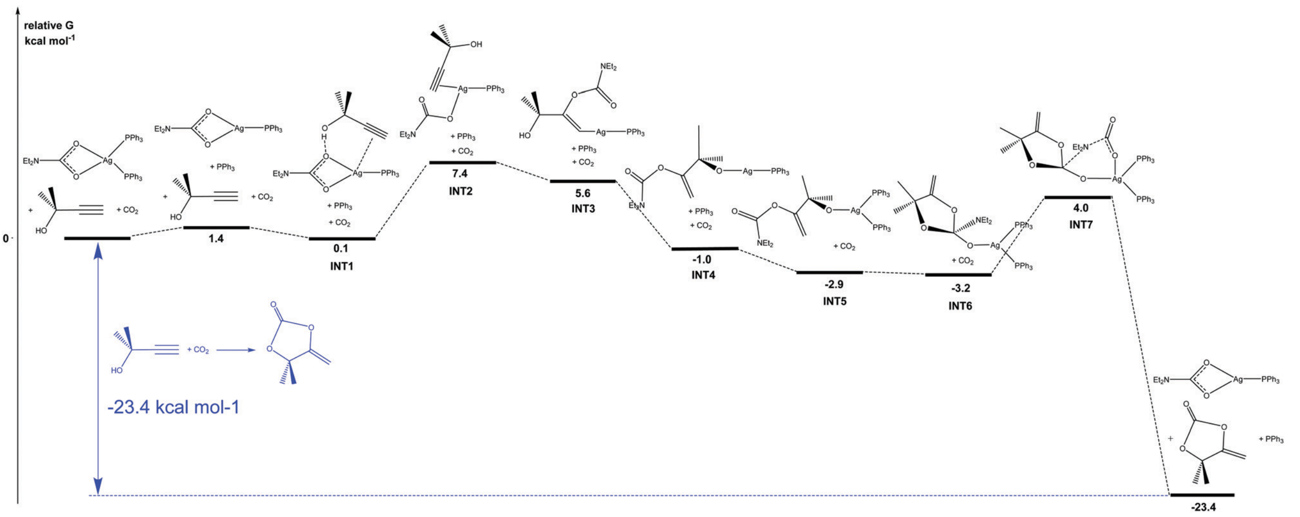
The optimized structures of the mono- and bis-phosphine silver complexes are comparatively shown in Fig. S1 in the ESI.† It is reasonable that the removal of one phosphine ligand from the latter, to produce the former, is required in order to reduce the steric hindrance around the metal center and thus enable to approach the alkyne reactant. According to DFT, the initial interaction is essentially through a hydrogen bond between the alkyne –OH group and one carbamato oxygen of $[Ag(\kappa^2\text{-}O_2CNEt_2)(PPh_3)]$ (computed OH–O distance = 1.701 Å), while the center of the $C{\equiv}C$ bond is 3.145 Å far from the silver atom. The resulting $[Ag(\kappa^2\text{-}O_2CNEt_2)(PPh_3)(HC{\equiv}CCMe_2OH)]$ intermediate (**INT1**, Fig. S2, ESI†) approximately holds the same Gibbs energy as the reactants. It is remarkable that the inclusion of a second triphenylphosphine ligand raises the Gibbs energy by about 4.4 kcal mol^{-1}, leaving the alkyne unable to interact with the complex. In order to allow alkyne activation, η^2-coordination is expected to take place, and this seems viable upon switching the coordination mode of the carbamate from κ^2 to κ^1. Indeed, the resulting species $[Ag(\kappa^1\text{-}O_2CNEt_2)(PPh_3)(\eta^2\text{-}CH{\equiv}CCMe_2OH)]$ (**INT2**, Fig. S3, ESI†) is accessible (relative Gibbs free energy = 7.4 kcal mol^{-1}), showing Ag–C bond lengths of 2.359 and 2.507 Å for the unsubstituted and substituted carbon, respectively. Again, attempts to optimize the related adduct with two coordinated PPh_3 molecules led to alkyne dissociation. The following nucleophilic attack of diethylcarbamate to the

Table 3 Silver-catalyzed carboxylative cyclization of propargyl alcohols affording α-alkylidene cyclic carbonates[a]

Run	Catalyst[bc]	Yield[d] (%)	Propargyl alcohol	α-Alkylidene cyclic carbonate
1	Ag_2O	85		
2	$[Ag(O_2CNEt_2)]$	>99		
3	$[Ag(O_2CNEt_2)(PPh_3)_2]$	65		
4	Ag_2O	85		
5	$[Ag(O_2CNEt_2)]$	88		
6	$[Ag(O_2CNEt_2)(PPh_3)_2]$	53		
7	Ag_2O	64		
8	$[Ag(O_2CNEt_2)]$	>99		
9	Ag_2O	>99		
10	$[Ag(O_2CNEt_2)]$	>99		
11[e]	Ag_2O	45		
12[e]	$[Ag(O_2CNEt_2)]$	87		
13[f]	Ag_2O	10		
14[f]	$[Ag(O_2CNEt_2)]$	>99		
15[g]	Ag_2O	5		
16[g]	$[Ag(O_2CNEt_2)]$	40		
17[h]	Ag_2O	97		
18[h]	$[Ag(O_2CNEt_2)]$	>99		
19[i]	Ag_2O	95		
20[i]	$[Ag(O_2CNEt_2)]$	>99		

[a] Reaction conditions: propargyl alcohol 1.0 mL; T = 25 °C; p(CO_2) = 1 atm; reaction time = 5 hours. [b] Ag_2O 0.5 mol%, $[Ag(O_2CNEt_2)]$ 1 mol%. [c] Co-catalyst: PPh_3, 1 mol% and 2 mol% associated to Ag_2O and $[Ag(O_2CNEt_2)]$, respectively. [d] Determined by ^1H NMR using 1,1,2,2-tetrachloroethane as internal standard (selectivity >99% in all cases). [e] T = 35 °C. [f] Propargyl alcohol 5.8 mmol in 1.0 mL of CD_3CN. [g] Propargyl alcohol 5.4 mmol in 1.0 mL of CD_3CN. [h] Propargyl alcohol 3.6 mmol in 1.0 mL of CD_3CN. [i] Propargyl alcohol 2.5 mmol in 1.5 mL of CD_3CN.

η^2-coordinated alkyne affords **INT3**, lowering the Gibbs energy by about 1.8 kcal mol^{-1}; **INT3** is a roughly linear Ag vinyl-complex (C–Ag–P angle = 166.8°, C=C bond length = 1.335 Å), and its structure is shown in Fig. S4 (ESI†). The coordination of a second phosphine to **INT3** was ruled out, being the resulting complex less stable by 8.0 kcal mol^{-1}. Starting from **INT3**, many attempts were done in order to find a feasible route to deprotonate the alcohol moiety, which is regarded as an essential requisite for the cyclization process. These calculations ruled out the possible role of either triphenylphosphine or free carbamate. Instead, on thermodynamic grounds, $[Ag\{OCMe_2C(CH_2)OC(O)NEt_2\}(PPh_3)]$ (**INT4**, Fig. S5, ESI†) is an accessible intermediate, being generated by OH to vinyl proton migration. In **INT4**, the anionic ligand is coordinated to the metal through a



Scheme 2 DFT-computed intermediates along the reaction of dimethylpropargyl alcohol with CO_2 catalyzed by Ag(I) carbamate. C-PCM/ωB97X/def2-SVP calculations, acetonitrile as continuous medium.

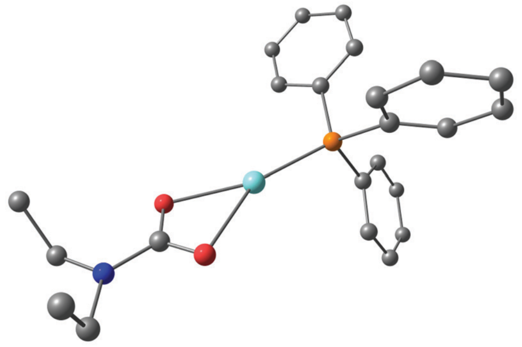


Fig. 1 DFT-optimized geometry of $[Ag(\kappa^2\text{-}O_2CNEt_2)(PPh_3)]$. C-PCM/ωB97X/def2-SVP calculations, acetonitrile as continuous medium. Color map: Ag, cyan; P, orange; O, red; N, blue; C, grey. Hydrogen atoms are omitted for clarity. Selected computed bond lengths (Å): Ag–O 2.281, 2.414; Ag–P 2.381.

negatively charged oxygen atom. The **INT3** to **INT4** conversion step is thermodynamically favorable, and further stabilization is supplied by the addition of a second phosphine ligand. This computational feature is in alignment with the experiment and justifies the advantageous use of $PPh_3/[Ag(\kappa^2\text{-}O_2CNEt_2)] = 2$ molar ratio (Table 2, run 15). The resulting complex **INT5** (Fig. S6, ESI†) is stabilized by about 2.9 kcal mol^{-1} with respect to the reactants. The successive, presumed cyclization, consisting in the electrophilic attack of the alkoxido oxygen to the carbonyl moiety, is slightly exergonic and yields **INT6** (Fig. S7, ESI†). The subsequent steps must pass through the cleavage of the C–NEt_2 bond, but the formation of a silver-amido moiety was excluded. More probably, the interaction of the amino group with the carbon dioxide reactant generates a semi-carbamate (**INT7**, Fig. S8, ESI†), and the $\{NEt_2\}$ fragment starts to dissociate from the cyclic compound (C–N distance = 1.642 Å in **INT7**, 1.468 Å in **INT6**). The N–CO_2 distance is 1.604 Å. **INT7** is less stable than the reactants by only 4.0 kcal mol^{-1}, and the completion of the $\{NEt_2\}$ migration produces the alkylidene cyclic carbonate and restores the carbamato complex. The process is globally exergonic by 23.4 kcal mol^{-1}.

In summary, combined experimental facts and DFT outcomes have allowed to identify the presumable active catalytic species; moreover, despite the reaction mechanism is hard to rationalize due to the heavy computational effort required to elucidate the kinetics, plausible reaction intermediates have been recognized, highlighting the versatile role of the carbamato ligand. In particular, the latter can switch its coordination mode from bi- to monodentate, and then behave as an oxygen nucleophile towards the alkyne, thus providing the {COO} fragment incorporated in the cyclic carbonate. The subsequent CO_2 capture from the reaction environment regenerates the carbamate.

Conclusions

α-Alkylidene cyclic carbonates are valuable fine chemicals with important applications, and there is a great interest in the development of sustainable catalytic systems to obtain this class of compounds from propargyl alcohols *via* CO_2 fixation. In general, silver species, in association with a Lewis base, represent a suitable choice, however high temperatures, pressurized CO_2 and/or a solvent are frequently required to make the process efficient. Here, we have evaluated for the first time the catalytic performance of an easily available and cost-effective silver compound, *i.e.* the carbamato complex $[Ag(O_2CNEt_2)]$. In contrast to silver carbamate, other metal based carbamates did not work in the carboxylation reaction, clearly indicating that the nature of the metal center, favouring alkyne activation *via* coordination, is crucial. $[Ag(O_2CNEt_2)]$, in combination with PPh_3, promotes the synthesis of a range of α-alkylidene cyclic carbonates in generally high yields, working at atmospheric CO_2 pressure and ambient temperature. The use of the solvent is avoided, except for high melting-point propargyl alcohols. A comparative study has highlighted that [Ag(O_2CNEt_2)] is more active compared to its commercial synthetic precursor, *i.e.* Ag_2O, at the same silver concentration. The promising catalytic activity of the silver carbamate seems ascribable to the multitasking role of the ligand. DFT calculations support, on thermodynamic grounds, the viability of dynamic incorporation of carbon dioxide within the carbamate, providing the {COO} fragment to the organic product. This work confirms the interesting potential of metal carbamates, which constitute a form of pre-activated carbon dioxide, in promoting CO_2-fixation reactions in mild conditions, and encourages further studies in this direction.

Conflicts of interest

There are no conflicts to declare.

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