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ARTICLE

Carboxylation of terminal alkynes with CO_2 catalyzed by novel silver N-heterocyclic carbene complexes

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Four novel N-heterocyclic carbene (NHC) silver complexes **I-IV** have been synthesized and characterized. The single X-ray crystal diffraction data indicate a dinuclear solid-state structure for **I** and **III**, and mononuclear structure for **II** and **IV**. These complexes have been successfully used as efficient catalyst for the C-H activating carboxylation of terminal alkynes with CO_2. A wide range of substrates with various functional groups afforded the corresponding aryl or alkyl substituted propiolic acids in good yields under mild conditions. Moreover, the role of bases and the reaction mechanism are also fully discussed.

Introduction

The utilization of abundant, nontoxic and cheap CO_2 as a C1 feedstock for the production of raw chemicals is of huge industrial interest.[1] However, CO_2 is a thermodynamically and kinetically stable molecule with a low energy level, which makes its transformation particularly difficult. A major goal is to develop efficient catalysts for the activation of this inert molecule. Great efforts have been made in the past decades and some remarkable progresses have been achieved in this rapidly emerging area, such as the cyclic addition of CO_2 to epoxide to yield cyclic carbonates,[2] copolymerization of CO_2 and epoxides to prepare polycarbonates,[3] hydrogenation of CO_2 to formic acid,[4] the carboxylation of ethylene and methyl iodide with CO_2 to afford acrylates,[5] the carboxylation of alkynes with CO_2 to form saturated or unsaturated carboxylic acids or esters.[6] Among various transformations, the transition metal catalyzed carboxylation of terminal alkynes with CO_2 has been regarded as one of the most advantageous and promising route.[7] By C-H activating carboxylation of terminal alkynes with CO_2, various functionalized propiolic acids can be obtained,[8] the products of which are valuable intermediates in the manufacture of medicine, synthetic fiber, and industrial preservatives.[9] Pioneering contributions to this area have been made by Grooβen,[10] Nolan,[11] Zhang,[12] Lu,[7a] He[13] and other groups.[14] Although the carboxylation of terminal alkynes with CO_2 is able to proceed under metal-free conditions, high temperature or high pressure is usually required.[15] Copper(I) and silver(I) halides or their complexes are found to be highly active to catalyze the carboxylation of various aryl and alkyl terminal alkynes with CO_2 in the presence of strong base under very mild conditions.[16] The main steps of this transformation are the coordination of alkyne to Ag(I), the deprotonation of alkyne affording silver(I) acetylide, the insertion of CO_2 into C-Ag bond and the acidification to the desired propiolic acids.[7a] Among various reported copper(I) or silver(I) catalytic systems, N-heterocyclic carbene (NHC)-copper or silver complexes have shown remarkable activity and selectivity. Moreover, it has been found that the presence of NHC ligands in the catalytic system can also widen the substrate of the carbxylation reactions, which may due to the formation of intermediate CO_2 adduct.[6a] Despite this fact, the carboxylation of terminal alkynes with CO_2 catalyzed by silver(I)- or copper(I)-NHC complexes is so far rather limited in scope. Zhang et. al. have reported the carboxylation of terminal alkynes with CO_2 using poly-NHC-Cu(I) or poly-NHC-Ag(I) as catalyst, and the catalytic systems showed high activity and good stability affording various functionalized propiolic acids in good to excellent yields in the presence of Cs_2CO_3 at ambient conditions.[12] Lu reported a three-component carboxylative coupling of terminal alkynes, allylic chlorides and CO_2 using 10 mol% of Cu(I)-NHC complex (IPrCuCl) as catalyst,[17] and a variety of functionalized allylic 2-alkynoates can be obtained in good yield and high selectivity. Li described an morpholine-functionalized Ag(I)-NHC catalyzed carboxylation reaction with high catalyst loading (10 mol%).[18] To the best of our knowledge, those are the only examples regarding the silver(I) and copper(I) NHC catalyzed carboxylation of terminal alkynes with CO_2. Nevertheless, these established transition metal NHC catalytic systems are not ideal since the carboxylation reactions were either carried out in high catalyst loading or resulted in only low to moderate carboxylic acid yields. Despite excellent product yields could be achieved with a very low metal loading (0.3 mol%) in the case of using poly-NHC-Ag(I),

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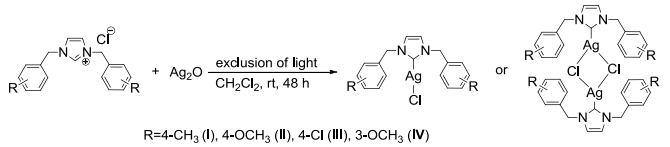
the preparation of this catalyst is somehow not very convenient.[12b]

Recently, several novel Ag-NHC complexes have been prepared and fully characterized in our laboratory. To our delight, these simple and stable complexes can catalyze the carboxylation of aryl and alkyl terminal alkynes with CO_2 efficiently, affording various functionalized propiolic acids in good yields with only 1 mol% of catalyst loading. The reaction mechanism was also fully discussed. Therefore, we wish to report our preliminary results of this work herein.

Results and discussion

Synthesis of Ag-NHCs I-IV

Ag-NHC complexes **I**-**IV** were obtained by mixing a solution of imidazolium salts with 0.55 equiv. of Ag_2O with exclusion of light at room temperature. Details on the synthesis and characterization of **I**-**IV** can be found in the experimental section. All products were isolated as white solids in good yields (Scheme 1).



Scheme 1. Synthesis of Ag-NHCs **I**-**IV**.

The complexes have been fully characterized by FT-IR, ^{1}H and ^{13}C NMR spectra (ESI). Comparing to the imidazolium salt precursors, the H^2 proton signal of imidazolium ring (at about 9.5 ppm) is disappeared in the ^{1}H NMR spectra for Ag-NHCs **I**-**IV**, indicating the formation of silver carbene complexes. Meanwhile, the H^4 and H^5 proton signals of the imidazolium ring are a bit high-field shifted as compared to the corresponding imidazolium salt precursors. The ^{13}C NMR spectra for Ag-NHCs **I**-**IV** exhibit feature resonance signals at 178-180 ppm, which can be attributed to the carbenic carbon atoms. The data are also in good accordance with the carbenic carbon atoms of other reported silver heterocyclic carbene complexes.[19]

X-ray crystal structures of Ag-NHCs I-IV

Single crystals for Ag-NHCs **I**-**IV** were obtained by slow evaporation of diethyl ether / chloroform mixing solution of the respective silver complex at room temperature. The X-ray crystal structures of **I**-**IV** are depicted in Figures 1-4. It is interesting to note that **I** and **III** display dinuclear solid-state structures, while **II** and **IV** - which bear somehow bulky methoxy group on the ligand - represent mononuclear solid-state structures. Both mono- and dinuclear complexes show Ag–C bond distances around 2.10 Å, comparable to those in other silver–carbene complexes.[19] For **II** and **IV**, Ag-Cl bond distances are 2.357 (1) and 2.338 (1) Å respectively. For the dimer **I** and **III**, two NHC-AgCl moieties are present around an inversion center to give a dinuclear species with side-on Ag...Cl interaction. However the planar 4-membered Ag_2Cl_2 indicate very different bridging Ag-Cl bond distances. The Ag (1)- Cl (1) bond distances are 2.441 (5) Å for **I** and 2.415 (2) Å for **III**, whereas the Ag (1)- Cl (1)# bond distances are 2.773 (5) Å for **I** and 2.851 (2) Å for **III**. This indicates that the dimer complexes **I** and **III** are formed via a weak Ag...Cl interaction of the respective monomer.

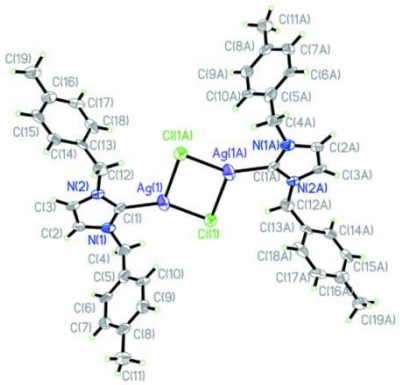


Figure 1. The molecular structure of **I**. Selected bond distances (Å) and angles (°): Ag(1)-C(1) 2.110 (2), Ag(1)-Cl(1) 2.441 (5), Ag(1)-Cl(1)#1 2.773 (5), Cl(1)-Ag(1) #1 2.773 (5); C(1)-Ag(1)-Cl(1) 149.5 (4), C(1)-Ag(1)-Cl(1)#1 114.9 (4), Cl(1)-Ag(1)-Cl(1)#1 95.41 (14), Ag(1)-Cl(1)-Ag(1)#1 84.59 (14), N(1)-C(1)-Ag(1) 124.0 (11), N(2)-C(1)-Ag(1) 130.4 (12). Symmetry code: #1 -x+2, -y, -z. CCDC: 1413846.

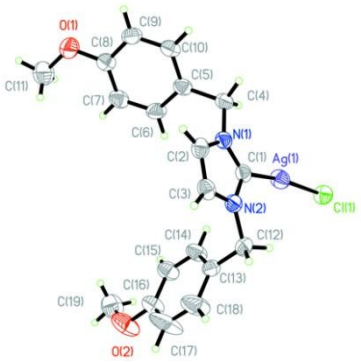


Figure 2. The molecular structure of **II**. Selected bond distances (Å) and angles (°): Ag(1)-C(1) 2.093 (3), Ag(1)-Cl(1) 2.357 (1); C(1)-Ag(1)-Cl(1) 169.00 (7), N(1)- C(1)-Ag(1) 29.58 (18), N(2)-C(1)-Ag(1) 126.1 (2). CCDC: 1432048.

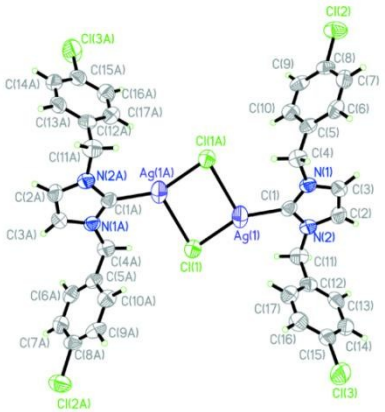


Figure 3. The molecular structure of **III**. Selected bond distances (Å) and angles (°): Ag(1)-C(1) 2.104 (5), Ag(1)-Cl(1) 2.415 (2), Ag(1)-Cl(1)#1 2.851 (2), Cl(1)-Ag (1)#1 2.8512 (17); C(1)-Ag(1)-Cl(1) 153.95 (15), C(1)-Ag(1)-Cl(1)#1 110.89 (15), Cl(1)-Ag(1)-Cl(1)#1 95.09 (5), Ag(1)-Cl(1)-Ag(1)#1 84.91 (5), N(1)-C(1)-Ag(1) 131.0 (4), N(2)-C(1)-Ag(1) 124.8 (4). Symmetry code: #1 -x+2, -y, -z+1. CCDC: 1413845.

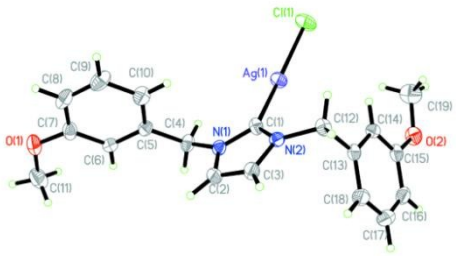
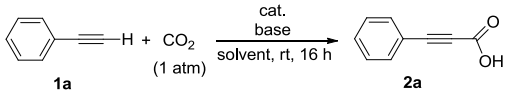


Figure 4. The molecular structure of **IV**. Selected bond distances (Å) and angles (°): Ag(1)-C(1) 2.101 (4), Ag(1)-Cl(1) 2.338 (1); C(1)-Ag(1)-Cl(1) 165.55 (12), N(1)-C (1)-Ag(1) 131.3 (3), N(2)-C(1)-Ag(1) 123.4 (3). CCDC: 1413847.

Carboxylation of terminal alkynes with CO_2

To explore the reactivity, the carboxylation of 1-phenylethyne **1a** with CO_2 was initially studied as a model reaction. Blank reaction showed that the reaction could not proceed without the involvement of catalyst (Table 1, entry 1). To our delight, when 1 mol % of Ag-NHC **I** was applied, the reaction resulted in good yield of the desired product **2a** under the condition of 1.5 equiv. of Cs_2CO_3 in DMF (entry 2). When the catalyst loading was increased to 3 mol %, the yield of **2a** was not increased, and 5 mol % of **I** could even decrease the product yield (entries 3 and 4), which might be ascribed to the decarboxylative activity of Ag-NHCs.[20] Under the condition of 1 mol % catalyst loading, catalysts **II-IV** were also highly effective and afforded similar isolated yields of **2a** (entries 5-7) as **I**. The time-dependent experiments on the yields of **2a** using **I** or **II** as catalyst were compared. Both **I** (dimer) and **II** (monomer) display similar time-dependent curves (Figure 5), with the product yields increase rapidly within 8 hours of the reaction and then slow down. Despite **I** represents a dimer solid-structure, no induction period could not be observed at the initial period of the reaction. This reflects that the examined dimer Ag-NHC complex possess a rather weak Ag...Cl interaction and they might represent as monomers in solution (especially in the polar DMF medium)[21]. Therefore, no obvious differences on the catalytic activities could be observed between monomeric and dimeric Ag-NHCs. Increasing the reaction temperature from room temperature to 40 °C, the yield was only slightly increased, and 60 °C even led to a lower product yield (entries 8 and 9). The influence of bases on the reaction was also carefully studied (entries 1, 10-15). The results show that the inorganic K_2CO_3, Cs_2CO_3, and the organic base DBU are effective bases. However, good yield could only be obtained by using Cs_2CO_3. Moreover, when reducing the amount of Cs_2CO_3 to 1.2 or 1.0 equiv., the yields were also significantly decreased (entries 16 and 17). Increasing the amount of Cs_2CO_3 to 2.0 equivalents, no obvious increase of yield was observed (entry 18). The reaction was also examined by using different solvents (entries 19-22). However, only poor to medium yields could be obtained in CH_2Cl_2, CH_3CN and DMSO, and the reaction was not able to proceed in THF. Based on the above studies, a standard condition **A** (1 mol% of Ag-NHC, 1.5 equiv. of Cs_2CO_3, 1 atm of CO_2 at rt in DMF for 16 h) was obtained.

Table 1. Optimization of reaction conditions[a]



1a 2a

Entry	Cat. (mol%)	Base (equiv.)	Solvent	Isolated yield (%)b
1	-	Cs_2CO_3 (1.5)	DMF	0
2	**I** (1)	Cs_2CO_3 (1.5)	DMF	82
3	**I** (3)	Cs_2CO_3 (1.5)	DMF	82
4	**I** (5)	Cs_2CO_3 (1.5)	DMF	68
5	**II** (1)	Cs_2CO_3 (1.5)	DMF	81
6	**III** (1)	Cs_2CO_3 (1.5)	DMF	81
7	**IV** (1)	Cs_2CO_3 (1.5)	DMF	82
8[c]	**I** (1)	Cs_2CO_3 (1.5)	DMF	83
9[d]	**I** (1)	Cs_2CO_3 (1.5)	DMF	69
10	**I** (1)	DBU (1.5)	DMF	38
11	**I** (1)	K_2CO_3 (1.5)	DMF	20
12	**I** (1)	KO^tBu (1.5)	DMF	5
13	**I** (1)	NaO^tBu (1.5)	DMF	trace
14	**I** (1)	NaOH (1.5)	DMF	trace
15	**I** (1)	-	DMF	0
16	**I** (1)	Cs_2CO_3 (1.0)	DMF	48
17	**I** (1)	Cs_2CO_3 (1.2)	DMF	71
18	**I** (1)	Cs_2CO_3 (2.0)	DMF	81
19	**I** (1)	Cs_2CO_3 (1.5)	DMSO	43
20	**I** (1)	Cs_2CO_3 (1.5)	CH_2Cl_2	8
21	**I** (1)	Cs_2CO_3 (1.5)	CH_3CN	37
22	**I** (1)	Cs_2CO_3 (1.5)	THF	0

[a] Reaction conditions: 1-phenylethyne (2.0 mmol), CO_2 (1 atm), solvent (10 mL), rt, 16 h. [b] Isolated yield. [c] 40 °C. [d] 60 °C.

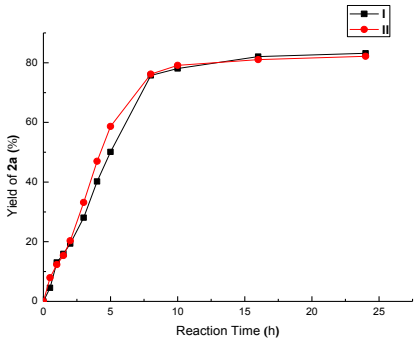
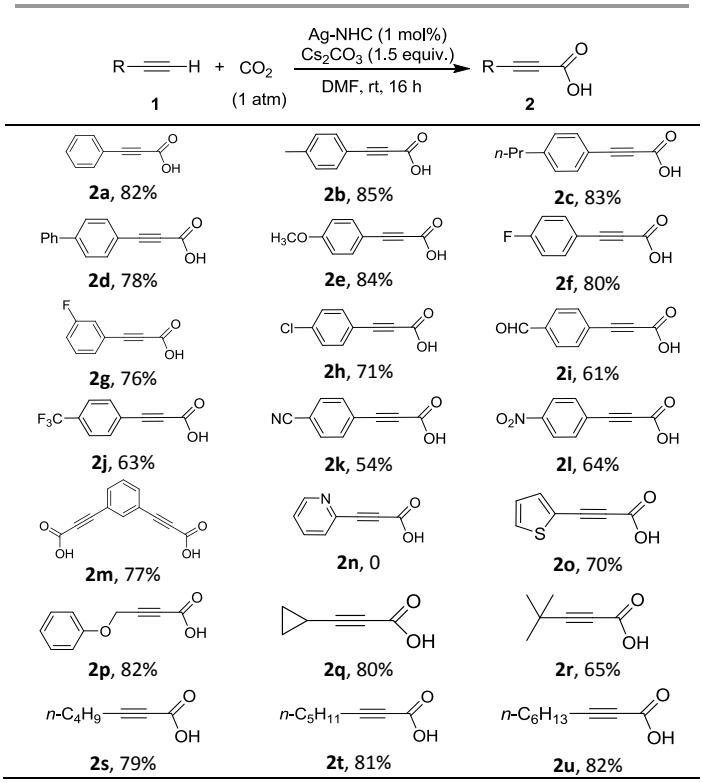


Figure **5.** Time-dependent yields of **2a** in the presence of **I** or **II** as catalyst. Reaction conditions: 1-phenylethyne (2.0 mmol), CO_2 (1 atm), **I** or **II** (1 mol%), Cs_2CO_3 (1.5 equiv.), DMF (10 mL), rt.

The scope of this carboxylation was then further studied using various alkynes as substrates under condition **A**, and the results are summarized in Table 2. It is satisfactory to see that the reaction shows high substituent-loading capability and tolerance of various substituents. For 1-phenylethyne without substituent, and aromatic alkynes bearing electron-donating groups such as methyl, propyl, phenyl and methoxyl groups, good yields of the corresponding carboxylic acids ranging from 78 % to 85 % can be achieved (**2a**-**2e**). A comparable good yield can also be obtained for weak electron-withdrawing fluro or chloro substituted aromatic alkynes (**2f**-**2h**). However, the

Table 2. Ag-NHC-catalyzed carboxylation of terminal alkynes with CO_2[a]

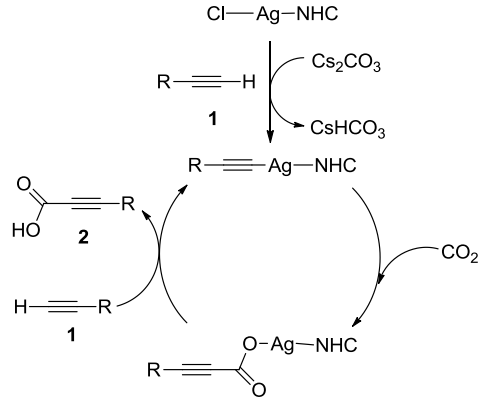


[a] Reaction conditions: alkynes **1** (2.0 mmol), Ag-NHC **I** (0.02 mmol, 1 mol% Ag), Cs_2CO_3 (3.0 mmol), DMF (10 mL), rt, 16 h; isolated yield.

yields of the corresponding products are somehow lower when using aromatic alkynes bearing strong electron-withdrawing groups such as CHO, CF_3, CN and NO_2, which may due to the low nucleophilicity of α carbon of these alkynes (**2i**-**2l**). Nevertheless, 1,3-diethynylbenzene results in 77% of the desired pheyl-1,3-dipropilic acid yield (**2m**). For heterocyclic substituted alkynes, the 2-ethynylpyridine resulted in a complicated mixture of products and the targeted pyridyl propiolic acid could not be isolated from the reaction system (**2n**).[22] Nevertheless, 70 % of thienyl propiolic acid (**2o**) can be isolated when using 2-ethynylthiophene as the substrate. It is satisfactory to see that the reaction is also effective for terminal aliphatic alkynes, whereas moderate to good yields of **2p**-**2u** can be achieved under condition **A**.

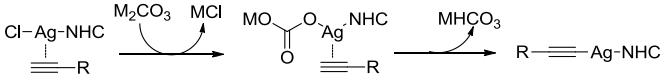
Mechanistic considerations

Based on the literature precedents,[6a,7a,13,17,23] a possible catalytic mechanism outlined in scheme **2** is proposed. Firstly, the terminal alkyne is deprotonated by the strong base Cs_2CO_3. The following coordination of the deprotonated alkynl group with Ag-NHC catalyst leads to the formation of the silver(I) acetylide, which is assumed to be the key catalytic species for the reaction. The subsequent insertion of CO_2 into Ag-C bond of the silver(I) acetylide results in the formation of a silver(I) propiolate intermediate. Finally, silver(I) propiolate reacts with another terminal alkyne molecule and regenerates the silver(I) acetylide, meanwhile releasing the desired product **2**. In such a transformation, the base plays a very important role. As has been found, Cs_2CO_3, K_2CO_3 and DBU are effective bases, in which Cs_2CO_3 proved to be the most efficient (Table 1). However, other bases such as KO^{t}Bu, NaO^{t}Bu and KOH proved to be not effective. The pKa value for CO_3^{2-} and DBU are 10.33 and 13.4 respectively[24], while pKa value for ^{t}BuOH is around 20[25]. Thus, the basicity of KO^{t}Bu and NaO^{t}Bu are much higher than that of Cs_2CO_3, K_2CO_3 and DBU. Obviously, the carboxylation reactivity does not correlate directly with the basicity. The nature of Cs_2CO_3, K_2CO_3 and DBU should be very important. Lv et al. has made DFT calculations on the AgI catalyzed carboxylation of phenyl acetylene with CO_2 using Cs_2CO_3 as the base[26]. Meanwhile, Lin et al. also studied the mechanism for copper(I) carbene (IPr)CuCl catalyzed carboxylative coupling of terminal alkyne, CO_2 and allylic chloride using K_2CO_3 as the base[23a]. Their calculation data suggest that the base Cs_2CO_3 or K_2CO_3 may participate in generation of the catalytically active species. Moreover, it is known that the pKa value of terminal alkyne is about 25, and the pKa values of HCO_3^- is about 10, thus it is impossible for a terminal alkyne to be directly deprotonated by Cs_2CO_3 or K_2CO_3[12b]. Based on these considerations, it is assumed that the coordination of alkyne to Ag-NHC may first occur in our catalytic reaction, which would make the alkyne significantly more acidic. Then, the deprotonation of alkyne can be facilitated by the coordination of anion MCO_3^- (M = Cs or K) of the base to silver forming a MCO_3^- ligated intermediate, followed by the removal of $MHCO_3$ and generation of the desired silver(I) propiolate (Scheme 3).



Scheme 2. Proposed mechanism for the carboxylation of terminal alkynes with CO_2.

While in the case of using DBU, the carboxylation generally assumes to undergo the DBU-CO_2 intermediate pathway.[8f,13]



Scheme 3. Mechanism for the deprotonation of terminal alkyne by M_2CO_3.

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Experimental

General Method

All manipulations were carried out using standard Schlenk techniques under a dry nitrogen or CO_2 atmosphere. All the experiments were performed in flame-dried Schlenk tubes. NMR spectra were obtained on a Bruker Ascend HD 500 (^{1}H NMR, 500 MHz; ^{13}C NMR, 125 MHz) spectrometer using $CDCl_3$ or DMSO-d_6 as solvents. IR spectra were recorded on a Spectrum GX FT-IR spectrometer. Elemental analysis were performed on a perkin-Elemer PE 2400 elemental analyzer. DMF was distilled from CaH_2 at 60 °C under reduced pressure and stored over 4Å molecular sieves. The cesium carbonate was dried for 12h in vacuo at 120 °C prior to use. CO_2 (99.999%) was dried by 4Å molecular sieves before use. All other commercially available compounds of analytical grade were used without further purification. Imidazolium salts and Ag-NHCs were prepared according to literature procedures.[27-29]

Synthesis and characterization of Ag-NHCs I-IV

A flame-dried, nitrogen-flushed, 100 mL Schlenk tube was charged with the imidazolium chlorides (2.0 mmol), Ag_2O (0.26 g, 1.1 mmol, 0.55 equiv.), and stirred in CH_2Cl_2 (20 mL) for 48 h at room temperature under exclusion of light. The resulting mixture was filtered and crystallized by a certain amount of ethyl ether to afford white crystals **I-IV.**

1,3-Bis(4-methylbenzyl)imidazol-2-ylidene silver(I) chloride (I): Yield: (0.69 g, 83%). ^{1}H NMR (DMSO-d_6, 500 MHz) δ (ppm): 7.52 (s, 4H), 7.20-7.13 (m, 16H, Ar-H), 5.25 (s, 8H), 2.26 (s, 12H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 179.29 (Ag-C), 137.78, 134.65, 129.78, 128.07, 122.87, 54.56, 21.16. IR (KBr): 3082, 2940, 1567, 1519, 1440; $C_{38}H_{40}Ag_2Cl_2N_4$ calcd. C 54.37, H 4.80, N 6.67; found C 54.34, H 4.82, N 6.65.

1,3-Bis(4-methoxybenzyl)imidazol-2-ylidene silver(I) chloride (II): Yield: (0.68 g, 75%). ^{1}H NMR (DMSO-d_6, 500 MHz) δ (ppm): 7.50 (s, 2H), 7.27 (d, *J* = 8.0 Hz, 4H, Ar-H), 6.90 (d, *J* = 8.5 Hz, 4H, Ar-H), 5.23 (s, 4H), 3.72 (s, 6H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 178.80 (Ag-C), 159.51, 129.63, 129.55, 122.72, 114.63, 55.59, 54.31. IR (KBr): 3129, 2934, 2829, 1615, 1512, 1449; $C_{19}H_{20}AgClN_2O_2$ calcd. C 50.52, H 4.46, N 6.20; found C 50.50, H 4.43, N 6.22.

1,3-bis(4-chlorobenzyl)imidazol-2-ylidene silver(I) chloride (III): Yield: (0.57 g, 62%). ^{1}H NMR (DMSO-d_6, 500 MHz) δ (ppm): 7.57 (s, 4H), 7.44 (d, *J* = 8.0 Hz, 8H, Ar-H), 7.31 (d, *J* = 8.5 Hz, 8H, Ar-H), 5.34 (s, 8H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 179.85 (Ag-C), 136.64, 133.16, 129.88, 129.22, 123.17, 53.91. IR (KBr): 3043, 2940, 1591, 1488; $C_{34}H_{28}Ag_2Cl_6N_4$ calcd. C 44.34, H 3.06, N 6.08; found C 44.30, H 3.05, N 6.05.

1,3-Bis(3-methoxybenzyl)imidazol-2-ylidene silver (I) chloride (IV): Yield: (0.72 g, 79%). ^{1}H NMR (DMSO-d_6, 500 MHz) δ (ppm): 7.57 (s, 2H), 7.25 (t, *J* = 8.0 Hz, 2H, Ar-H), 6.90-6.82 (m, 6H, Ar-H), 5.28 (s, 4H), 3.71(s, 6H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 178.92 (Ag-C), 159.33, 138.60, 129.81, 122.44 ,119.50, 113.32, 113.14, 54.93, 54.08. IR (KBr): 3129, 2940, 2829, 1598, 1473; $C_{19}H_{20}AgClN_2O_2$ calcd. C 50.52, H 4.46, N, 6.20; found C 50.50, H 4.42, N, 6.21.

General procedure for the carboxylation of terminal alkynes with CO_2

In a typical procedure, Ag-NHC **I** (8.4 mg, 0.02 mmol, 1.0 mol%), Cs_2CO_3 (978 mg, 3.0 mmol), and DMF (10 mL) were added to a Schlenk tube. CO_2 (1 atm) and terminal alkynes (2.0 mmol) were then introduced into the reaction mixture under stirring. The mixture was stirred at room temperature for 16 h. Then the resulting mixture was transferred to the potassium carbonate solution (2 N, 10 mL) and stirred for 30 min at room temperature. The mixture was extracted with dichloromethane (3 × 10 mL), the aqueous layer was acidified with concentrated HCl to pH=1, then extracted with diethyl ether (3 × 10 mL). The combined organic layers were dried with anhydrous $MgSO_4$ and filtered; the solution was concentrated in vacuo, affording the corresponding products **2**.

3-Phenylpropiolic acid (2a)[15]: white solid (242 mg, 82%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 11.52 (br, s, 1H, -COOH), 7.62 (d, *J* = 7.0 Hz, 2H, Ar-H), 7.48 (t, *J* = 7.5 Hz, 1H, Ar-H), 7.39 (t, *J* = 7.5 Hz, 2H, Ar-H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 158.99 (-COOH), 133.34, 131.22, 128.70, 119.07, 89.28, 80.08.

3-*p*-Tolylpropiolic acid (2b)[15]: white solid (269 mg, 85%). ^{1}H NMR (DMSO-d_6, 500 MHz) δ (ppm): 13.74 (br, s, 1H, -COOH), 7.52 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.29 (d, *J* = 8.0 Hz, 2H, Ar-H), 2.36 (s, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 154.84 (-COOH), 141.64, 133.06, 130.13, 116.36, 85.34, 81.87, 21.65.

3-(4-Propylphenyl)propiolic acid (2c)[9]: white solid (316 mg, 83%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 10.80 (br, s, 1H, -COOH), 7.53 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.20 (d, *J* = 8.0 Hz, 2H, Ar-H), 2.62 (t, *J* = 7.5 Hz, 2H), 1.70-1.60 (m, 2H), 0.94 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 158.86 (-COOH), 146.68, 133.38, 128.89, 116.20, 89.88, 79.80, 38.14, 24.17, 13.73.

3-([1,1'-Biphenyl]-4-yl)propiolic acid (2d)[15]: white solid (351 mg, 78%). ^{1}H NMR (DMSO-d_6, 500 MHz) δ (ppm): 13.83 (br, s, 1H, -COOH), 7.80-7.76 (m, 2H, Ar-H), 7.75-7.70 (m, 4H, Ar-H), 7.53-7.47 (m, 2H, Ar-H), 7.45-7.40 (m, 1H, Ar-H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 154.78 (-COOH), 142.81, 139.21, 133.73, 129.59, 128.80, 127.65, 127.33, 118.32, 84.84, 82.85.

3-(4-Methoxyphenyl)propiolic acid (2e)[15]: white solid (296 mg, 84%). ^{1}H NMR (DMSO-d_6, 500 MHz) δ (ppm): 13.62 (br, s, 1H, -COOH), 7.59 (d, *J* = 9.0 Hz, 2H, Ar-H), 7.03 (d, *J* = 8.5 Hz, 2H, Ar-H), 3.82 (s, 3H, OCH_3); ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 161.69, 154.98 (-COOH), 135.10, 115.19, 111.05, 85.78, 81.53, 55.89.

3-(4-Fluorophenyl)propiolic acid (2f)[11a]: white solid (260 mg, 80%). ^{1}H NMR (DMSO-d_6, 500 MHz) δ (ppm): 13.80 (br, s, 1H, -COOH), 7.72-7.67 (m, 2H, Ar-H), 7.33-7.27 (m, 2H, Ar-H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 163.75 (d, *J* = 249.1 Hz), 154.69 (-COOH), 135.84, 116.92 (d, *J* = 22.4 Hz), 115.93, 83.90, 82.05.

3-(3-Fluorophenyl)propiolic acid (2g)[11a]: white solid (248 mg, 76%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 10.65 (br, s, 1H, -COOH), 7.42-7.35 (m, 2H, Ar-H), 7.31 (d, *J* = 8.5 Hz, 1H, Ar-H), 7.20 (t, *J* = 8.5 Hz, 1H, Ar-H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 162.23 (d, *J* = 247.1 Hz), 158.20 (-COOH), 130.44, 129.16, 120.89, 119.93 (d, *J* = 23.4 Hz), 118.72 (d, *J* = 21.0 Hz), 87.32, 80.39.

3-(4-Chlorophenyl)propiolic acid (2h)[15]: white solid (226 mg, 71%). ^{1}H NMR (DMSO-d_6, 500 MHz) δ (ppm): 13.90 (br, s, 1H, -COOH),

7.66 (d, *J* = 8.5 Hz, 2H, Ar-H), 7.55 (d, *J* = 8.5 Hz, 2H, Ar-H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 154.58 (-COOH), 136.29, 134.82, 129.73, 118.34, 83.56, 83.02.

3-(4-Formylphenyl)propiolic acid (2i)[15]: white solid (221 mg, 61%). ^{1}H NMR (DMSO-d_6, 500 MHz) δ (ppm): 13.40 (br, s, 1H, -COOH), 10.07 (s, 1H, -CHO), 7.99 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.85 (d, *J* = 8.0 Hz, 2H, Ar-H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 193.03 (CHO), 154.43 (-COOH), 137.42, 133.65, 130.13, 125.05, 84.58, 83.40.

(4-Triflouromethylphenyl)-propynoic acid (2j)[9]: white solid (265 mg, 63%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 9.48 (br, s, 1H, -COOH), 7.73 (d, *J* = 8.5 Hz, 2H, Ar-H), 7.67 (d, *J* = 8.0 Hz, 2H, Ar-H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 156.90 (-COOH), 133.42, 132.71 (d, *J* = 32.8 Hz), 125.68, 124,54, 122.63(d, *J* = 64.4 Hz), 86.64, 81.31.

3-(4-Cyanophenyl)propiolic acid (2k)[15]: white solid (181 mg, 54%). ^{1}H NMR (DMSO-d_6, 500 MHz) δ (ppm): 14.12 (br, s, 1H, -COOH), 7.95 (d, *J* = 8.5 Hz, 2H, Ar-H), 7.83 (d, *J* = 8.5 Hz, 2H, Ar-H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 154.32 (-COOH), 133.67, 133.24, 124.28, 118.52, 113.50, 84.95, 82.62.

3-(4-Nitrophenyl)propiolic acid (2l)[15]: white solid (246 mg, 64%). ^{1}H NMR (DMSO-d_6, 500 MHz) δ (ppm): 8.29 (d, *J* = 8.5 Hz, 2H, Ar-H), 7.91 (d, *J* = 9.0 Hz, 2H, Ar-H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 154.27 (-COOH), 148.70, 134.30, 126.07, 124.46, 85.53, 82.18.

3,3'-(1,3-Phenylene)dipropiolic acid (2m)[15]: white solid (321 mg, 77%). ^{1}H NMR (DMSO-d_6, 500 MHz) δ (ppm): 13.97 (br, s, 2H, -COOH), 7.86 (s, 1H, Ar-H), 7.78 (d, *J* = 7.5 Hz, 2H, Ar-H), 7.57 (t, *J* = 8.0 Hz, 1H, Ar-H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 154.50 (-COOH), 136.31, 135.11, 130.38, 120.49, 83.06, 82.95.

3-(Thiophen-2-yl)propiolic acid (2o)[15]: white solid (212 mg, 70%). ^{1}H NMR (DMSO-d_6, 500 MHz) δ (ppm): 13.84 (br, s, 1H, -COOH), 7.88 (d, *J* = 5.5 Hz, 1H), 7.67 (d, *J* = 3.5 Hz, 1H), 7.20 (t, *J* = 4.5 Hz, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 154.61 (-COOH), 137.44, 133.16, 128.74, 118.74, 86.30, 78.95.

4-Phenoxybut-2-ynoic acid (2p)[7a]: white solid (293 mg, 82%). ^{1}H NMR (DMSO-d_6, 500 MHz) δ (ppm): 13.89 (br s, 1H, -COOH), 7.33 (t, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 7.0 Hz, 3H), 5.03 (s, 2H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ (ppm): 157.44 (-COOH), 154.06, 130.06, 122.02, 115.20, 82.30, 79.76, 55.43.

3-Cyclopropylpropiolic acid (2q)[9]: white solid (178 mg, 80%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 10.69 (br, s, 1H, -COOH), 1.45-1.37 (m, 1H), 1.01-0.93 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 158.30 (-COOH), 96.75, 68.03, 9.57, -0.48.

4,4-Dimethylpent-2-ynoic acid (2r)[15]: white solid (163 mg, 65%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 1.30 (s, 9H, CH3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 158.10 (-COOH), 99.65, 71.18, 29.82, 27.68.

Hept-2-ynoic acid (2s)[9]: colorless liquid (199 mg, 79%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 11.04 (br, s, 1H, -COOH), 2.37 (t, *J* = 7.0 Hz, 2H, CH2), 1.60-1.54 (m, 2H, CH2), 1.48-1.39 (m, 2H, CH2), 0.93 (t, *J* = 7.5 Hz, 3H, CH3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 158.53 (-COOH), 92.71, 72.59, 29.34, 21.84, 18.33, 13.30.

2-Octynoic acid (2t)[15]: colorless liquid (225 mg, 81%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 10.21 (br, s, 1H, -COOH), 2.35 (t, *J* = 7.0 Hz, 2H, CH2), 1.63-1.55 (m, 2H, CH2), 1.43-1.29 (m, 4H), 0.90 (t, *J* = 7.5 Hz, 3H, CH3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 158.52 (-COOH), 92.76, 72.64, 30.91, 27.06, 22.04, 18.68, 13.78.

2-Nonynoic acid (2u)[9]: colorless liquid (251 mg, 82%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 11.52 (br, s, 1H, -COOH), 2.36 (t, *J* = 7.0 Hz, 2H), 1.58 (q, *J* = 7.5 Hz, 2H), 1.44-1.29 (m, 6H), 0.90 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 158.66 (-COOH), 92.74, 72.66, 31.15, 28.45, 27.34, 22.41, 18.71, 13.92.

Single crystal X-ray structure determination of I-IV

Details of the X-ray experiment, crystal parameters, data collections and refinements for **I-IV** can be found in Table S1 and S2 of ESI. Single crystals were mounted on a Bruker XRDR3M / ESYSTCM diffractometer operating at 50 kV and 30 mA equipped with a MoK$_\alpha$ radiation source (λ=0.71073 Å). Data collection were performed at 193 - 296 K with a ω/ϕ diffraction measurement method and reduction was performed using the SMART and SAINT software with frames of 0.3° oscillation in the θ range 1.5<θ<27.5°. The structures were solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on F^2 using the SHELXTL package.[30] Crystallographic data for the structures of **I-IV** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC-1413846 (**I**), CCDC-1432048 (**II**), CCDC-1413845 (**III**) and CCDC-1413847 (**IV**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk.

Conclusions

In conclusion, we have developed a novel Ag-NHC catalyzed highly active and selective carboxylation of alkynes with CO_2. The single X-ray crystal diffraction data indicate either dinuclear or mononuclear solid-state structure of the synthesized Ag-NHC complexes. Nevertheless, both monomer and dimer display similar activity for carboxylation. The developed method is applicable for a broad range of substrates, affording various functionalized propiolic acids in good yields. The role of bases and the carboxylation mechanism for the examined reaction is fully discussed.

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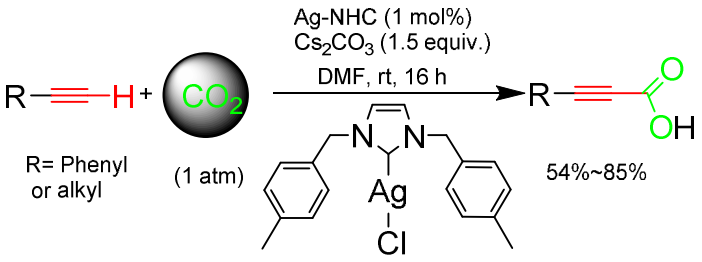
Figure:



Abstract: Carboxylation of terminal alkynes with CO_2 to propiolic acids using novel silver N-heterocyclic carbene complexes as efficient catalysts.