Expanded Ring NHC Silver Carboxylate Complexes as Efficient and Reusable Catalysts for the Carboxylative Cyclization of Unsubstituted Propargylic Derivatives

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Stabilized by a bulky N-heterocyclic carbene [^{BP}DPr, 1,3-bis(2,6-diisopropylphenyl)-1,3-diazonine-2-ylidene] ligand, new silver carboxylate complexes of the form ^{BP}DPrAgO_2C-R (R = Me, Ph) have been synthesized and fully characterized in solution and in the solid state and implemented as sole catalysts (base-, additive-, and, in some cases, solvent-free) in the challenging fixation of carbon dioxide to unsubstituted propargylic derivatives for the synthesis of oxazolidinones and α-methylene cyclic carbonates. Derived from X-ray diffraction studies, the molecular geometry and the concept of buried volume were employed to describe the structural and steric features of these silver complexes. Their stability and efficiency as catalysts have been demonstrated by the synthesis of 29 carboxylation products (72–98% yield) at low catalyst loadings (0.01–1.5 mol%). Characteristics are high turnover numbers (up to 9400), catalyst recyclability (up to 96% yield after the 7th cycle with no decomposition of the silver complex), and the possibility to scale-up the reaction.

Introduction

N-heterocyclic carbenes (NHCs) are an important class of ligands for transition metals.[1] The structural tunability of steric and electronic properties from either the backbone ring or the N-substituents enables distinct catalytic activities and selectivities.[2] Within these manifolds, new carbene ligands based on NHC backbones with larger ring sizes (more than five atoms) have been designed.[3] These expanded ring NHC (erNHC) ligands showcase enhanced σ-donor ability and a superior steric bulkiness, which provides high stability and protection to the metal center and consequently enlarges their catalytic lifetime.[4] In this regard, NHC silver complexes were initially considered as useful organometallic synthons due to their ligand transfer ability,[5] and a growing number of silver-catalyzed organic transformations proved their potential as catalysts as well.[6,7]

Carbon dioxide (CO_2) is the major greenhouse gas produced on earth, and its emission to the atmosphere has been related to the climate change.[8] Due to its high abundance, lack of toxicity, and low-cost, the attained interest of CO_2 as C_1 building block in both academia and industry relies on its tremendous potential as renewable carbon source.[9] In this respect, the fixation of CO_2 to propargylic alcohols or propargyl amines, promoted by organometallic catalysts, has received considerable attention during the last years.[10] This atom- and step-economic strategy gives access to privileged heterocyclic motifs such as α-methylene cyclic carbonates and oxazolidinones, which can be employed as reactive solvents, additives in Li-ion batteries, synthetic intermediates for the synthesis of polymers and fine chemicals, or can be found as substructures of biologically relevant molecules (e.g., pharmaceuticals).[11,12] In particular, the fixation of CO_2 to propargylic derivatives has been investigated in seminal work of Yamada, Sekine, and co-workers in the context of silver and gold catalysis.[7b,13]

The recent years have witnessed the growing use of several NHC metal catalysts in environmentally benign reactions due to their compatibility with eco-friendly solvents, solubility in water or under solvent-free conditions, enabling a straightforward recovery that eases their recyclability.[14] Although many examples of supported or immobilized metals on 3D frameworks [e.g., metal-organic frameworks (MOFs)], phosphines, ionic liquids, or NHCs, are effective for the cycloaddition of CO_2 with propargylic derivatives, many of them are restricted to the use of bases or additives, and allow the conversion of only secondary or tertiary propargylic substrates, hence limiting their application profile.[15–17] Indeed, the Thorpe–Ingold effect in substrates bearing gem-dialkyl substituents in propargylic position offers the optimal geome-

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try for the cyclization step, while for unsubstituted propargylic derivatives HC≡C–CH_2–Y–H, the Y–H (Y = NR, O) and π-activation of the C≡C bond are significantly more difficult.[18] Therefore, the development of mild, operationally simple and alternate carboxylation protocols that operate with a wide substrate scope by employing readily available catalysts that significantly improve the synthetic and catalytic processes, are highly desirable.

In this work, we present the synthesis, structure evaluation, and spectroscopic characterization of the first expanded ring NHC silver carboxylate complexes, as well as their catalytic properties in the cycloaddition of CO_2 with primary propargylic alcohols or propargyl amines. These reactions can be conducted at room temperature and do not require a base or another additive, thus representing a user-friendly protocol for obtaining α-methylene cyclic carbonates or oxazolidinones from readily available precursors. Furthermore gram-scale reactions and catalyst recyclability experiments were conducted to shed light upon the potential relevance of the silver complexes as tool for environment-friendly industrial applications.

Results and Discussion

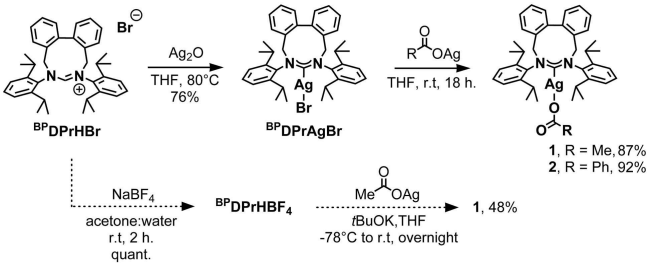
Synthesis and characterization of silver complexes

The initial motivations for this study stemmed from our recent discovery that the sterically bulky ^{BP}DPr [1,3-bis(2,6-diisopropylphenyl)-1,3-diazonine-2-ylidene] ligand[19] was able to efficiently stabilize a catalytically active copper fluoride species for the π-activation of the C≡C bond of propargylic alcohols that, in the presence of CO_2, led to the cycloaddition products. This strategy provided the first effective and diastereoselective copper-catalyzed carboxylative cyclization of unsubstituted propargylic alcohols.[20] To the best of our knowledge, there exists at most one silver-based catalyst for the conversion of these challenging primary propargylic substrates in the current literature.[21] Building on these precedents, we wondered whether a silver complex stabilized by the ^{BP}DPr ligand could provide a practical catalytic tool for activating the C≡C bond in unsubstituted propargylic derivatives. Derived from the attractive structural and steric features of this carbene ligand and the known catalytic utility of other silver carboxylates,[22] we envisioned the preparation of ^{BP}DPrAgO_2C-R (R = Me, Ph) complexes to subsequently evaluate their catalytic performance in CO_2 fixation to propargylic substrates at room temperature in the absence of any co-catalyst (e.g., base, additive).

Our study began with the preparation of the known silver complex ^{BP}DPrAgBr followed by ligand transfer reactions (Scheme 1) to silver carboxylate salts (i.e., acetate, benzoate).[5f] Initial attempts to synthesize complex **1** via the direct deprotonation of the NHC-HBF_4 salt resulted in a moderate yield under the selected experimental conditions.

Transmetalation reactions afforded the corresponding silver complexes in good yields and their identity was confirmed in solution by NMR spectroscopy and MS, and in the solid state by IR spectroscopy, elemental analysis, and single-crystal X-ray diffraction (XRD) analysis. Both complexes are bench-stable colorless solids with melting points above 220 °C and can be indefinitely stored in the freezer. No decomposition signs like "silver mirror" or colloidal black spots were visible when stored under light at room temperature. Complex **1** is soluble in CH_2Cl_2, $CHCl_3$, CH_3CN, and THF, among other commonly used organic solvents. Complex **2** has good solubility in THF or AcOEt, is sparingly soluble in CH_2Cl_2 or $CHCl_3$ (< 12 mg mL^{-1}), and remains essentially insoluble above 5.0 mM concentration in CH_3CN at room temperature. Both complexes are insoluble in Et_2O or hydrocarbon solvents (e.g., pentane, hexane, petroleum ether). In the mass spectra [matrix assisted laser desorption ionization (MALDI+)] the presence of peaks belonging to the $(NHC\text{-}H)^+$ and $(NHC\text{-}Ag)^+$ fragments indicate a linear mononuclear geometry. Other detectable $[(NHC)_2\text{-}AgO_2C\text{-}R]^+$ or $[(NHC)_2Ag]^+$ fragments suggest that intermolecular silver-hydrogen or silver-silver interactions might exist.[23] Based on ^{13}C NMR spectra these interactions might be trivial in solution, since the presence of the carbene carbon (C_{NHC}) signal as two doublets at around $\delta = 232$ ppm confirms that the complexes do not exhibit a fluxional behavior of the silver-carbene carbon (Ag-C_{NHC}) bond.[5,23b] The observed C_{NHC} resonances are significantly shifted to lower fields compared to their IPr analogues ($\delta \approx 184$ ppm).[22] The couplings $^1J(^{107}Ag\text{-}^{13}C) = 238\text{–}241$ Hz and $^1J(^{109}Ag\text{-}^{13}C) = 275\text{–}278$ Hz, increased with respect to the NHC silver bromide complex [^{13}C NMR $\delta = 230.0$ (dd, $^1J(^{107}Ag\text{-}^{13}C) = 228$ Hz, $^1J(^{109}Ag\text{-}^{13}C) = 263$ Hz], demonstrate a significant influence of the carboxylate anion to the Ag-C_{NHC} bond upon halide abstraction.

The values for the gyromagnetic ratio ($\gamma = 1.15$) of both NMR-active silver isotopes in **1** and **2** are still in accordance to the spin-spin interactions of the ^{109}Ag/^{107}Ag with the singlet C_{NHC}.[4c,5f,24] IR absorption frequencies, $\nu(CO_2)$, for the asymmetric (ν_{asym}) and symmetric (ν_{sym}) stretches of the carboxylate where found at $\nu_{asym} = 1607$ and 1599 cm^{-1}, and $\nu_{sym} = 1386$ and 1371 cm^{-1} for **1** and **2**, respectively. The difference between ν_{asym} and ν_{sym} values ($\Delta\nu$) in **1** ($\Delta\nu = 228$ cm^{-1}) and **2** ($\Delta\nu = 221$ cm^{-1}) are significantly larger than those of the corresponding non-coordinated silver carboxylates ($\Delta\nu = 129\text{–}134$ cm^{-1})[22,25] consistent with a monodentate O-coordination of the carboxylate unit.[26]



Scheme 1. General synthesis of ^{BP}DPrAgOAc (**1**) and ^{BP}DPrAgOBz (**2**).

Single crystals suitable for X-ray analysis were obtained by slow evaporation of solvent mixtures (e.g., THF/hexane, CH_2Cl_2/pentane) from saturated solutions of the complex at room temperature overnight.[27] The solid-state molecular structures of **1** and **2** are shown in Figure 1a. With the information from the CIF files, the buried volume values and topographic maps (Figure 1c) were calculated using Samb*V*ca 2.1 (with the default settings: bondi radii scaled by 1.17, sphere radius 3.5 Å, mesh spacing 0.10 Å, distance from the center 2.0 Å, hydrogen atoms omitted).[28] Selected structural parameters are deposited in Table 1. The X-ray crystal structures denote a monodentate O-coordination of the carboxylate anion to the silver atom and this was previously deducted from the stretching frequencies in their IR spectra. It is interesting to note, that neither the nature of the carboxylate anion nor the N-aryls seem to alter the Ag-C_{NHC} bond length. Noteworthy, a significant deviation from linearity was found in the C_{NHC}-Ag-O angles for both complexes (by ≈8°) and the N-C_{NHC}-N angles (118–119°) overcome those of other silver carboxylate complexes bearing five-membered (IPr, SIPr, IPent) ligands (108–113°).[22]

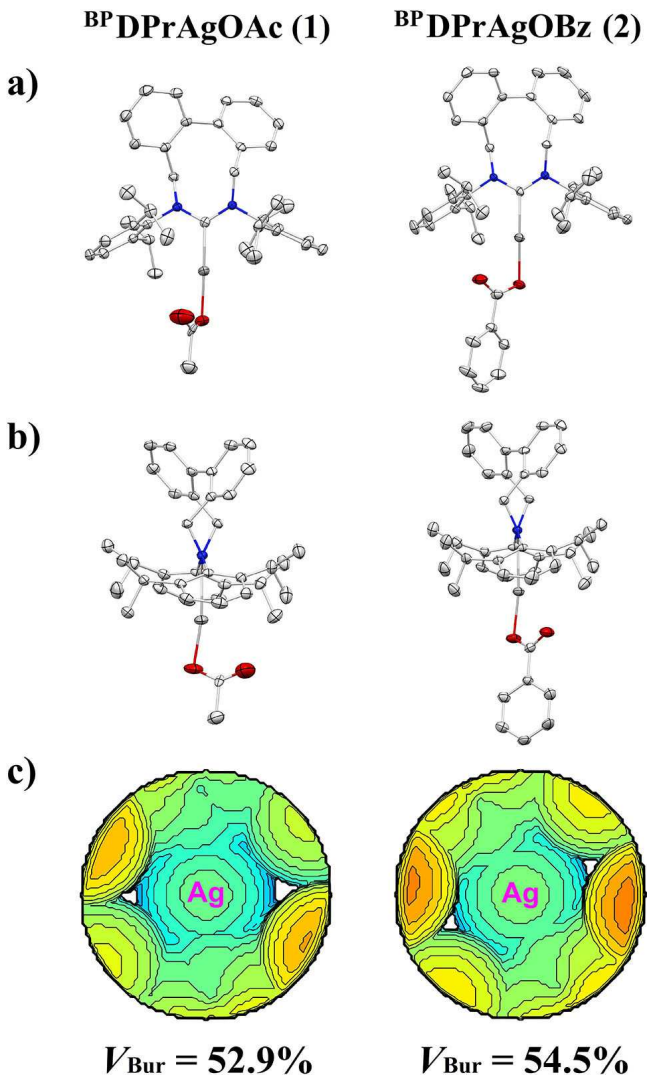


Figure 1. Solid-state molecular structure (ORTEP diagram) from a front view (a), side view at 90° rotation over the C2-axis (b), and steric map (c) of ^{BP}DPrAgOAc (**1**, left) and ^{BP}DPrAgOBz (**2**, right), respectively. Ellipsoids are set at 40% probability level. Hydrogen atoms and one crystallized H_2O molecule (in **2**) are all omitted for clarity.

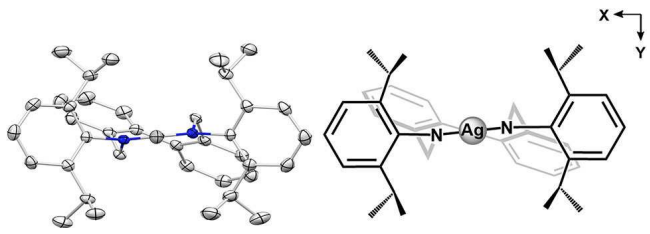


Figure 2. Bottom view along C_2-axis (*z*-axis) of **1** in the solid state accompanied by its bidimensional representation. Hydrogen atoms and [OAc] anion are omitted for clarity.

As illustrated in Figure 2, the twisting of the C_2-symmetric biphenyl moiety influences the folding of the adjacent methylene spacers giving origin to a distorted non-planar NHC backbone, characteristic of the expanded ring carbene ligands.[2a,19] The torsion (dihedral angle) between both N-aryl planes and the N–N axis reveals a considerably more twisted molecular geometry of **1** ($\alpha = 35.09°$) than that of **2** ($\alpha = 26.90°$) and this could be explained by a stabilizing effect of the carboxylate anions. These also affect the steric distribution around the silver center as reflected by the buried volume values (**2**, $V_{Bur} = 54.5\%$; **1**, $V_{Bur} = 52.9\%$). In **1**, the methyl group of the acetate exerts a poor steric influence over the *ortho iso*-propyl substituents of the N-aryls in contrast to the phenyl group, in silver benzoate complex **2**, which diminishes the distortion of the N-aryls and consequently favors the homogeneous structural arrangement of the NHC ligand boosting the overall steric distribution of the complex.

Cycloaddition of CO_2 with unsubstituted propargylic alcohols or propargyl amines

Preliminary experiments confirmed our initial hypothesis. In the cyclization of a test substrate (**3**) with CO_2 under atmospheric pressure at room temperature, using 5 mol% loading of ^{BP}DPrAgOAc (**1**) as the catalyst, the expected product was formed in 15% yield (see the Supporting Information for details). By screening both catalysts in a set of conditions we established complex ^{BP}DPrAgOBz (**2**) as the best choice for the carboxylative cyclization of propargylic alcohols

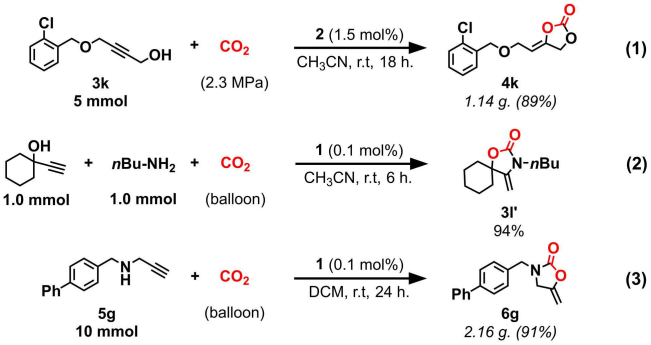
Table 1. Selected geometrical parameters (bond lengths and angles) of complexes **1** and **2**.

	^{BP}DPrAgOAc (**1**)	^{BP}DPrAgOBz (**2**)
Ag-C_{NHC} [Å]	2.089(2)	2.089(3)
Ag-O [Å]	2.112(2)	2.122(2)
N-C_{NHC}-N [°]	118.4(2)	119.3(3)
C_{NHC}-Ag-O [°]	172.07(9)	172.88(11)
C_{Ar}-N_2···N_5-$C_{Ar'}$ (α) [°]	35.09	26.90

(Table S1). We therefore conducted further optimization experiments with complex **2** as the catalyst. The experiments were carried out for 18–24 h in CH_3CN as the solvent (Table S2). From beginning to end the catalyst remained insoluble at the examined concentrations of substrate (1.0 M). Nevertheless, an unanticipated catalytic activity was observed, and the product was obtained in all cases in the CH_3CN phase and the NMR analysis of the solid residue corresponded to the intact silver complex. The reaction was promoted at lower catalyst loadings as expected albeit at the expense of higher CO_2 pressure. Along with these experiments, we could not detect any traces of the ring-opened side product. These observations indicate that the limiting parameter is not the catalyst loading, but rather the applied CO_2 pressure. At present, we believe that the bulky NHC ligand stabilizes the transient silver-alkenyl species within the catalytic cycle, thus preventing the ring opening pathway.[20]

Under the optimized reaction conditions described in Table S2, entry 10, we then evaluated the generality of the silver-catalyzed carboxylative cyclization (Figure 3). A variety of unsubstituted propargylic alcohols (**3**), derived from 2-butyn-1,4-diol, a low-cost and commercially available chemical, were converted. Various substitution patterns on the aryl ring in **3** were tested. The presence of alkyl (**4c**, 90%) or aryl (**4f**, 84%) substituents in the *para* position of the aryl ring of **3** provided slightly higher yields than for an electron-withdrawing group (*p*-CF_3, **4p**, 72%). Likewise, the presence of *para*-substituted halogen gave a good yield (**4k**, 84%). No significant difference was observed for *ortho*-, *meta*-, and *para*-chloro-substituted aryl moieties (78–84% yield). And the presence of an alkyl *ortho* substituent in **3** led to a slightly diminished yield (e.g., **4d**, 83%), compared to its *para*-substituted isomer (**4c**, 90%) suggesting a marginal steric effect. Encouraged by these results, we assessed a gram scale experiment using complex **2** as catalyst under our reaction conditions to gain more insight into its catalytic performance [Scheme 2, Eq. (1)]. A good efficiency was maintained when running the reaction on a 10 mmol scale under 2.3 MPa CO_2 pressure to furnish **3g** (2.28 g) in 89% yield. Nucelar Overhauser effect (NOE) experiments confirmed the stereochemistry of the *Z*-alkylidene products, consistent with previous results using bulky silver and copper catalysts.[20,21]

Prompted by our success with unsubstituted propargylic alcohols as substrates, we then sought to explore the transformation of unsubstituted propargyl amines **5** (Figure 4).



Scheme 2. Scale-up experiments.

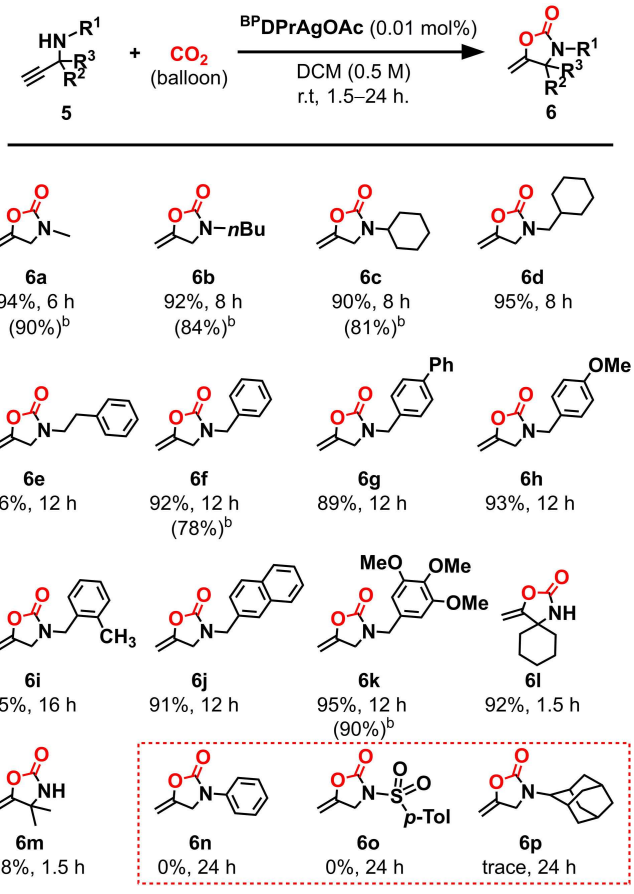


Figure 4. Substrate scope for solvent-free carboxylative cyclization of propargyl amines **5**. [a] Isolated yields are presented. [b] Performed in the absence of solvent for 12 h.

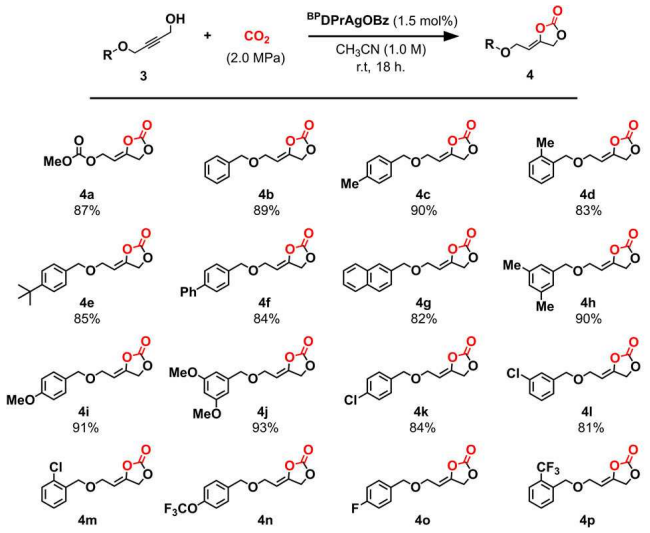


Figure 3. Survey of unsubstituted propargylic alcohols **3** in the carboxylative cyclization. [a] Isolated yields are presented.

Silver complexes **1** and **2** were also used as catalysts. Preliminary screenings (see Supporting Information, Table S3) showed that 1 mol% catalyst could promote the transformation of **5a** into **6a** in 99% NMR yield after 10 min using CO_2 at atmospheric pressure. Under the studied experimental conditions full and clean conversions were observed, which indicates the resilience of the silver species in non-dried solvents, without the need for the prevention of oxygen. In the absence of a catalyst, no conversion of the propargyl amine occurred, and the ligand-free AgOAc-catalyzed reaction (1 mol%, 24 h, r.t.) required the addition of 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU; 5 mol%) to deliver a commensurable yield. This observation, together with the results disclosed in Figure 4, clearly evidence the intimate interplay between the carbene ligand and substrate in our catalytic proposal. The influence of the catalyst loading (Table S4) was therefore investigated. The conversion of substrate **5a** did not decrease with reduced amounts of the catalyst (0.1–0.5 mol%) and 90% yield was still observed by using only a 0.05 mol% catalyst loading after 2 h. The stability and good solubility of the complexes in CH_2Cl_2, allowed for the preparation of stock solutions to employ even lower loadings of the catalyst. Based on these preliminary experiments, we found that the use of a 0.01 mol% loading of complex **1** was found to be ideal for the catalysis.

To verify the applicability of the optimized conditions, a library of propargyl amines was subjected to the current silver catalysis at room temperature. In a typical experiment, a Teflon-coated screw-cap vial was charged with substrate, solvent and catalyst, and a CO_2-filled balloon ($\approx$1.5 L) was coupled via cannula and the mixture was stirred at room temperature until no starting material was detected [as judged by thin layer chromatography (TLC) or GC-MS analysis]. The results are summarized in Figure 4. Isolated yields are presented after flash chromatography, and for selected substrates, isolated yields of solvent-free reactions are presented (in parentheses). In all examined cases, the conversion was higher than 98% (as revealed by NMR analysis of crude samples). Total reaction times span from 0.5 to 16 h, although for some substrates (**5n**, *N*-phenyl, and **5p**, *N*-2-adamantyl) no product or only traces were observed after 24 h. Interestingly, upon exposure of unprotected propargyl amine or *N*-tosyl-protected propargyl amine (**5o**) no detectable product was obtained. This can be explained by the low N-nucleophilicity of both the aniline-type nitrogen in **5n** and the tosyl-protected **5o**, and the significant steric bulk of the N-substituent in **5p**. As predicted, substrates with additional *gem*-substituents in the propargylic position, smoothly afforded the carboxylation products **6l** and **6m** in 92–98% yield after 1.5 h reaction. The X-ray crystal structure of **6k** is presented in Figure 5.

Strikingly, the catalytic system did not allow the conversion of primary propargyl amines bearing internal alkynes (e.g., methyl- or phenyl-terminated alkynes); nonetheless, when compared to other successful state-of-the-art silver-based catalytic systems for the carboxylative cyclization of unsubstituted propargyl amines (Figure S1), the herein developed NHC silver complexes are a promising and more efficient catalytic alternative.

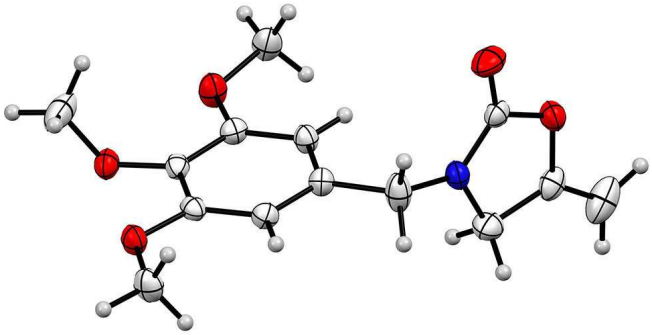


Figure 5. X-ray crystal structure (ORTEP representation) of **6k** at 45% thermal probability.[26]

It is worth noting that, our described protocols can be carried out at room temperature under base-, additive-, or (even) solvent-free conditions, constituting an additional bonus from a practical and operational point of view. On the basis of our latter results, we anticipated that our carboxylative cyclization protocol could be amenable for a three-component reaction. Thus, an experiment was run on a 1 mmol scale using 1-ethynyl-1-cyclohexanol and *n*-butylamine as the substrates, in the presence of 0.1 mol% catalyst under our standard reaction conditions [Scheme 2, Eq. (2)]. Nearly full conversion of both substrates was observed and 94% isolated yield of oxazolidinone **3l'** was obtained. Like the activation of C≡C bonds in propargylic alcohols at the gram-scale was found to be clean and efficient, the use of propargyl amines as substrates under silver catalysis at a large-scale is highly relevant. In this respect, a scale-up experiment was carried out using propargyl amine **5g** (10 mmol) with 0.1 mol% loading of complex **1** under CO_2 at atmospheric pressure producing **6g** (2.16 g) in 91% yield [Scheme 2, Eq. (3)].

With regard to the mechanism, the reaction should follow the reaction path already computed for other ligands, with the cyclization step being the rate-limiting step.[21]

Catalyst recycling

From the point of view of sustainable catalysis, it is interesting that the silver complexes could also be recovered and reutilized (Figure 6). α-Methylene cyclic carbonates are usually soluble in polar organic solvents (e.g., CH_3CN, AcOEt, etc.) whereas the silver catalyst **2** remains insoluble above 1.0 M concentration of the substrate/product. This case of heterogeneous catalysis opens up the opportunity for product separation from the catalyst by simple filtration through a membrane or decanting the liquor containing the product, which makes it possible to recover and recycle the silver catalyst. To validate this hypothesis, the carboxylative cyclization experiments were performed with **3j** under our conventional protocol

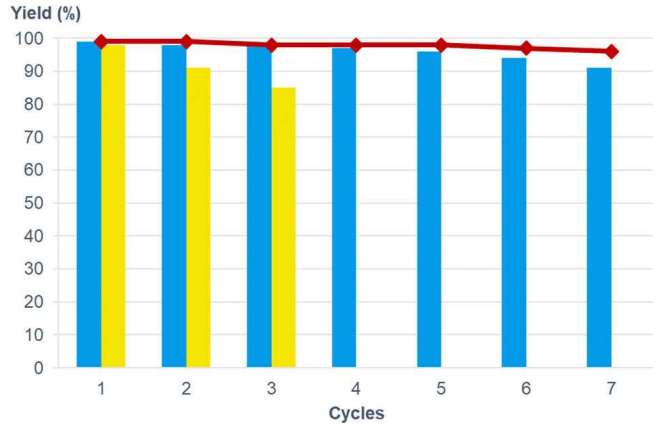


Figure 6. Catalysts recyclability. Performed with 1.5 mol% of complex **1** (yellow bars) or **2** (blue bars) under batch conditions, and by successive additions of substrate using complex **1** (red marks) with a final 0.16 mol% catalyst loading.

using CH_3CN as the solvent. At the end of the reaction, the suspension was kept on the bench for 0.5 h and the solution containing the product was separated by syringe. We checked that this procedure also allowed the residual, unconverted substrate to be separated from the catalyst. The solid residue was washed with cold CH_3CN to leave the active silver catalyst in the reaction vessel (typical loss of catalyst in each run about 1.4% of the initial catalyst loading; overall 14% of the silver were lost over the 10 runs, see the Supporting Information), and a fresh load of substrate was added. The procedure was repeated several times to evaluate the catalyst performance. Acetate **1** and benzoate **2** both exhibited excellent catalytic activity in the first run, nevertheless, the yield afforded by catalyst **1** gradually decreased although no decomposition was observed. We assume that upon treatment of the crude reaction, some catalyst could be solubilized in CH_3CN and withdrawn from residue, making a lower quantity available for the next run. Under the same experimental conditions, complex **2** displayed a good recyclability and could be recovered and reused at least 7 times without a strong loss of activity (90% yield after the 7th cycle) and no decomposition of the catalyst was observed in the NMR spectra (see the Supporting Information, Figure S2). Given the good solubility of **1** in CH_3CN, we decided to make successive additions instead of working up the reaction mixture after each cycle. We selected propargylic alcohol **3z** (6 mmol per addition) as the substrate and set 1 mol% of catalyst loading under CO_2 (2.3 MPa) at room temperature for 24 h. Under these conditions, complex **1** displayed high catalytic activity with no decomposition signals (as judged by NMR spectroscopy) affording 96% yield after 7 cycles with a final catalyst loading of 0.16 mol% and a turnover number of 584.

Conclusion

New silver carboxylate complexes bearing a sterically demanding carbene ligand of expanded ring backbone have been synthesized and fully characterized. A task-specific catalytic application, the challenging carboxylative cyclization of unsubstituted propargyl derivatives, demonstrated their potential as efficient catalysts. The obtained results suggest that the use of an expanded ring N-heterocyclic carbene (NHC)-silver carboxylate-based architecture is a promising catalytic approach for the π-activation of C≡C bonds[21] for the chemical fixation of CO_2. The molecular geometry and steric features of the bulky NHC ligand and the presence of a stabilizing monodentate carboxylate unit in a linear arrangement with the silver center, provide a unique stability to the complex enhancing its catalytic activity. The easy catalyst recovery after the clean transformation, can make these complexes adequate for environmentally friendly metal-catalyzed reactions because of their recyclability property. In consequence, we have synthesized stable and robust NHC silver complexes for the cycloaddition of CO_2 with primary propargylic alcohols or propargyl amines at room temperature. Without any doubt, the success of these new silver catalysts could provide new impulses for other related silver-catalyzed reactions.

Experimental Section

General procedure for α-methylene cyclic carbonates: A 20 mL scintillation vial provided with a Teflon-coated stirring bar was charged with substrate **3** (1 mmol), regular CH_3CN (1 mL), and silver complex **2** (11.6 mg, 1.5 mol%) at room temperature under open-air conditions. Vial was transferred into an autoclave and pressurized with CO_2 at approximately 2.0 MPa for 18 h under stirring (>550 rpm). Overpressure was slowly released; the suspension was filtered through a plug of celite to remove the catalyst. In some cases, we observed that the presence of silver catalyst traces in the crude product after filtration can catalyze its decomposition and the release of benzylic alcohol derivative (as detected by NMR spectroscopy). To avoid this, the crude product was taken up in AcOEt (2.5 mL), stirred in the presence of activated carbon (spatula tip) for 0.5 h and again filtering through a plug of celite. Additional CH_3CN (1 mL) was used to wash the solid residue and the plug of celite. The filtrate was concentrated in vacuo and crude products were purified by flash chromatography (AcOEt/petroleum ether, 2:8) to yield α-methylene cyclic carbonates as colorless oils or a colorless solid (**4f**).

(*Z*)-methyl (2-(2-oxo-1,3-dioxolan-4-ylidene)ethyl) carbonate (4a): Colorless oil (163 mg, 87% yield). ^{1}H NMR (301 MHz, $CDCl_3$): δ = 4.98–4.91 (m, 3H), 4.71–4.67 (m, 2H), 3.70 ppm (s, 1H).^{13}C NMR (76 MHz, $CDCl_3$)): δ = 155.40, 151.96, 146.11, 96.83, 67.43, 60.82, 54.82 ppm.

(*Z*)-4-(2-(benzyloxy)ethylidene)-1,3-dioxolan-2-one (4b): Colorless oil (196 mg, 89% yield). ^{1}H NMR (301 MHz, $CDCl_3$): δ = 7.28–7.18 (m, 5H), 4.90–4.85 (m, 3H), 4.45 (s, 2H), 4.14–4.10 ppm (m, 2H). ^{13}C NMR (76 MHz, $CDCl_3$): δ = 152.28, 143.95, 137.78, 128.49, 127.88, 100.32, 72.77, 67.34, 63.36 ppm.

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Conflict of Interest

The authors declare no conflict of interest.

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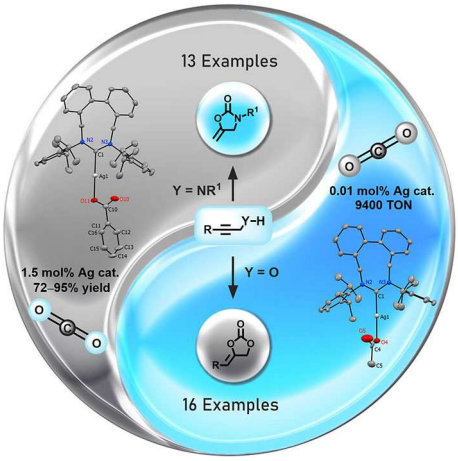

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CO_2 fixation: The first expanded ring N-heterocyclic carbene silver carboxylate complexes are efficient and reusable catalysts in the chemical fixation of carbon dioxide to unsubstituted propargylic derivatives under homogeneous or heterogeneous reaction conditions.