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Review

Recent Advances in N-Heterocyclic Carbene Coinage Metal Complexes in A^3-Coupling and Carboxylation Reaction

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Abstract: Owing of their accessibility and wide range of reactivities, alkynes make for fascinating building blocks. Either a selective alkyne carbon-carbon triple bond reaction or activation of the terminal alkyne C-H bond may be employed to functionalize them. Monocationic coinage metal complexes with a d10 electronic configuration are effective catalysts for alkyne activation. Silver(I) and gold(I) N-heterocyclic (NHC) systems are emerging as promising catalysts in multicomponent alkyne activation reactions; this review paper focuses on A^3 (aldehyde-amine-alkyne)-coupling reaction and carbon dioxide fixation, furnishing a systematic overview of the scientific advances achieved during the last two decades. This study will carefully compare the corresponding silver and gold complexes employed in the two processes. The differences in reaction routes brought about by the catalyst ligand structure will be investigated with an emphasis on evaluating the benefits provided by the easily tuneable NHC backbone, in terms of chemo- and stereo-selectivity.

Keywords: NHC complexes; silver complexes; gold complexes; A^3-coupling; CO_2 fixation

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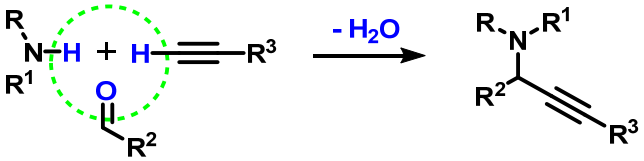
1. Introduction

Alkynes provide for intriguing building blocks as they are easily accessible and display a variety of reactivities. Their functionalization can be carried out either with a selective alkyne carbon-carbon triple bond reaction or as activation of the terminal alkyne C-H bond. A single or multiple functional groups can be introduced by π-bond breaking; on the other hand, alkynyl C-H bonds (pKa = 25) are particularly responsive, since they are significantly more acidic than their equivalent alkenyl and alkyl C-H bonds (pKa = 43 and >50, respectively). Hence, under various basic circumstances, base-promoted additions of terminal alkynes to carbonyl compounds can occur [1]. Classical, stoichiometric alkyne addition have been taken over by more sustainable processes, which take into account atom economy and chemoselectivity. Innovative, effective procedures that take use of the substrate's coexisting π-donor and π-acceptor features are transition metal-catalyzed insertion techniques across the triple bond of alkynes [1–3]. Monocationic coinage metal complexes with a d10 electronic configuration are effective catalysts for alkyne activation due to metal donation from *p* to s and metal to *p** back-bonding. Although copper catalysis is the most investigated in the literature, silver(I) and gold(I) systems are emerging as efficient alternatives, thanks to their enhanced stability and ease management [3–5]. N-Heterocyclic Carbenes (NHCs) are ideal systems for suitably modifying ligands to fine-tune reactivity, chemo-, and stereo-selectivity; these two-electron donor ligands combine strong σ-donating properties with a steric profile that permits both stabilisation of the metal centre and improvement of its catalytic activity [6,7]. The synthesis of such complexes has been extensively investigated over the past couple of decades, as well as their catalytic applications, which are widespread [8–10]. The main focus of this review article is the application

of NHC-silver(I) and gold(I) complexes in multicomponent (MC) reactions, with a specific attention to A^3 (aldehyde-amine-alkyne)-coupling reaction and carbon dioxide fixation. Such processes have gained more and more attention over the past decade, as testified by the exponential growth in published papers. One-pot catalysis, performed in classical organic solvents, as well as neat conditions or even polar solvents such as water, renders for efficient, atom-economic processes. The main products, namely propargylamines and propiolic acids, constitute interesting, versatile building blocks towards more complex chemical architectures, some of which are mentioned in this paper. The variations in catalyst performance brought on by the various NHC backbones will be addressed, and a careful comparison of the analogous silver and gold complexes used in the two MC reactions will be conducted. With a focus on examining the reaction mechanism, the variations in reaction pathways brought about by the catalyst structure will be explored with the purpose of generating fresh ideas for the design and development of novel and ever more efficient catalytic complexes.

2. A^3–Coupling Reaction

The A^3-reaction is a three-component coupling involving an aldehyde, a terminal alkyne and an amine (Scheme 1). It represents the most efficient method to obtain propargylamines.

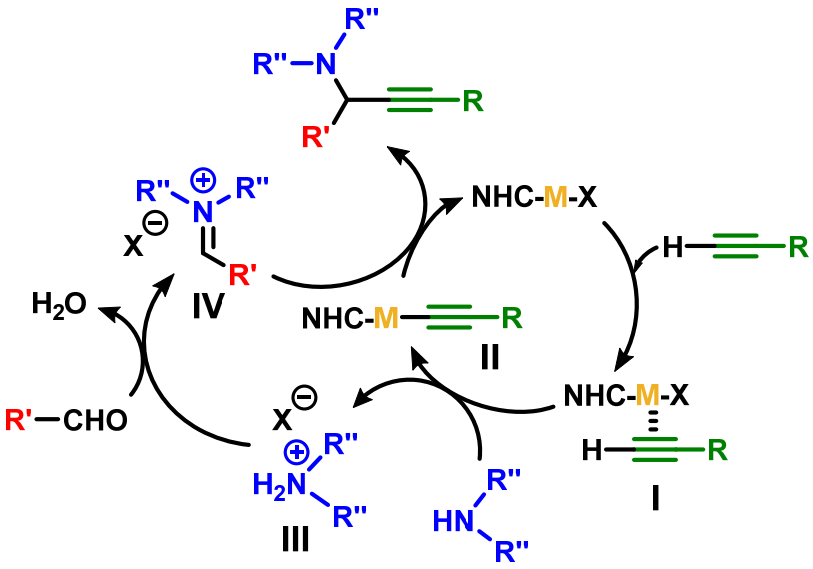


Scheme 1. A^3–coupling reaction.

Propargylamines constitute an important family of chemicals employed as organic building blocks and for realizing medicinal drugs such as Selegenine [11] and Rasagiline [12], that are currently used in the early treatment of Parkinson's and Alzheimer's diseases. The classical route for the synthesis of propargylamines is the nucleophilic addition of a metal acetylide to an imine. The acetylide is obtained by reaction of terminal alkynes with a strong base, such as butyllithium. The need to use stoichiometric amounts of acetylide, anhydrous conditions, and low temperatures, makes this method inconvenient. An alternative synthetic strategy has been developed over the past decade; catalytic amounts of transition metal inorganic salts can be used in the coupling reaction of equimolar quantities of aldehydes, amines and alkynes (A^3) [13,14]. Thanks to its atom economy and high chemical selectivity, this synthetic strategy has received more and more attention.

The first catalysts used in the A^3-coupling reactions [15] displayed a few drawbacks: high catalyst loading percentages and high temperatures. Copper [16], silver and gold complexes with N-heterocyclic carbenes (NHCs) were synthesized and tested as valid catalytic alternatives meant to overcome these downsides [5].

A proposed plausible mechanism for this three-components reaction, catalyzed by a late-transition metal NHC complex, is reported in Scheme 2 [15,17]. After the formation of an intermediate complex by side-on coordination of the alkyne to the metal, the weakly basic amine deprotonates the alkyne (whose acidity is now increased) and thus generates the corresponding metal acetylide. Lastly, the addition of this intermediate to an in situ generated imine (or iminium ion), leads to the desired propargylamine [18–22].



Scheme 2. Proposed reaction mechanism for NHC-M-X catalyzed A^3-coupling reactions.

In 2008, Wang and co-workers reported the synthesis of a series of NHC-Ag(I) (**1a**–**d**) and polystyrene supported PS-NHC-Ag(I) (**2a**–**d**) complexes (Figure 1) [23].

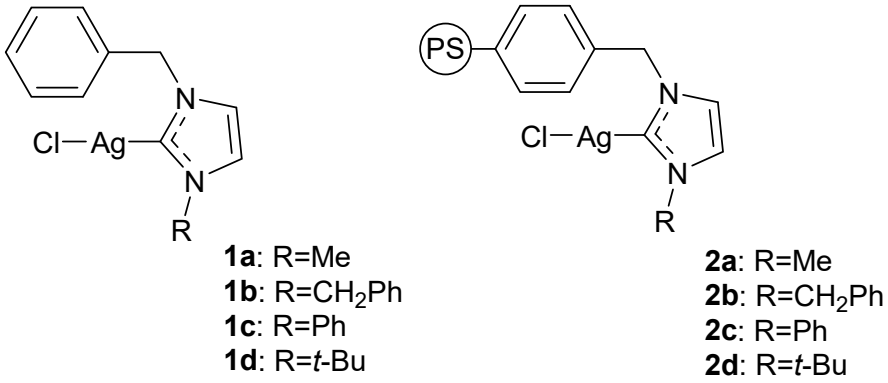
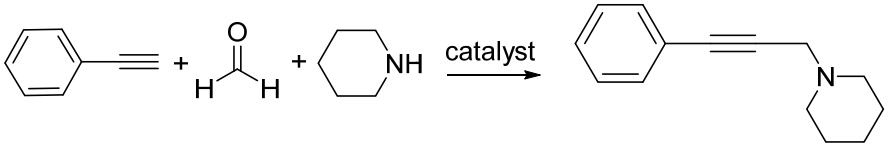


Figure 1. NHC-Ag(I) and PS-NHC-Ag(I) synthesized by Wang [23].

They were employed in the A^3-coupling reaction of paraformaldehyde (1.0 mmol), phenylacetylene (1.1 mmol) and piperidine (1.1 mmol) at room temperature for 24 h, with a 2 mol% amount of the silver catalyst in CH_2Cl_2, under nitrogen atmosphere. The results are summarized in Table 1. The catalytic activity of NHC-Ag(I) and PS-NHC-Ag(I) complexes decreased in this order: **1b** > **1c** > **1d** > **1a** and **2b** > **2c** > **2d** > **2a**, and this was the result of the influence of the substituted groups of the imidazolium salts: CH_2Ph > Ph > *t*-Bu > Me.

Thus, 1b and 2b (Table 1, Entries 2 and 6) resulted as the best catalysts for the A^3-coupling reaction. Low catalytic activities were observed with Ag_2O or AgI (Table 1, Entries 9 and 10); moreover, there was no propargylamine formation in the absence of the silver source.

Table 1. Effect of Silver catalysts on A^3-coupling reaction.

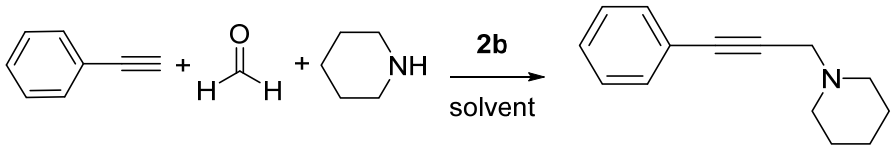


Entry [a]	Catalyst	Yield (%) [b]
1	**1a**	61
2	**1b**	80
3	**1c**	74
4	**1d**	68
5	**2a**	69
6	**2b**	90
7	**2c**	80
8	**2d**	75
9	**Ag_2O**	37
10	**AgI**	31

[a] Reaction conditions: paraformaldehyde (1.0 mmol), piperidine (1.1 mmol), phenylacetylene (1.1 mmol), silver catalyst (2 mol%), CH_2Cl_2 (0.5 mL), nitrogen atmosphere, room temperature, 24 h. [b] Isolated yields.

The authors evaluated the effect of the solvent on the A^3-coupling reaction as well, using catalyst **2b**. Among the various solvents tested, acetone, acetonitrile, dimethyl sulfoxide, and dichloromethane proved to be the best, but the highest yield (97%) was obtained under neat conditions (Table 2, Entry 10).

Table 2. Effect of the solvent on A^3-coupling reaction using **2b** as catalyst.

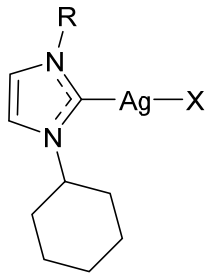


Entry [a]	Solvent	Yield (%) [b]
1	Acetone	95
2	Acetonitrile	91
3	Dimethyl sulfoxide	90
4	Dichloromethane	90
5	Dimethylformamide	84
6	Toluene	69
7	Tetrahydrofuran	62
8	Ethanol	49
9	Water	42
10	Neat	97
11 [c]	Neat	71

[a] Reaction conditions: paraformaldehyde (1.0 mmol); piperidine (1.1 mmol); phenylacetylene (1.1 mmol); **2b** (2 mol%); solvent (0.5 mL); nitrogen atmosphere; room temperature; 24 h. [b] Isolated yields. [c] **2b** (1 mol %) was used.

Furthermore, the recyclability of PS-NHC-Ag(I) catalyst **2b** was also investigated. The catalyst recovered by filtration maintained its ability to give A^3-coupling reaction for 12 consecutive cycles. The catalysis tests with these complexes were extended to different combinations of amines, aldehydes and alkynes obtaining the corresponding propargylamines in good to excellent yields (85–98%).

In 2010, Zou et al. [15] described the synthesis of some NHC-Ag-X complexes: 1-cyclohexyl-3-benzylimidazolylidene and 1-cyclohexyl-3-naphtylimidazolylidene chloride and bromide (**3a**–**d**) that are reported in Figure 2.



3a: R= CH_2Ph, X=Cl
3b: R= CH_2Ph, X=Br
3c: R= naphthalen-2-ylmethyl, X=Cl
3d: R= naphthalen-2-ylmethyl, X=Br

Figure 2. NHC-Ag-X complexes synthesized by Zou et al. [15].

These compounds were obtained by reaction of silver oxide with the corresponding imidazolium salts in dichloromethane, following a procedure reported previously in the literature [24].

One equivalent of sodium nitrate was added to the reaction mixture of silver oxide and 1-cyclohexyl-3-benzylimidazolylidene in tetrahydrofuran to give a weakly coordinating anion; in this way the desired biscarbene silver nitrate (**4**) was obtained (Figure 3).

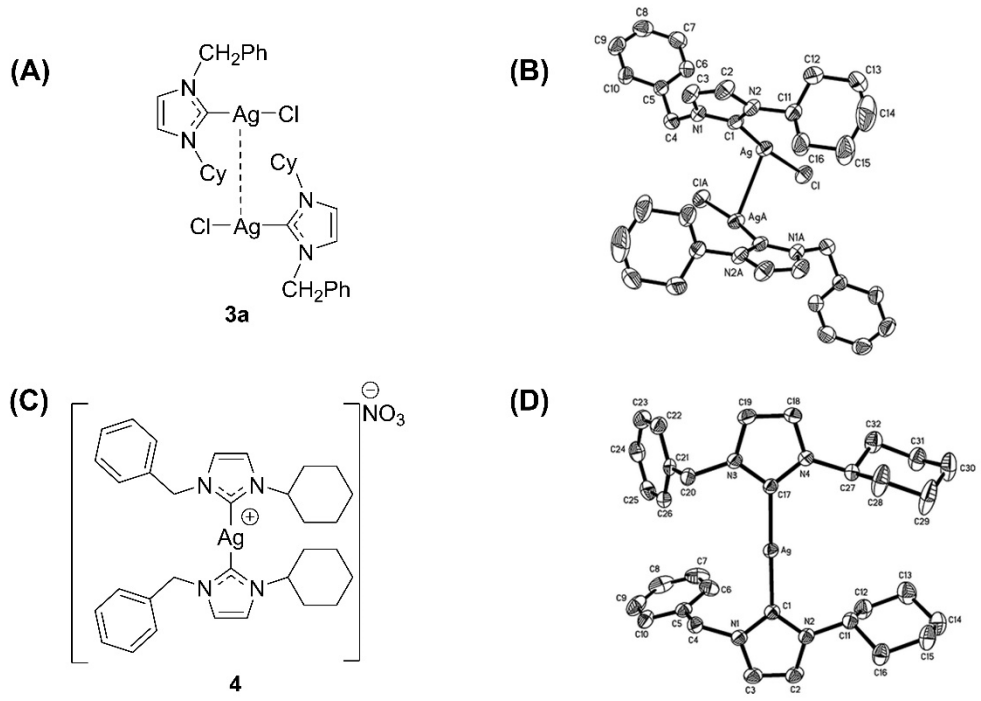
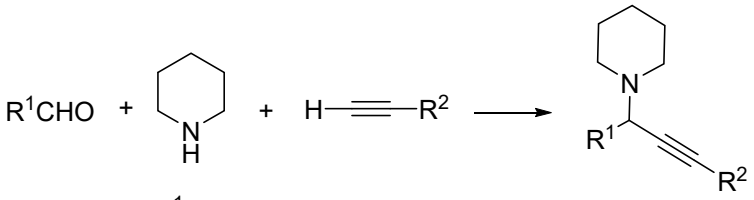


Figure 3. (**A**) $[(CyBn\text{-}NHC)AgCl]_2$ complex **3a** structure and relative (**B**) dimeric *trans* conformation crystal structure; (**C**) $[(CyBn\text{-}NHC)_2Ag]^+ NO_3^-$ complex **4** structure and relative (**D**) dimeric *cis* conformation crystal structure (anion omitted).

NMR and elemental analyses provided only a few information on the NHC silver complexes' molecular structure, thus single crystal X-ray diffraction analysis was performed. The analysis revealed that the complexes **3a** and **3b** have a *trans* conformation dimeric structure with a non-polar Ag-Ag bond (Figure 3A,B) report the exemplificative structure for complex **3a**); the complex **4** contains two NHC ligands with a *cis* orientation (Figure 3C,D), while the complexes **3c** and **3d** show the desired monomeric structure complexes **3a**–**d** and **4** were tested as catalysts in the A^3-coupling reaction of 3-phenylpropionaldehyde,

phenylacetylene and piperidine; the same were used, at 100 °C in air, also with alkyl alkynes, such as octyne, and aromatic aldehydes, both electron rich and deficient ones, giving the desired propargylamine in good yields. The results are shown in Table 3.

Table 3. Complexes **3a–d** and **4** catalytic activity in the A^3-coupling reaction.



R^1= $PhCH_2CH_2$, 4-ClC_6H_4, Piperonyl
R^2= Ph, H, n-C_6H_{13}

Entry [a]	Catalyst	Aldehyde	Alkyne	Temp. (°C)	Time (h)	Yield (%) [b]
1	**3a**	3-phenylpropionaldehyde	phenylacetylene	100	2	79
2	**3b**	3-phenylpropionaldehyde	phenylacetylene	100	2	61
3	**4**	3-phenylpropionaldehyde	phenylacetylene	100	2	77
4	**3c**	3-phenylpropionaldehyde	phenylacetylene	100	2	99
5	**3d**	3-phenylpropionaldehyde	phenylacetylene	100	2	84
6	**AgCl**	3-phenylpropionaldehyde	phenylacetylene	100	2	80
7	**AgBr**	3-phenylpropionaldehyde	phenylacetylene	100	2	64
8	**AgI**	3-phenylpropionaldehyde	phenylacetylene	100	2	49
9	**$AgNO_3$**	3-phenylpropionaldehyde	phenylacetylene	100	2	61
10	**Ag_2O**	3-phenylpropionaldehyde	phenylacetylene	100	2	78
11	**3c**	3-phenylpropionaldehyde	phenylacetylene	50	12	81
12	**3c**	3-phenylpropionaldehyde	phenylacetylene	r.t.	72	69
13 [c]	**3c**	3-phenylpropionaldehyde	phenylacetylene	100	12	31
14	**3c**	3-phenylpropionaldehyde	octyne	100	6	64
15	**3c**	4-chlorobenzaldheyde	phenylacetylene	100	12	77
16	**3c**	Piperonaldheyde	phenylacetylene	100	12	49

[a] Reaction conditions: aldehyde (1.0 mmol); piperidine (1.2 mmol); alkyne (1.5 mmol); NHC-Ag-X catalysts (3 mol%); dioxane (3 mL). [b] Isolated Yield. [c] Run in water. r.t. Room temperature.

The activities of NHC silver halides **3a** and **3b** were scarce when compared with simple inorganic silver halides AgCl and AgBr (Table 3, Entries 1–2 and 6–7). The yields increased with the complexes **3c** and **3d** thanks to the improved steric hindrance of 1-cyclohexyl-3-naphthalen-2-ylmethylimidazolylidene: in particular, the reaction with complex **3c** completed in 2 h giving the product in a 99% yield (Table 3, Entries 4–5). Although cationic complexes are reported to exhibit high catalytic activity in the A^3-coupling reaction, the cationic biscarbene silver nitrate complex **4** did not show better catalytic performance than the one observed with silver halides, due to the steric hindrance of the silver in the biscarbene cation $[(NHC)_2Ag]^+$ (Table 3, Entry 3). Reaction times were longer at lower temperatures (Table 3, Entries 11–12).

In 2012 Navarro and co-workers [25] reported a study on A^3-coupling reaction using analogous silver complexes with carbenes as ligands. They described the synthesis of NHC-Ag-X complexes starting from commercially available NHCs or their precursors, imidazolium salts [26–29]. These complexes, reported in Figure 4 (**5a–d** and **6a–b**), were tested in the reaction of cyclohexanecarboxaldehyde (1.0 mmol), piperidine (1.1 mmol) and phenylacetylene (1.1 mmol) at 25 °C, with an amount of the catalyst of 1–2 mol% and with different solvents.

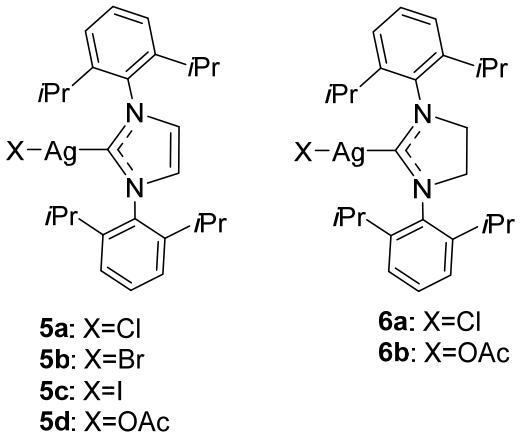
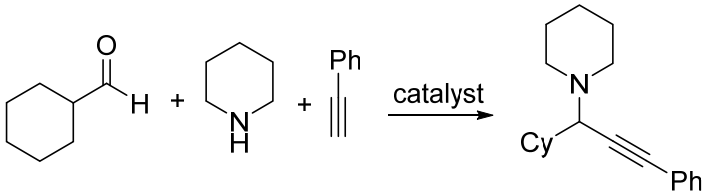


Figure 4. NHC-Ag(I) complexes synthesized by Navarro and co-workers [25].

The authors used **5a** ((IPr)AgCl) complex to optimize the reaction conditions. As shown in Table 4 (Entry 11, the use of methanol as solvent led to the highest yields when 1 mol% of the complex was employed.

Table 4. Effect of the solvent on the A^3-coupling reaction.



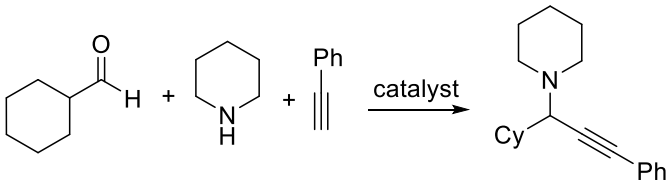
Entry [a]	Solvent	Time (h)	Yield (%) [b]
1	Neat	3	62
2	Acetone	3	63
3	Dichloromethane	3	69
4	Acetonitrile	3	96
5	Toluene	3	9
6	Dimethylformamide	3	57
7	Water	3	19
8	Isopropanol	1	88
9	Methanol	1	98
10	Isopropanol	0.25	68
11	Methanol	0.25	94

[a] Reaction conditions: cyclohexanecarboxaldehyde (1.0 mmol); piperidine (1.1 mmol); phenylacetylene (1.1 mmol); catalyst **5a** (1.2 mol%); solvent (0.5 mL); 25 °C. [b] GC yield (hexamethylbenzene as internal standard); average of 2 runs.

Subsequently, they carried out a study using methanol as solvent to evaluate the activity of the synthesized catalysts, i.e., **5a–d** and **6a–b.** The counterion has a notable effect, in fact the acetate ion gives the highest activity, while the halides follow the order Cl > Br >> I. Probably the polarizability of the counterion and its electronegativity are important factors. It should be noted that there are no important differences in the formation of the propargylamine, using a complex with saturated N-heterocyclic carbene based ligand (**6a–b**), compared to the complex with unsaturated ones (**5a–d**).

As shown in Table 5, the highest yield (96%, in 20 min) was obtained with 1 mol% of the complex **6b**. The study was extended to different amines, aldehydes and alkynes. The complex **6b** was able also to catalyze the coupling reaction of inactivated aryl aldehydes at room temperature, even if the reaction times resulted longer. Times could be shortened by increasing the temperature and/or the catalyst loading.

Table 5. Effect of the catalyst on the A^3-coupling reaction after 20 min.



Entry [a]	Complex	Yield (%) [b]
1	**5a**	86
2	**6a**	88
3	**5b**	70
4	**5c**	9
5	**5d**	91
6	**6b**	96

[a] Reaction conditions: cyclohexanecarboxaldehyde (1 mmol); piperidine (1 mmol), phenylacetylene (1.1 mmol); catalyst (1 mol%); methanol (0.5 mL); 25 °C; 20 min. [b] GC yield (hexamethylbenzene as internal standard); average of 2 runs.

The synthesis and the catalytic activity in A^3-coupling reactions of a supported Ag(I)-NHC-MOF complex was reported in 2013 [30]. Metal-organic frameworks (MOFs) are efficient heterogeneous catalysts featuring a metallic core and malleable organic linkers (see Figure 5). They display large pores, high surface area, and can selectively adsorb small molecules. To combine the advantageous properties of MOFs and NHCs, the latter can be integrated into MOFs. In this way, systems with multiple, embedded catalytic sites in a single structure can be obtained. According to a previous work by Kitagawa et al., Mousavi, Verpoort and co-workers [31] reported the synthesis of the **MOF A**, consisting of the [Zn_8O] clusters with six metallomacrocycles and NHC moieties, as shown in Figure 5 [30].

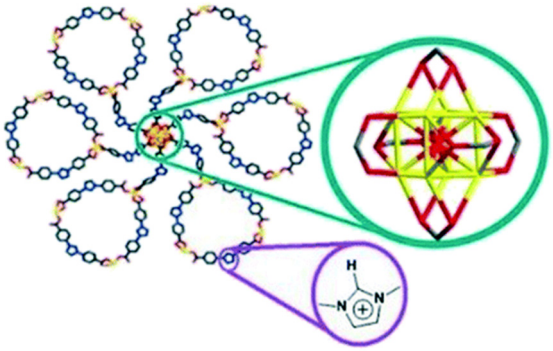


Figure 5. MOF A consisting of the [Zn_8O] clusters with six metallomacrocycles and NHC moieties.

The NHC carbon of the **MOF A** was deprotonated and, then, different amounts of Ag(OAc) were added in order to obtain MOF-NHC-Ag(I) complexes (**7**–**10**), as shown in Table 6.

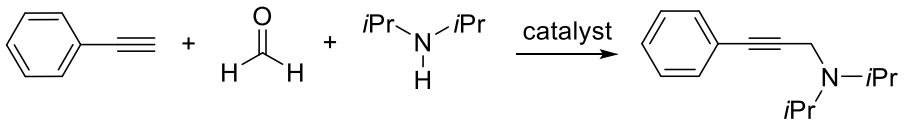
Table 6. MOF-NHC-Ag(I) synthesized complexes with different amounts of silver.

Entry [a]	Catalyst	Ag(OAc)	MOF A
1	**7**	25.0 mg, 0.15 mmol	60.0 mg, 0.1 mmol
2	**8**	20.0 mg, 0.12 mmol	60.0 mg, 0.1 mmol
3	**9**	12.5 mg, 0.075 mmol	60.0 mg, 0.1 mmol
4	**10**	7.5 mg, 0.045 mmol	60.0 mg, 0.1 mmol

[a] Reaction conditions: Ag(OAc) (different amounts), MOF (60.0 mg, 0.1 mmol), CH_2Cl_2 (60 mL), nitrogen atmosphere, room temperature, 12 h; and then 39 °C, 24 h.

These complexes were tested in A^3-coupling reaction of phenylacetylene (1.1 mmol), para-formaldehyde (1.0 mmol) and diisopropylamine (1.1 mmol) at room temperature in dichloromethane as solvent. In Tables 7 and 8, the activities of **MOF A** and MOF-NHC-Ag(I) complexes in the A^3-coupling reaction are reported.

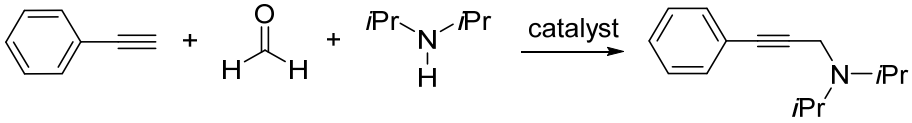
Table 7. Effect of the catalyst on A^3-coupling reaction.



Entry [a]	Catalyst	Time	Conversion (%) [b]	Yield (%) [b]
1	No catalyst	2 h	0	0
2	**MOF A**	24 h	>99	96
3	**10**	2 h	>99	97
4	**9**	1 h	>99	97
5	**8**	1 h	>99	97

[a] Reaction conditions: paraformaldehyde (1.0 mmol); diisopropylamine (1.1 mmol); phenylacetylene (1.1 mmol); MOF or MOF-NHC-Ag(I) (5 mg); CH_2Cl_2 (2.0 mL); nitrogen atmosphere; room temperature. [b] Conversions and yields were determined by ^{1}H-NMR.

Table 8. Time-dependent conversion of catalysts **MOF A** and **9** in A^3-coupling reaction.



Entry [a]	Catalyst	Time	Conversion (%) [b]
1	**MOF A**	2 h	30
2	**MOF A**	6 h	57
3	**MOF A**	15 h	86
4	**MOF A**	24 h	>99
5	**MOF A**	36 h	>99
6	**9**	15 min	22
7	**9**	30 min	67
8	**9**	45 min	83
9	**9**	1 h	>99

[a] Reaction conditions: paraformaldehyde (1.0 mmol); diisopropylamine (1.1 mmol); phenylacetylene (1.1 mmol); MOF or MOF-NHC-Ag(I) (5 mg); CH_2Cl_2 (2.0 mL); nitrogen atmosphere; room temperature. [b] Conversions were determined by ^{1}H-NMR.

Complex **9** led to a full conversion of the reagents into the propargylamine after 1 h unlike the **MOF A** which led to the complete conversion in 24 h. This demonstrated that silver plays a crucial role in the catalysing the A^3-coupling reaction. This is evident by observing Figure 6, which shows the conversions as a function of the amount of catalyst.

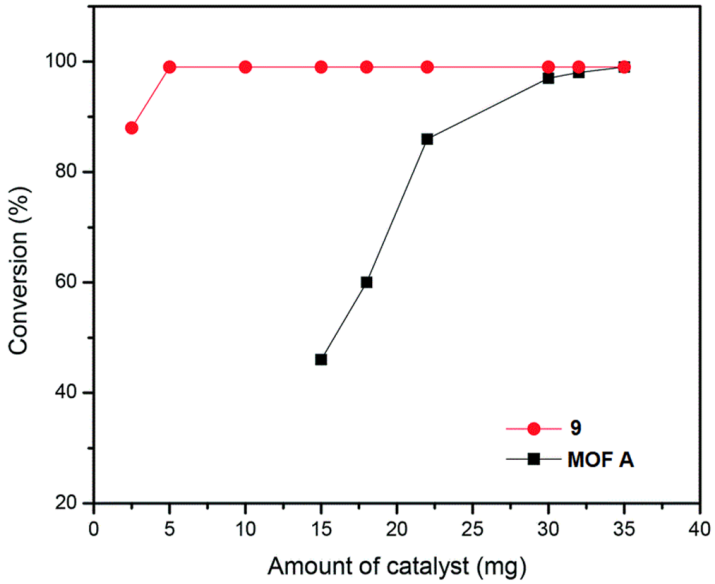
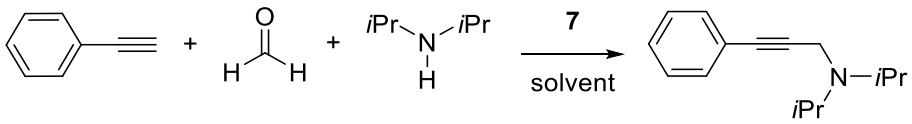


Figure 6. Effect of the amount of the catalyst on the A^3-coupling reaction.

Using complex **9** as catalyst, the effect of the solvent on the A^3-coupling reaction was also studied, and the results are summarized in Table 9. Reactions carried out in dichloromethane, acetone, acetonitrile gave the highest conversions. Toluene produced modest results and the reaction did not occur at all in solvents such as dimethyl sulfoxide and dimethylformamide. Reactions in tetrahydrofuran and in neat conditions generated the desired product.

Table 9. Effect of the solvent on A^3-coupling reaction using complex **7**.



Entry [a]	Solvent	Conversion (%) [b]	Yield (%) [b]
1	Dichloromethane	>99	97
2	Acetone	78	75
3	Acetonitrile	92	89
4	Dimethyl sulfoxide	n.d. [c]	n.d.
5	Dimethylformamide	n.d.	n.d.
6	Tetrahydrofuran	62.5	59
7	Toluene	29	25
8	Neat	53	50

[a] Reaction conditions: paraformaldehyde (1.0 mmol); diisopropylamine (1.1 mmol); phenylacetylene (1.1 mmol); complex **7** (5 mg); CH_2Cl_2 (2.0 mL); nitrogen atmosphere; room temperature. [b] Conversions and yields were determined by ^{1}H-NMR. [c] Not detectable.

In the years 2015–2017, Bantreil, Mètro, and co-workers [32–34] reported the solvent-free synthesis of NHC complexes bearing non-coordinating tetrafluoroborate or hexafluorophosphate counter-anions (**11a–d**, **12a–d**, **13a–d**, and **14a–b**; Figure 7).

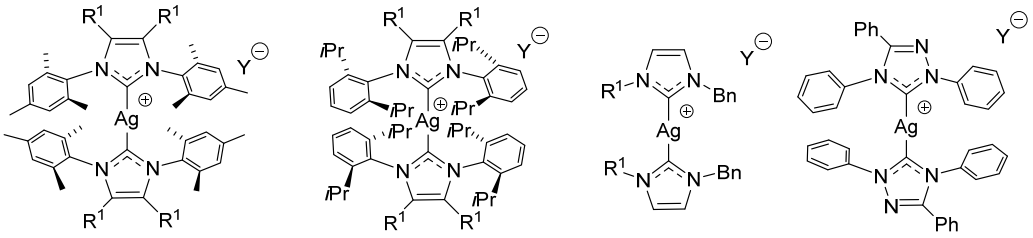
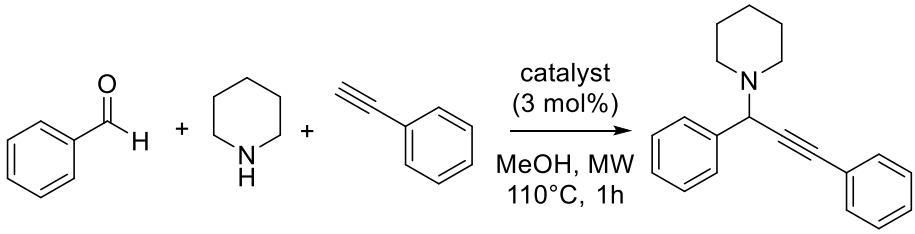


Figure 7. NHC–silver(I) complexes synthesized by Bantreil, Mètro et al. [32–34].

In 2017, they tested these complexes in the A^3-coupling reaction of benzaldehyde (1.0 equiv.), piperidine (1.2 equiv.) and phenylacetylene (1.5 equiv.) in order to obtain the respective propargylamine [35]. The complexes were used at 3 mol% and the reactions were performed in methanol at 110 °C under microwave irradiation for 1 h. The results are shown in Table 10.

Table 10. Catalytic activity of synthesized complexes in A^3-coupling reaction.

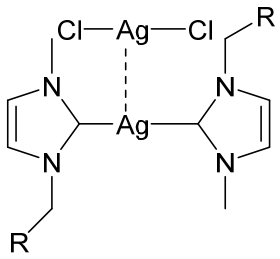


Entry [a]	Catalyst	Yield (%) [b]
1	**13a**	51
2	**13b**	36
3	**13c**	11
4	**13d**	30
5	**14a**	8
6	**14b**	12
7	**11a**	66
8	**11b**	53
9	**11c**	52
10	**11d**	55
11	**12a**	24
12	**12b**	81 [c], 77 [d]
13	**12c**	14
14	**12d**	7

[a] Reaction conditions: benzaldehyde (1.0 mmol); piperidine (1.2 equiv.); phenylacetylene (1.5 equiv.); catalyst (3 mol%); MeOH (2 mL); microwave irradiation; 110 °C; 1 h. [b] Determined by HPLC analysis by using mesitylene as an internal standard. [c] Yield of isolated product. [d] Yield of isolated product upon using 1.1 equiv. of both piperidine and phenylacetylene along with 4 mol% of the complex **12b**.

The best yield was obtained with complex **12b** which led to the desired propargylamine in 81% yield. (Table 10, Entry 12). Considering these good results, the catalytic activity of the complex **12b** was evaluated for the synthesis of a wide range of propargylamines. This catalyst turned out to be versatile and compatible with aliphatic and aromatic aldehydes and alkynes. Propargylamines were obtained with good yield (73–95%) in fast reaction times (1–4 h) with reduced catalyst loads (4 mol%) and in a low-toxicity solvent, methanol (2 mL).

In 2017 Kılınçarslan and co-workers [36] reported the synthesis and catalytic activity in A^3-coupling reaction of NHC-Ag(I) complexes based on 1-(methyl)-3-(alkyl)imidazole: 15a-c depicted in Figure 8.

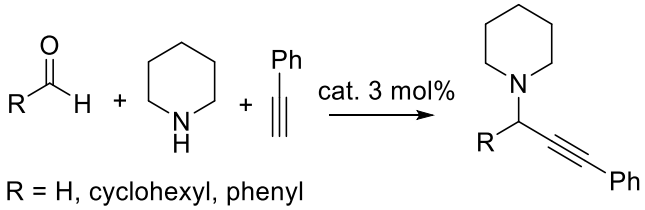


15a: R=2,4,6-trimethylphenyl (Mes)
15b: R=2,3,5,6-tetramethylphenyl (Duryl)
15c: R=2,3,4,5,6-pentamethylphenyl

Figure 8. NHC-Ag(I) complexes synthesized by Kılınçarslan et al. [36].

These complexes were tested using piperidine (1.2 mmol), several aldehydes (1.0 mmol) and phenylacetylene (1.5 mmol); the results are shown in Table 11. The complex **15a** showed scarce catalytic activity in the presence of benzaldehyde, and high efficiency with paraformaldehyde. The reaction was carried out in different solvents and in neat conditions, at 80 °C, achieving yields ranging from 12% to 88%.

Table 11. Catalytic activity in A^3-coupling reaction.



R = H, cyclohexyl, phenyl

Entry [a]	Aldehyde	Solvent	Catalyst	Yield (%) [b,c]
1	Paraformaldehyde	Dioxane	**15a**	84
2	Cyclohexanecarboxaldehyde	Dioxane	**15a**	76
3	Cyclohexanecarboxaldehyde	Dioxane	**15b**	70
4	Cyclohexanecarboxaldehyde	Dioxane	**15c**	68
5	Benzaldehyde	Dioxane	**15a**	12
6	H	Dioxane	**Ag_2O**	47
8 [d]	H	Acetone	**15a**	80
9	H	Dimethyl sulfoxide	**15a**	82
10 [e]	H	Water	**15a**	13
11 [f]	H	Ethanol	**15a**	14
12	H	Neat	**15a**	88
13	Cyclohexanecarboxaldehyde	Neat	**15a**	82
14	Benzaldehyde	Neat	**15a**	27

[a] Reaction conditions: aldehyde (1.0 mmol); piperidine (1.2 mmol); phenylacetylene (1.5 mmol); NHC-Ag(I) catalyst (3 mol%); dioxane (2.0 mL); argon atmosphere; 80 °C; 8 h. [b] Isolated yields. [c] Average of two runs. [d] At 56 °C. [e] For 12 h. [f] At 78 °C.

In the same year Quayle et al. [37] reported a study concerning synthesis, characterization and evaluation of the catalytic activity of the gold complexes reported in Figure 9.

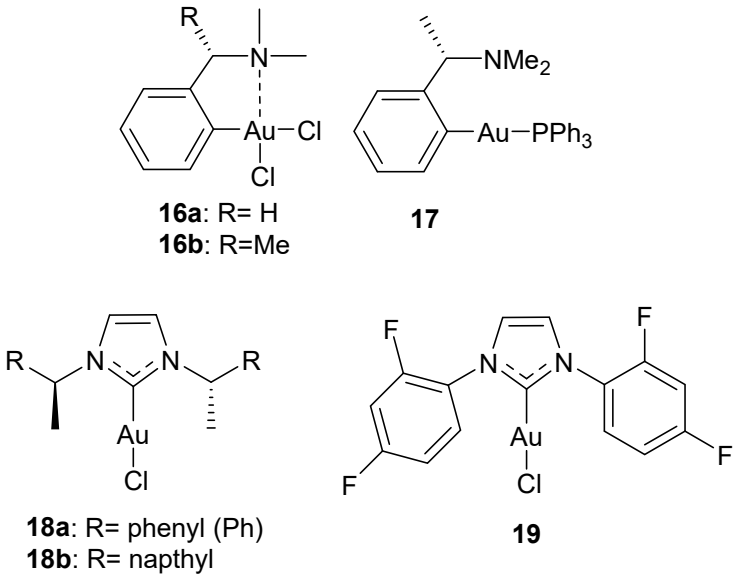


Figure 9. Gold complexes tested in A^3-coupling reaction.

These complexes were tested as catalysts in the A^3-coupling reaction of a variety of aldehydes, alkynes and amines. [$AuCl_2(\eta^{2\text{-}}C,N\text{-}C_6H_4CH_2NMe_2)$] **16a** and (*S*)-[$AuCl_2(\eta^{2\text{-}}C,N\text{-}C_6H_4CH(Me)NMe_2)$] **16b**, used at 1 mol%, in water at 40°C, led to quantitative conversion after 24 h. Instead, only 9 and 10% of aldehyde conversion was reported when the NHC-Au complexes **18a**–**b** and **19** were tested, thus showing low activity in the A^3-coupling reaction. In addition, a lack of enantioselectivity was also observed with the chiral complexes **16a**, **17**, and **18a**–**b** and this was in line with what has been reported in the literature about obtaining enantiomers with gold complexes[38].

In 2019 A. Neshat et al. [22] presented a study on the synthesis of novel NHC-Ag(I) complexes **21** and **22** by substitution of chlorides in the previously reported complex **5a** with homoscorpionate sulphur donor borate ligands (Figure 10). Complex **21** was tested in A^3-coupling reactions, and its catalytic activity was compared with that of the complexes **5a** and **20** already known. Since complexes **21** and **22** have close characteristics, the catalytic activity of complex **22** was not tested.

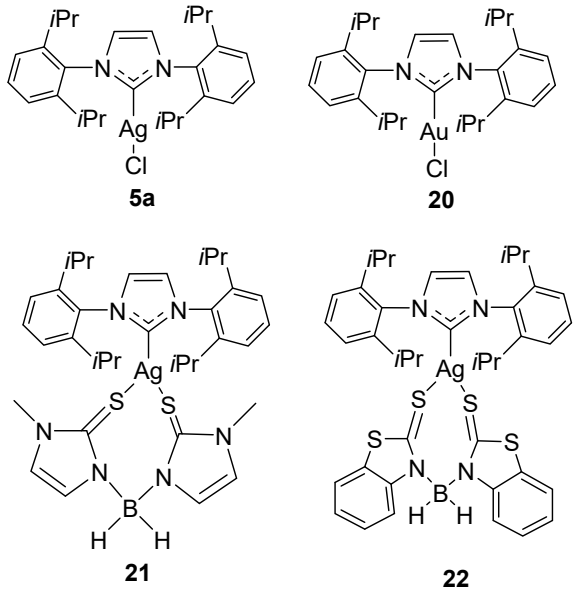
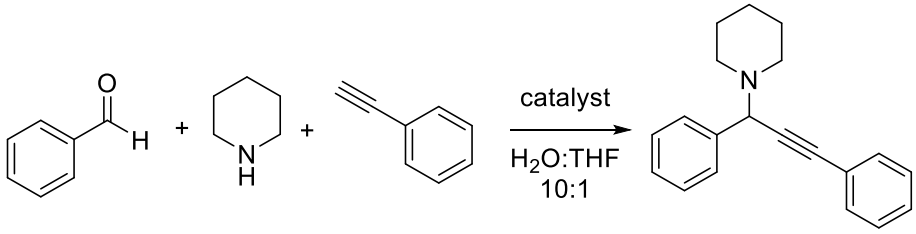


Figure 10. Ag-NHC and Au-NHC complexes tested by Neshat et al. [22].

Various amount of the complexes **5a**, **20**, **21** were tested in A^3-coupling reaction of benzaldehyde (0.5 mmol), piperidine (0.75 mmol) and phenylacetylene (0.75 mmol) under different temperatures and reaction times. Employing a 1% mol amount of the **5a**, **20**, **21** catalysts, and running the reaction at 50°C and for 24 h, yields of 95%, >99% and >99%, were, respectively, obtained (Table 12, Entry 1).

Table 12. A^3-coupling of benzaldehyde, piperidine and phenylacetylene with catalysts **5a**, **20**, **21** under different reaction conditions.



Entry [a]	Catalyst	Cat. (mol%)	Temp. (°C)	Time (h)	Yield (%) [b]
1	**5a**	1	50	24	95
	20				>99
	21				>99
2	**5a**	1	r.t.	24	87
	20				>99
	21				>99
3	**5a**	0.5	r.t.	24	30
	20				>99
	21				>99
4	**5a**	0.2	r.t.	24	<5
	20				>99
	21				>99
5	**5a**	0.2	r.t.	12	<5
	20				82
	21				45
6	**5a**	0.1	r.t.	24	0
	20				50
	21				39

[a] Reaction conditions: benzaldehyde (0.5 mmol); piperidine (0.75 mmol); phenylacetylene (0.75 mmol); catalyst (indicated in the column); H_2O:THF (10:1, 2 mL). [b] Yield determined by ^{1}H-NMR. r.t. Room temperature.

Subsequent decrease of the temperature to ambient, with complex **5a**, caused a drop in the yield from 95 to 87%, while it remained unchanged by employing complexes **20** and **21** (Table 12, Entry 2). A similar trend was observed by stitching the amount of catalyst from 1% to 0.5% and 0.2% (Table 12, Entries 3–4). They also tried reducing the reaction time from 24 to 12 h, employing the 0.2% catalysts, but, again, lower yields were obtained (Table 12, Entry 5) and the same occurred when they tried to lower the percentage of catalyst by going to 0.1% (Table 12, Entry 6).

As a conclusion, NHC-Ag(I) complexes with bidentate sulphur donor ligands (i.e., complex **21**), showed great catalytic activity in A^3-coupling reactions. The catalytic activity of the novel catalyst **21** was comparable with that of complex **20** and higher than that of the complex **5a**.

In 2020 Mariconda and co-workers [19] synthetized two novel complexes of silver and gold bearing 4,5-dichloro-N-methyl-N′-(2-hydroxy-2-phenyl)ethyl-imidazole-2-ylidine ligand (**23a**, **24a**) (Figure 11).

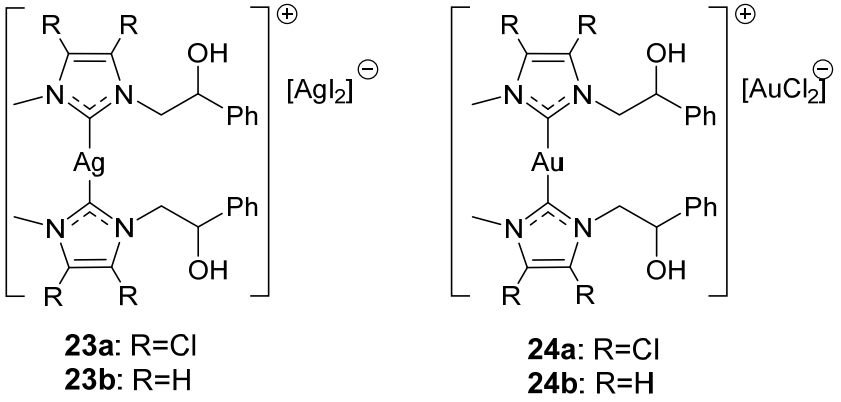


Figure 11. Silver(I) and gold(I) catalysts used in A^3-coupling reactions.

According to the results of conductivity measurements, these complexes can be present in solution as ionic species $[M(NHC)_2]^+$ $[MX_2]^-$ or neutral species M(NHC)X, where the last were considered responsible of the catalytic activity in A^3-coupling reaction (Figure 12).

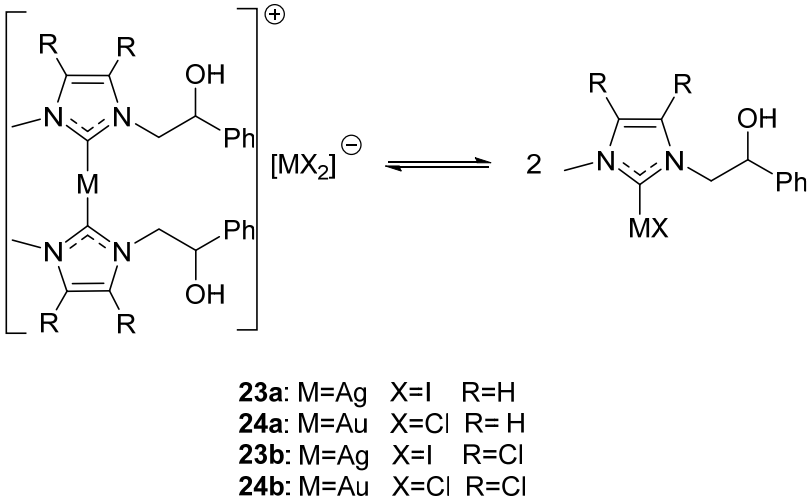
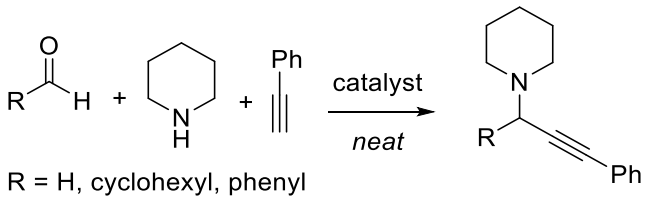


Figure 12. Equilibrium between ionic and neutral species of NHC-M complexes.

They were tested as catalysts in A^3-coupling reaction of aldehydes (i.e.,: formaldehyde or paraformaldehyde or cyclohexanecarboxaldehyde or benzaldehyde, 1.0 mmol) with piperidine (1.2 mmol) and phenylacetylene (1.5 mmol), in the absence of solvent or using dioxane (Tables 13 and 14). The activity of complexes **23a** and **24a** were compared with two analogous complexes with hydrogens on the backbone (**23b** and **24b**) synthesized by the same group [39,40]. The results, in neat conditions, are reported in Table 13.

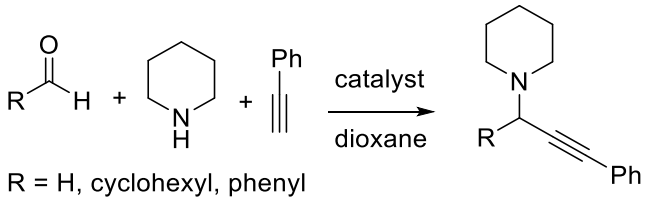
Table 13. Solvent free synthesis of propargylamines via A^3- coupling reactions catalyzed by NHC-Ag(I) (**23a**–**b**) and NHC-Au(I) (**24a**–**b**).



Entry [a]	Catalyst	Aldehyde	Conversion (%) [b]
1	**23b**	Formaldehyde solution (38%)	58
2		Paraformaldehyde	13
3		Cyclohexanecarboxaldehyde	99
4		Benzaldehyde	13
5	**24b**	Formaldehyde solution	96
6		Paraformaldehyde	99
7		Cyclohexanecarboxaldehyde	99
8		Benzaldehyde	83
9	**23a**	Formaldehyde solution	64
10		Paraformaldehyde	94
11		Cyclohexanecarboxaldehyde	99
12		Benzaldehyde	38
13	**24a**	Formaldehyde solution	81
14		Paraformaldehyde	99
15		Cyclohexanecarboxaldehyde	96
16		Benzaldehyde	86

[a] Reaction conditions: aldehyde (1.0 mmol); piperidine (1.2 mmol); phenylacetylene (1.5 mmol); catalyst (3 mol%); nitrogen atmosphere; 80 °C; 6 h. [b] Conversions were determined by ^{1}H-NMR analysis using 2-bromo mesitylene as internal standard.

Table 14. Synthesis of propargylamines via A^3-coupling reactions catalyzed by silver and gold NHC complexes in the presence of dioxane as solvent.



Entry [a]	Catalyst	Aldehyde	Conversion (%) [b]
1	**23b**	Formaldehyde solution (38%)	n.d.
2		Paraformaldehyde	n.d.
3		Cyclohexanecarboxaldehyde	71
4		Benzaldehyde	n.d.
5	**24b**	Formaldehyde solution	65
6		Paraformaldehyde	67
7		Cyclohexanecarboxaldehyde	68
8		Benzaldehyde	22
9	**23a**	Formaldehyde solution	62
10		Paraformaldehyde	30
11		Cyclohexanecarboxaldehyde	99
12		Benzaldehyde	14
13	**24a**	Formaldehyde solution	99
14		Paraformaldehyde	71
15		Cyclohexanecarboxaldehyde	99
16		Benzaldehyde	68

[a] Reaction conditions: aldehyde (1.0 mmol); piperidine (1.2 mmol); phenylacetylene (1.5 mmol); catalyst (3 mol %); nitrogen atmosphere; 80 °C; 6 h. [b] Conversion determined by ^{1}H-NMR analysis using 2-bromo mesitylene as internal standard. n.d. Not detected.

All complexes were found to be capable to catalyze the A^3-coupling reaction. By comparing Entries 1–16 of Table 12, it was evident that the gold catalysts were much more efficient than silver ones. Cyclohexanecarboxaldehyde and paraformaldehyde were the most reactive in presence of all the catalysts (except **23b** for the paraformaldehyde), whereas the benzaldehyde resulted the least reactive. As far as formaldehyde in aqueous solution is concerned, this was moderately reactive in the presence of silver complexes (Table 13, Entries 1 and 9), while good reactivity was observed with gold-based complexes (Table 13, Entries 5 and 13).The same reactions were performed using dioxane as solvent and the results are reported in Table 14. A trend of reactivity emerged from the results in Table 14: **24a** > **24b** > **23a** > **23b**. In conclusion, gold-based complexes were more performing than silver ones and the new complexes with chlorines on NHC backbone (**23a** and **24a**) were more active than the previously synthesized complexes (**23b** and **24b**).

Recently [21], a green approach for A^3-coupling reactions using water as solvent or working in neat condition was proposed. In order to enhance the solubility of catalysts in water, four new complexes (**25a–b**, **26a–b**) were designed by substitution of the alcohol group of the previously described **23b** and **24b** with sodium alcoholate or methoxyl group, as shown in Figure 13.

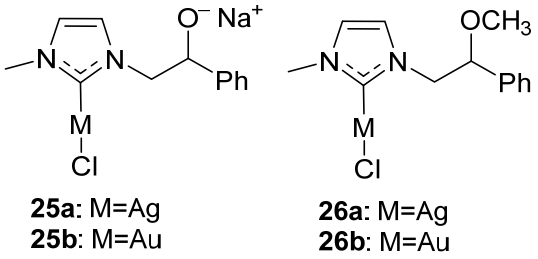
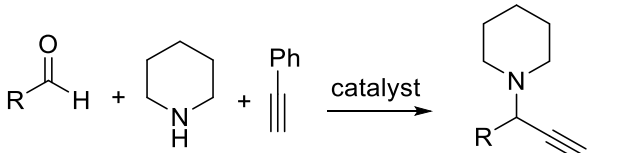


Figure 13. Silver and gold complexes with sodium alcoholate or methoxyl groups.

These complexes were tested as catalysts in A^3-coupling reactions of an aldehyde (i.e.,: paraformaldehyde, butyraldehyde, cyclohexanecarboxaldehyde, and benzaldehyde) with piperidine and phenylacetylene in neat conditions or using water as solvent.

In Table 15 the catalytic activity of these new complexes, in the absence of solvents, are depicted. Gold complexes (**25b** and **26b**) have shown better catalytic activity than silver analogues: **26b** ≥ **25b** > **26a** ≥ **25a**.

Table 15. NHC–Ag(I) and NHC–Au(I) catalyzed A^3-coupling reaction.

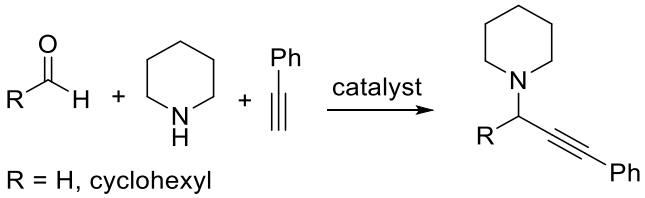


Entry [a]	Aldehyde	Yield (%) [b]			
		25a	**25b**	**26a**	**26b**
1	Formaldehyde	20	90	29	88
2	Butyraldehyde	43	74	46	87
3	Cyclohexanecarboxaldehyde	40	60	43	76
4	Benzaldehyde	10	47	11	43

[a] Reaction conditions: aldehyde (1.0 mmol); piperidine (1.2 mmol); phenylacetylene (1.5 mmol); catalyst (3 mol%); nitrogen atmosphere; 80 °C; 6 h. [b] Conversions were determined by ^{1}H-NMR analysis using 2-bromo mesitylene as internal standard.

In particular, paraformaldehyde was the most reactive substrate when gold complexes were used. Both gold and silver complexes with a methoxyl group performed better than the ones with sodium-alcoholate groups. The catalytic behaviour of the gold complexes **25b** and **26b** in the A^3-coupling reaction of cyclohexanecarboxaldehyde and benzaldehyde with piperidine and phenylacetylene was investigated, in water. Comparing the activity of the complexes **25b** and **26b** with that of the previously reported **24b** and **24a** analogues (see Table 14), catalyst **24a**, bearing chlorines on the NHC backbone, showed to be the most active (Table 16).

Table 16. NHC–Au(I) catalyzed A^3-coupling reaction.



Entry [a]	Aldehyde	Yield (%) [b]			
		24b	**24a**	**25b**	**26b**
1	Cyclohexanecarboxaldehyde	66	70	43	37
2	Benzaldehyde	19	25	20	11

[a] Reaction conditions: aldehyde (1.0 mmol); piperidine (1.2 mmol); phenylacetylene (1.5 mmol); catalyst (3 mol%), water (3.0 mL), nitrogen atmosphere; 80 °C; 6 h. [b] Conversions were determined by ^{1}H-NMR analysis using 2-bromo mesitylene as internal standard.

Further improvement of the catalysts' structure [41] resulted in four new complexes having an hydroxyl functional group on each of the nitrogen atoms of the imidazole ring (Figure 14). These complexes were even more soluble in green solvents and in physiological environments.

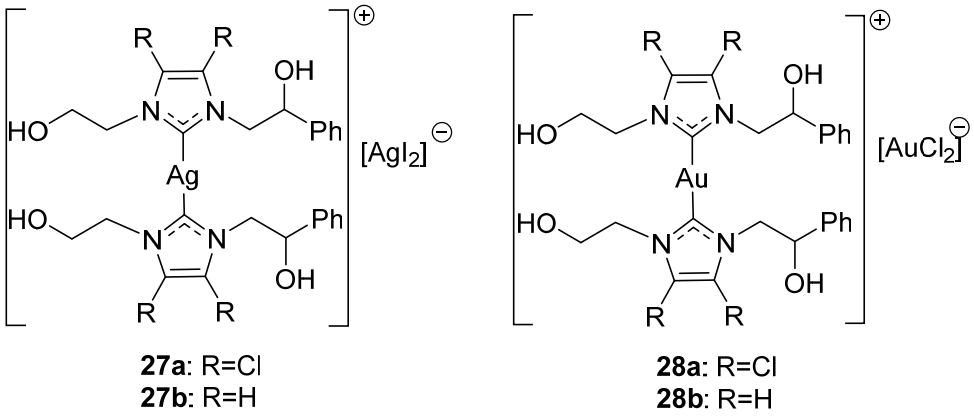
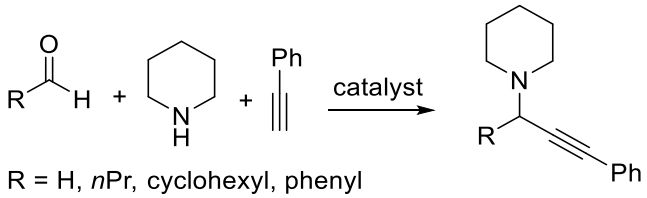


Figure 14. Water-soluble NHC-Ag(I) and NHC-Au(I) complexes.

As shown in Figure 14, silver and gold complexes **27a** and **28a** differ from complexes **27b** and **28b** for the presence of the chlorines on the backbone. These complexes were tested as catalysts in A^3-coupling reactions of phenylacetylene, piperidine and three different aldehydes (paraformaldehyde, cyclohexanecarboxaldehyde, and benzaldehyde), at 80 °C in neat conditions. As shown in Table 17, all complexes were able to catalyze the coupling of aldehydes, piperidine, and phenylacetylene. By comparing Entries 1–12, it was evident that silver complexes (**27a**–**b**) having N-heterocyclic carbene with hydrogens on the backbone were less active than the gold complexes (**28a**–**b**) with chlorine atoms on the backbone.

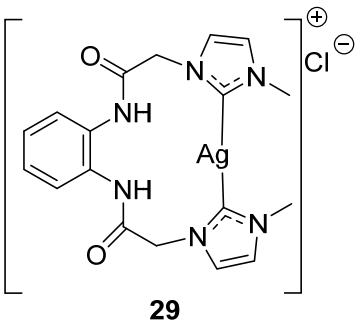
Table 17. Catalytic activity of the water-soluble NHC-Ag(I) and NHC-Au(I) complexes in A^3-coupling reactions.



Entry [a]	Catalyst	Aldehyde	Yield (%) [b]
1	**27b**	Paraformaldehyde	25
2	**27b**	Cyclohexanecarboxaldehyde	47
3	**27b**	Benzaldehyde	23
4	**27a**	Paraformaldehyde	65
5	**27a**	Cyclohexanecarboxaldehyde	52
6	**27a**	Benzaldehyde	36
7	**28b**	Paraformaldehyde	86
8	**28b**	Cyclohexanecarboxaldehyde	65
9	**28b**	Benzaldehyde	60
10	**28a**	Paraformaldehyde	99
11	**28a**	Cyclohexanecarboxaldehyde	99
12	**28a**	Benzaldehyde	60

[a] Reaction conditions: aldehyde (1.0 mmol), piperidine (1.2 mmol), phenylacetylene (1.5 mmol), catalyst (3 mol%); nitrogen atmosphere; 80 °C; 6 h. [b] Conversions were determined by ^{1}H-NMR analysis using as internal standard 2-bromo mesitylene.

In 2022 Mateus et al. [42] reported the synthesis of a chelating bidentate NHC-based silver complex containing bisamides linkers (29) (Figure 15).



29

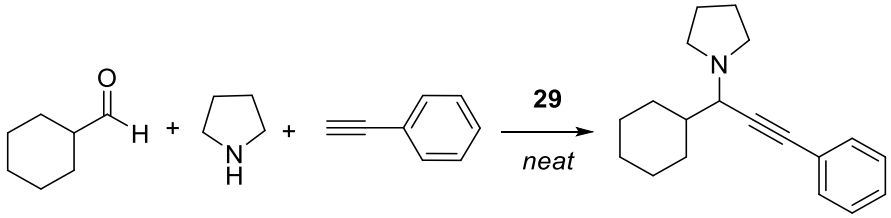
Figure 15. Chelating bidentate NHC-Ag(I) complex.

The catalytic activity of the complex **29** has been evaluated in the A^3-coupling reaction of cyclohexanecarbaldehyde, pyrrolidine and phenylacetylene, as described in Table 18.

The reaction conducted with 1 mol% of the catalyst **29** at 80 °C, led to a full conversion of the starting reagents and the desired propargylamine was isolated in 89% (Table 18, Entry 1). Given this interesting result, the catalyst load was lowered to 0.5 mol% and, even in this case, the full consumption of the reactants occurred leading to 85% of the desired product (Table 18, Entry 2). The scientists decided to proceed by lowering the reaction temperature and, then, by decreasing the catalyst load up to 0.1 mol%.

So, by extending the reaction times to 36 h and by using 0.5 mol% of the catalyst, the reaction gave high yields at temperatures lower than 80 °C (Table 18, Entries 3–6), even at room temperature (Table 18, Entry 6). It was also possible to obtain good yields when the catalyst load was decreased to 0.1 mol% in 36 h at 80 °C (Table 18, Entry 7).

Table 18. Chelating bidentate NHC–Ag(I) complex catalyzed A^3-coupling reaction.



Entry [a]	Catalyst (mol%)	Temperature (°C)	Time (h)	Yield (%) [b]
1	1	80	5	89
2	0.5	80	5	85
3	0.5	60	5	-
4	0.5	60	36	88
5	0.5	40	36	87
6	0.5	25	36	72
7	0.1	80	36	74
8	-	80	36	<5

[a] Reaction conditions: cyclohexanecarbaldehyde (1.5 mmol), pyrrolidine (1.5 mmol), phenylacetylene (1.5 mmol). [b] Isolated yield.

3. Carboxylation Reaction

The greenhouse effect and relative change in climate have been causing concern in the scientific community, public opinion, and governments for the past few decades. The massive production of carbon dioxide (CO_2) is among the principal causes of climate change [43]. The increase in CO_2 levels is attributable to many factors such as intensive agriculture, transportation, industries, combustion of petroleum-based resources, and the rise of the population. In particular, India, China, the US, Russia, Canada, and Japan are the countries with the highest values of greenhouse emissions [43–45].

Reducing carbon dioxide levels has become a major global concern in the current scenario. Many research groups are involved in converting CO_2 into value-added molecules [46]. For example, photocatalysis and electrocatalysis can consent the conversion of carbon dioxide into methane, methanol, and carbon monoxide [47]. Furthermore, diverse toxic carbonylation agents, such as carbon monoxide and phosgene, can be replaced by carbon dioxide for the construction of C-C and C-X bonds (X=H, O, N) [48]. Therefore, developing an efficient, inexpensive, and eco-sustainable carbon dioxide utilization method is crucial.

Unfortunately, the transformations of CO_2 are particularly difficult due to its kinetic inertia and thermodynamic stability. The primary focus is the development of catalytic systems that can activate this inert molecule. Over recent years, N-heterocyclic carbenes and their relative complexes have earned significant attention in the activation of carbon dioxide, thanks to their steric and electronic properties [49]. Moreover, compared to other catalysts, NHCs are more facile and inexpensive to develop. It has been demonstrated that there are two approaches by that CO_2 can be activated by N-heterocyclic carbene metal complexes: interaction of the π electrons of the carbon dioxide molecule with the empty d-orbital of the transition metals. In such manner, it is possible to extend the carbonaceous chain of alkynes (carboxylation of terminal alkynes) [50]; by oxidative coupling of metal complexes, carbon dioxide, and olefins to produce cyclic intermediates (2-oxazolidinone and carbonates) (Figure 16) [51,52].

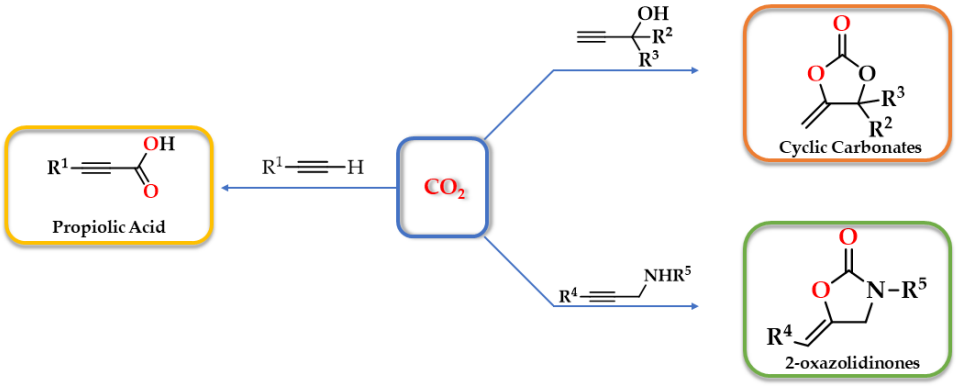


Figure 16. Carboxylation reaction catalyzed by Ag/Au(I) NHC complexes reported in this review.

This paragraph of the review summarizes and analyses the results in the functionalization/activation of carbon dioxide, obtained by silver(I) and gold(I) NHC complexes.

3.1. Carboxylation of Terminal Alkynes

Alkynyl carboxylic acids are a ubiquitous class of compounds due to their great utility in medicinal chemistry and in the production of synthetic fibres [53]. Different synthetic procedures have been developed for the preparation of this class of compounds including the oxidation of aldehydes or alcohols, or hydrolysis of bromide [54,55]. The carboxylation of terminal alkynes with carbon dioxide is the most powerful method for the synthesis of propiolic acids. Zhang's [56] and Grooben's [57] groups reported in 2010, for the first time, that the carboxylation of terminal alkynes, with carbon dioxide, can be catalyzed by copper or copper-NHC complexes (Figure 17A,B). Furthermore, Zhang and collaborators [50] have reported the direct carboxylation of alkynes with a transition metal-free catalytic system, at 120 °C and 2.5 atm (Figure 17C). Later, Zhang et al. [58] reported the development of a ligand-free Ag(I) catalyst, active in the carboxylation of the terminal alkynes under mild reaction conditions. (Figure 17D). The main limitations of these methods were that the yields obtained were generally moderate, and the reaction conditions (temperature and pressure) were quite harsh. In Figure 17 are reported all the early developed protocols to produce propiolic acids with alkynes and carbon dioxide.

In 2012, Zhang and collaborators [59] reported a heterogeneous catalytic system (poly-NHC-Ag nanoparticles, Poly-NHC-Ag-NPs) **30**, active in the carboxylation of terminal alkynes with carbon dioxide (Figure 17E). The synthesis of poly-imidazolium salts and its relative AgNPs catalytic system are reported in Scheme 3 [60].

The nano-composite catalytic system showed excellent yields with different aryl alkynes, under ambient reaction conditions. In an initial screening the desired propiolic acid was recovered up to 98% (0.3 mol% of the Ag catalyst). Based on this interesting result, the authors tested its reusability. Centrifugation and filtering of the reaction mixture allowed for the recovery of the catalytic system. The solid residue was washed with DMF and reused in the sequent runs. More than 93% of the yield was produced every five times the catalytic system was being used, evidencing its high activity. A fraction of the catalyst was lost throughout the recovery process, which was the cause of the activity's decline. The reaction scope was implemented testing the carboxylation reaction of different aryl alkynes (Table 19).

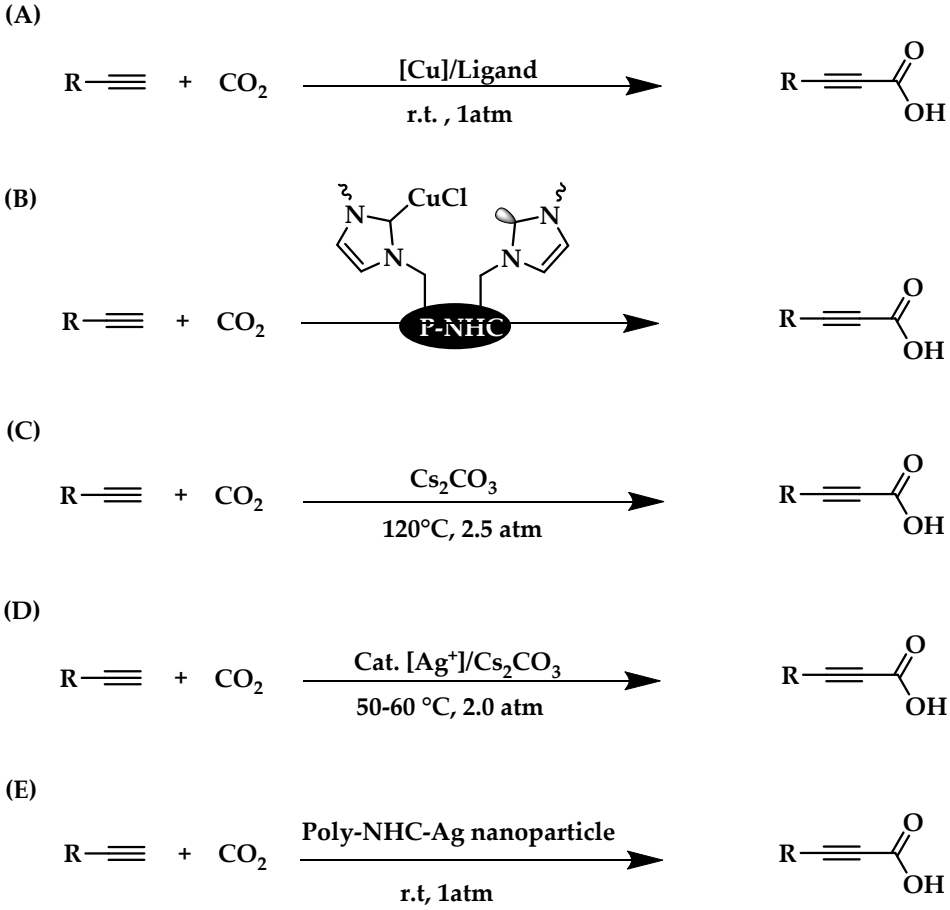
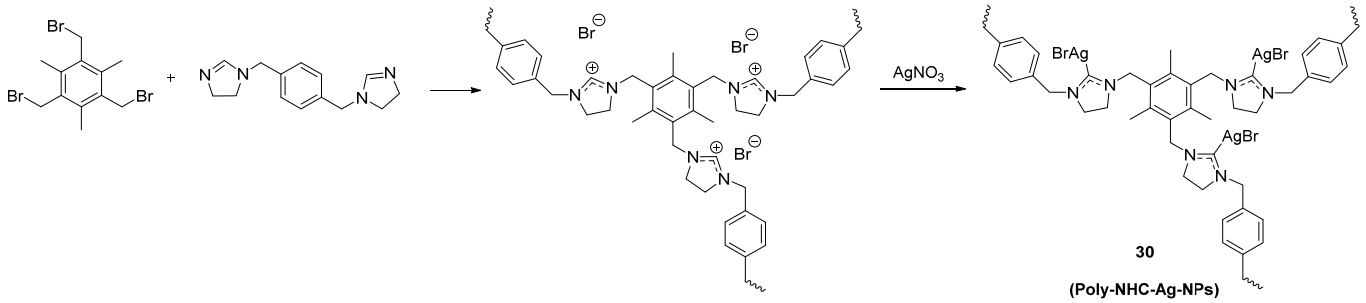


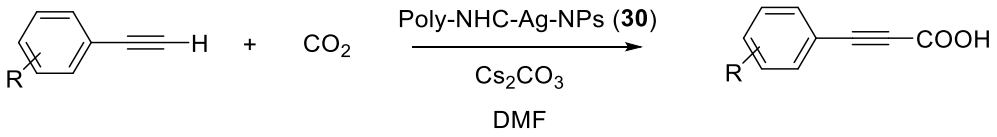
Figure 17. Protocols developed for the synthesis of substituted propiolic acids from alkynes. (**A**,**B**) copper or copper-NHC complexes; (**C**) transition metal-free; (**D**) ligand-free Ag(I) catalyst; (**E**) poly-NHC-Ag nanoparticles, Poly-NHC-Ag-NPs.



Scheme 3. Preparation of heterogeneous catalytic system (Poly–NHC–Ag–NPs **30**).

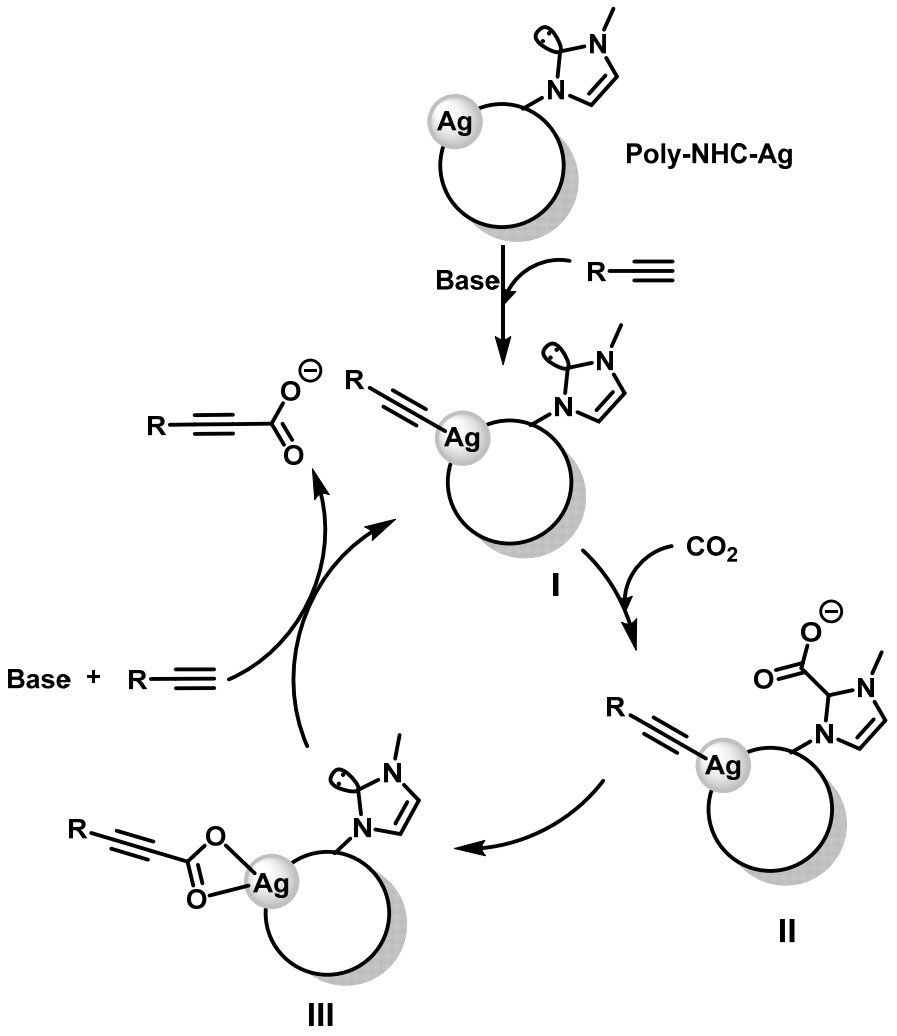
As shown in Table 19, excellent yields were obtained with both electron-donating groups (Entries 2, 3, 5, 6, 8), and electron-withdrawing groups (4, 7, 9, 10), demonstrating tolerance to diverse functional groups (OH, CHO, CN, NO_2, etc). The authors have not observed the formation of any by-products. They affirmed that the excellent catalytic activity is due to the synergistic action of the ligand (NHC) and Ag nanoparticles. Zhang et al. proposed a possible mechanism, shown in Scheme 4.

Table 19. Carboxylation of terminal alkynes with poly-NHC-Ag-NPs.



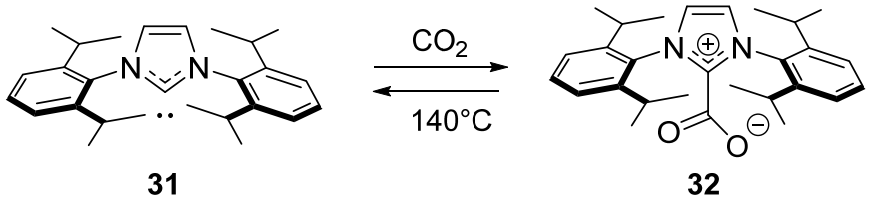
Entry [a]	R	Yield (%) [b]
1	H	98
3	4-Ph	96
4	4-Cl	97
5	4-OCH_3	95
2	4-CH_3	97
6	3-OH	95
7	4-CHO	95
8	4-CH_2OH	96
9	4-CN	96
10	4-NO_2	95

[a] Reaction conditions: alkyne (1.0 mmol), Poly-NHC-Ag NPs **30** (0.3 mol%), Cs_2CO_3 (1.2 mmol), CO_2 (1 atm), room temperature, DMF (5 mL), 20 h. [b] GC yields.



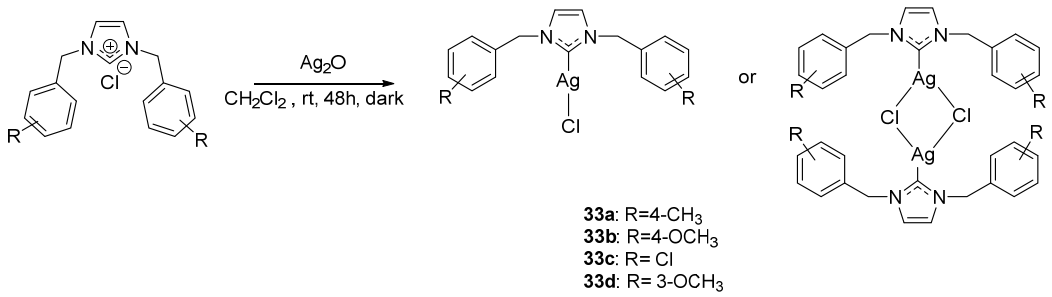
Scheme 4. Proposed mechanism for the carboxylation reaction of terminal alkynes catalyzed by poly-NHC–Ag-NPs catalyst.

They asserted that the first stage of the cycle is the formation of metal acetylide intermediate through the deprotonation of the alkyne by the base (**I**). Later, the carbene carbon atom reacts with CO_2, due to its nucleophilicity, to produce an NHC-carboxylate specie (**II**) [61,62]. Since Louie and colleagues [63] reported the activation of CO_2 with the generation of zwitterionic species in a reversible mechanism in 2004, the authors postulated the formation of carboxylate species (**32**, Scheme 5). Then, the coordination of the carboxylic group, near the silver centre, induces the nucleophilic attack by the acetylide species (**III**). Finally, the silver acetylide species is regenerated by the alkyne deprotonation by the base. The proposed mechanism highlights the synergic crucial role between the metal centre and the poly-NHC ligand.



Scheme 5. Activation of CO_2 by NHC, observed by Louie et al. [63].

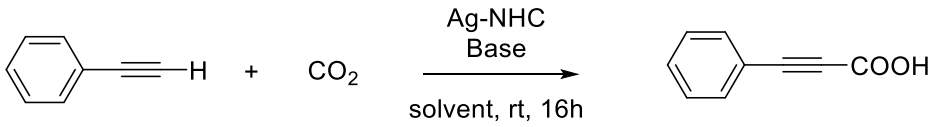
In 2016, Fang et al. [64] reported the synthesis, structural characterization and catalytic activity in the carboxylation of terminal alkynes of four Ag-NHC complexes **33a**–**d**. The synthesis of the complexes was reported in Scheme 6; they were obtained by the reaction of the corresponding imidazolium salt with 0.55 eq. of silver oxide (Ag_2O), with the exclusion of the light, at room temperature for 48 h.



Scheme 6. Synthesis of the complexes **33a**–**d**.

Single crystals of **33a**–**d** were obtained by slow evaporation of a diethyl ether/chloroform solution of the corresponding silver compounds at room temperature. Surprisingly, the authors found that whereas complexes **33b** and **33d** had a mononuclear structure, complexes **33a** and **33c** revealed a dinuclear structure. The reactivity of complexes was initially explored in the reaction of phenylacetylene with carbon dioxide. The results are reported in Table 20.

Table 20. Carboxylation reaction catalyzed by Ag(NHC) complexes.



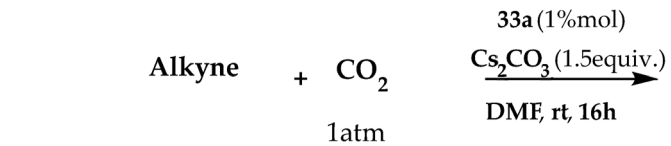
Entry [a]	Catalyst (% mol)	Base (Equiv.)	Yield (%) [b]
1	-	Cs_2CO_3 (1.5)	n.d.
2	**33a**(1)	Cs_2CO_3 (1.5)	82
3	**33a**(3)	Cs_2CO_3 (1.5)	82
4	**33a**(5)	Cs_2CO_3 (1.5)	68
5	**33b**(1)	Cs_2CO_3 (1.5)	81
6	**33c**(1)	Cs_2CO_3 (1.5)	81
7	**33d**(1)	Cs_2CO_3 (1.5)	82
8 [c]	**33a**(1)	Cs_2CO_3 (1.5)	83
9 [d]	**33a**(1)	Cs_2CO_3 (1.5)	69
10	**33a**(1)	DBU(1.5)	38
11	**33a**(1)	K_2CO_3(1.5)	20
12	**33a**(1)	KO^{t}Bu(1.5)	5
13	**33a**(1)	NaO^{t}Bu(1.5)	Trace
14	**33a**(1)	NaOH(1.5)	Trace
15	**33a**(1)	-	n.d.
16	**33a**(1)	Cs_2CO_3 (1.0)	48
17	**33a**(1)	Cs_2CO_3 (1.2)	71
18	**33a**(1)	Cs_2CO_3 (2.0)	81
19 [e]	**33a**(1)	Cs_2CO_3 (1.5)	43
20 [f]	**33a**(1)	Cs_2CO_3 (1.5)	8
21 [g]	**33a**(1)	Cs_2CO_3 (1.5)	37
22 [h]	**33a**(1)	Cs_2CO_3 (1.5)	n.d.

[a] Reaction conditions: 1-phenylacetylene (2.0 mmol), CO_2 (1 atm), DMF (10 mL), room temperature, 16 h. [b] Isolated yields. [c] 40 °C. [d] 60 °C. [e] In DMSO. [f] In DCM. [g] In acetonitrile. [h] In THF. n.d. Not detected.

The authors demonstrated that the reaction could not occur without the presence of the silver catalyst (Table 20, Entry 1). They also evaluated the suitable catalytic loading for the optimization of reaction conditions. The desired propiolic acid was isolated in good yield (82%), using 1–3 mol% of **33a**, in DMF, and using 1.5 equiv. of Cs_2CO_3 (Table 20, Entries 2,3). When the reaction was loaded with 5% mol of catalyst, the yield dropped, probably, as suggested by the authors, due to the ability of the Ag-NHC complexes to also catalyze the decarboxylation process. (Table 20, Entry 4). It is worth note that in the literature a few examples of decarboxylation reactions of carboxylic acids catalyzed by Ag_2CO_3 are reported [65,66]. Other silver complexes were tested in the carboxylation reaction of phenylacetylene, using 1 mol% loading; they displayed comparable activity (Table 20, Entries 5–7). Although the complex **33a** showed a dinuclear structure, and the complex **33b** exhibited a mononuclear structure, their time-dependent experiments were comparable. For silver complex **33a** any induction time during the initial period of the reaction was observed. The authors tried to explain this behaviour by asserting that the complexes **33a** and **33c**, in a polar medium, such as DMF, could display a monomeric structure, due to the weak Ag···Cl interaction [9,67]. The increase in temperature did not positively influence the reaction: when the reaction was conducted at 40 °C, the yield was mostly unvarying (Table 20, Entry 8), while a further increase in temperature (60 °C) gave yield decrease (Table 20, Entry 9). The authors then deepened the influence of the base (Table 20, Entries 1 vs. 10–15). The best results were obtained with the inorganic base Cs_2CO_3. DBU (1,8-Diazabicyclo(5.4.0)undec-7-ene) and K_2CO_3 were less efficient (Table 20, Entries 10 and 11), while KO^{t}Bu, NaO^{t}Bu, and NaOH were ineffective (Table 20, Entries 12–14). Based on these data, the authors asserted that the carboxylation reaction is not correlated to the basicity. However, the presence of the base is fundamental for the course

of the reaction (Table 20, Entry 15). The base loading was evaluated (Table 20, Entry 1 vs. Entries 15–18), e.g.,: when 1.2 or 1.0 equiv. of Cs_2CO_3 were employed, the quantity of propiolic acid diminished. Finally, the author explored carefully diverse solvents (Table 20, Entry 19–22). Once the best reaction conditions were assessed (1 mol% of silver complex, 1.5 equiv. of Cs_2CO_3, 1 atm of CO_2, room temperature, in DMF, 16 h), a scope of the alkyne substrates was performed. The results are summarized in Table 21.

Table 21. Carboxylation reaction with different terminal alkynes, catalyzed by silver complex **33a**.

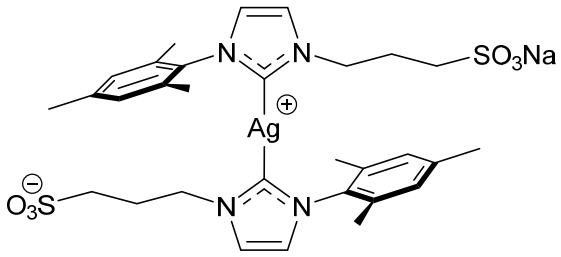


Entry [a]	Alkyne	Yield (%) [b]
1	Phenylacetylene	82
2	4-Ethynyltoluene	85
3	1-Ethynyl-4-propylbenzene	83
4	4-Ethynyl-1,'1-biphenyl	78
5	1-Ethynyl-4-methoxybenzene	84
6	1-Ethynyl-4-fluorobenzene	80
7	1-Ethynyl-3-fluorobenzene	76
8	1-Ethynyl-4-chlorobenzene	71
9	4-Ethynylbenzaldehyde	61
10	1-Ethynyl-4-(trifluoromethyl)benzene	63
11	4-Ethynylbenzonitrile	54
12	1-Ethynyl-4-nitrobenzene	64
13	1,3-diethylnylbenzene	77
14	2-ethynylpyridine	n.d.
15	2-ethynylthiophene	70
16	(Prop-2-yn-yloxy)benzene	82
17	Ethynylcyclopropane	80
18	3,3-dimethylbut-1-yne	65
19	1-hexyne	79
20	1-heptyne	81
21	1-octyne	82

[a] Reaction conditions: alkyne (2.0 mmol), **33a** (1% mol), solvent (10 mL), Cs_2CO_3 (3.0 mmol), room temperature, 16 h. [b] Isolated yields. n.d. Not detected.

The Ag-NHC complex **33a** demonstrated remarkable catalytic performances towards different substituents. Good yields were obtained with aromatic alkynes having electron-donating groups on the phenyl ring (e.g.,: CH_3, $CH_3CH_2CH_2$, Ph, OCH_3, Table 21, Entries 2–5). Analogous yields were achieved with aromatic alkynes having electron-withdrawing groups on the phenyl ring, i.e.,: fluoride and chloride. (Table 21, Entries 6–8) However, a lowering of the yields was observed with aromatic alkynes bearing strong withdrawing substituents (such as CHO, CF_3, CN, NO_2, Table 21, Entries 9–12) perhaps due to marked decrease in nucleophilicity of the α carbon. When the carboxylation reaction was conducted with 2-ethynyl pyridine (Table 21, Entry 14), the corresponding pyridyl propiolic acid was not isolated from the reaction mixture, as observed by Gooßet et al. [57]. Finally, good yields had been recorded with aliphatic terminal alkynes. (Table 21, Entries 16–21).

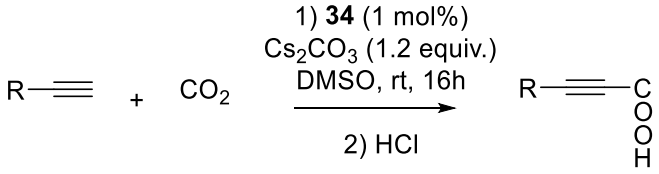
In 2017, Verpoort et al. [68] reported the catalytic activity of a bis (N-heterocyclic carbene) Ag complex **34** (Figure 18) in the carboxylation of diverse terminal alkynes with CO_2. The results are listed in Table 22.



34

Figure 18. Strucuture of the bis (NHC)Ag complex **34** tested by Verpoort et al. [68].

Table 22. Carboxylation reaction with different terminal alkynes, catalyzed by silver complex **34**.



Entry [a]	R	Yield (%) [b]
1	(4-MeO)-Ph	90
2	Ph-	85
3 [c]	HC≡C-Ph-	85
4 [c]	HC≡C-$(CH_2)_3CH_2$-	77
5	$(CH_3)_3Si$-	72
6	$(CH_3)_3C$-	65
7	H-	40

[a] Reaction conditions: alkyne (1.0 mmol), **34** (1% mol), solvent (1 mL), Cs_2CO_3 (1.2 mmol) room temperature, CO_2 (1 bar), 16 h. [b] Catalytic yield was obtained by ^{1}H-NMR integration, using 1,4-ethynylbenzene as the internal standard. [c] 2.4 equiv. of Cs_2CO_3.

As described in Table 22, best yields (upper 85%) were obtained with aromatic alkynes (Entries 1–3), while a sharp decrease was observed when aliphatic alkynes were tested (Entries 4–7). It should be noted that the carboxylation reaction of diynes required 2.4 equivalents of base for the formation of dicarboxylic acids (Entries 3,4).

Based on the results obtained by Zhang [59], on the synergistic effects between NHC and silver, seen above, Verpoort et al. tested a series of NHC/Ag systems (**P-L1**–**P-L4**, Figure 19) in the carboxylation reaction of terminal alkynes to give the corresponding carboxylic acids, using silver oxide as Ag source. The authors developed this series of catalytic systems, primarily to avoid the synthesis of the relevant photosensitive silver complexes, and to exploit the synergistic effects among Ag ions and the NHC-CO_2 adduct. Furthermore, in the catalytic system, different potassium salts were introduced, and the authors observed that the nature of the halogen played an important role in the catalysis. The authors have preliminary investigated the carboxylation reaction, using phenylacetylene as a standard substrate; the results are reported in Table 23.

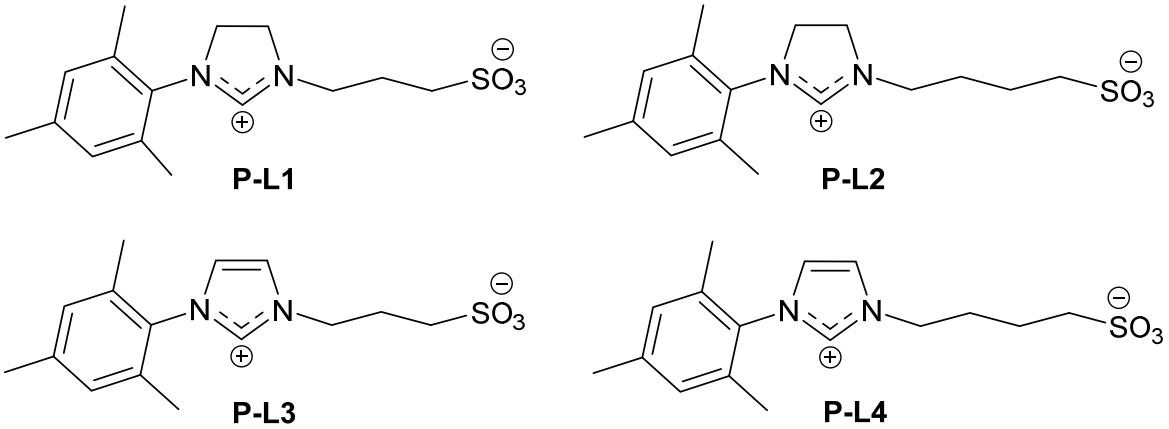
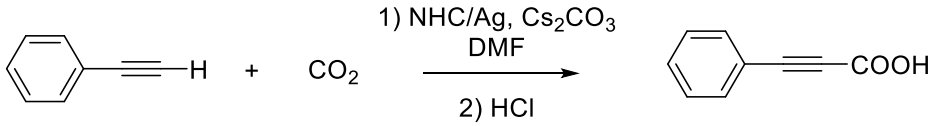


Figure 19. Zwitterionic NHC pro-ligands **P-L1**–**P-L4** tested in the carboxylation reaction.

Table 23. Investigation of the catalytic systems **P-L1**–**P-L4**/Ag.

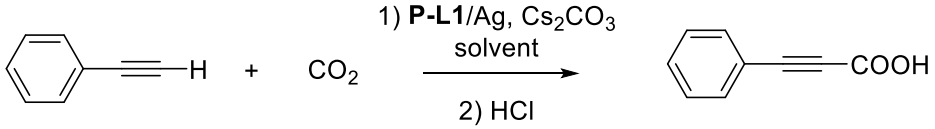


Entry [a]	Catalytic System	Yield (%) [b]
1	**P-L1** + Ag_2O + KI	98
2	**P-L2** + Ag_2O + KI	94
3	**P-L3** + Ag_2O + KI	97
4	**P-L4** + Ag_2O + KI	93
5 [c]	AgI	83
6 [d]	**P-L2** + Ag_2O + KCl	79
7 [d]	**P-L2** + Ag_2O + KBr	96
8	Ag_2O	18
9 [e]	-	10
10 [f]	-	10
11 [g]	-	25
12 [h]	**P-L2** + Ag_2O + KI	n.d.

[a] Reaction conditions: alkyne (10 mmol), NHC/Ag system (0.0125 mmol of Ag_2O, 0.025 mmol of **P-L1**–**P-L4**, 0.025 mmol KI), DMF (40 mL), Cs_2CO_3 (15 mmol) 35 °C, CO_2 (1 bar), 24 h. [b] Isolated yield. [c] AgI (0.1 mmol). [d] 0.025 mmol of Ag_2O, 0.05 mmol of **P-L1**–**P-L4**, KX 0.05 mmol. [e] 0.025 mmol of KI, 15 mmol of Cs_2CO_3, DMF (40 mL), 35 °C, 1 bar, 24 h. [f] 15 mmol Cs_2CO_3, DMF (40 mL), 35 °C, 1 bar. [g] 15 mmol of Cs_2CO_3, DMF (40 mL), 35 °C, 1bar, 72 h. [h] Absence of CO_2. n.d. Not detected.

The activity of **P-L1** and **P-L3** were slightly better than their corresponding imidazolinium salts (**P-L2**, **P-L4**, Table 23, Entries 1, 3 vs. Entries 2, 4). There was no discernible pattern that could be attributed to the aliphatic chain's length. High yields were attained utilising 0.5 mol% of the NHC salt (Table 23, Entries 6, 7); KBr could substitute KI as potassium salt efficiently. When Ag_2O was examined in the absence of NHC and KI, the carboxylic acid yield significantly decreased (Table 23, Entry 8). Only 10% of the phenyl-1-propionic acid was produced whether the base was used alone or in combination with KI (Table 23, Entries 10, 11). The authors optimized the reaction condition by evaluating the solvent effect, the time, and the loading of both base of the catalyst. The results are listed in Table 24.

Table 24. Optimization of the carboxylation reaction of phenylacetylene with **P-L1**/Ag system.



Entry [a]	Base	Solvent	Catalyst Loading (mol%)	Yield (%) [b]
1	Cs_2CO_3	DMF	0.25	98
2	Cs_2CO_3	DMSO	0.25	92
3	Cs_2CO_3	CH_3CN	1.00	11
4	Cs_2CO_3	H_2O	0.50	n.d.
5	Cs_2CO_3	CH_3OH	0.50	n.d.
6	K_2CO_3 [c]	DMF	0.50	41
7	KO^tBu	DMF	0.25	47
8 [d]	Cs_2CO_3	DMF	0.25	48
9 [e]	Cs_2CO_3	DMF	0.25	80
10	Cs_2CO_3	DMF	0.10	95
11	Cs_2CO_3	DMF	0.075	87

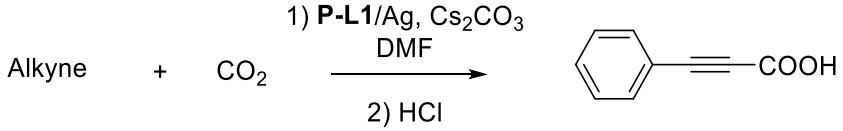
[a] Reaction conditions: phenylacetylene (10 mmol), **P-L1**/Ag system (0.0125 mmol of Ag_2O, 0.025 mmol of **P-L1**, 0.025 mmol KI), solvent (40 mL), Cs_2CO_3 (15 mmol) 35 °C, CO_2 (1 bar), 24 h. [b] Isolated yield. [c] Cs_2CO_3 (30 mmol). [d] 12 h, [e] 18 h. n.d. Not detected.

As seen above, the solvent plays a crucial role in the carboxylation reaction (Table 24, Entries 1–5). DMF and DMSO showed to be the most suitable for this type of reaction thanks to their high polarity and aproticity. Verpoort et al. attributed the higher yields with DMF to its weak alkalinity, which has a beneficial effect in the of the alkyne deprotonation and promoting the formation of the acetylide species. Another polar and aprotic solvent was tested (CH_3CN, Table 24, Entry 3), but yields in the presence of this solvent were much lower than those obtained with DMF. H_2O and MeOH were found to be unsuitable for the carboxylation of the terminal alkynes (Table 24, Entries 4,5). The base also plays an essential role in the catalytic system as well: as seen by Fang et al. [64] Cs_2CO_3 showed superior efficiency than the other tested bases such as K_2CO_3 or KO^tBu (Table 24, Entries 6–7). Twenty four hours was the suitable time for the reaction (Entry 1 vs. Entries 8–9). The P-L1/Ag system showed interesting activity even when the catalytic loading was lowered (Table 24, Entries 10–11).

Thus, once the reaction was optimized, the authors tested the catalytic system in the carboxylation of different terminal alkynes (Table 25).

The results show high tolerance of the catalytic system with a wide range of terminal alkynes. Aliphatic alkynes were more active towards the carboxylation than aromatics (Table 25, Entries 13–19 vs. 1–12, 21), owing to their significant electron-donating properties. Aryl alkynes with strong electron-withdrawing substituents reacted less easily than the aryl alkynes with electron-releasing substituents (Entries 9–12, 21 vs. Entries 1–8).

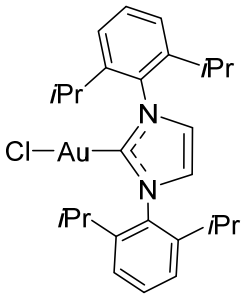
Table 25. Carboxylation reaction of terminal alkynes with **P-L1**/Ag.



Entry [a]	Alkyne	Yield (%) [b]
1	Phenylacetylene	95
2	4-Ethynyltoluene	99
3 [c]	1-Ethynyl-4-*n*-buthylbenzene	97
4	1-Ethynyl-4-*t*-buthylbenzene	99
5 [c]	1-Ethynyl-4-*n*-penthylbenzene	98
6	1-Ethynyl-4-methoxybenzene	98
7	1-Ethynyl-2-methoxybenzene	98
8	1-Ethynyl-4-penthoxybenzene	98
9	1-Ethynyl-2-fluorobenzene	72
10	1-Ethynyl-3-fluorobenzene	78
11	1-Ethynyl-4-fluorobenzene	96
12 [c]	1-Ethynyl-4-(trifluoromethyl)benzene	87
13	Ethynylcyclopropane	97
14	Ethynylcyclohexane	97
15	Prop-2-yn-1-ylcylohexane	97
16	3-methoxyprop-1-yne	94
17	1-hexyne	92
18	1-heptyne	98
19	1-octyne	99
20	2-ethynylthiophene	80
21 [c]	1-Ethynyl-4-nitrobenzene	72

[a] Reaction conditions: alkyne (25 mmol), **P-L1**/Ag system (0.0125 mmol of Ag_2O, 0.025 mmol of NHC proligand, 0.025 mmol KI), DMF (40 mL), Cs_2CO_3 (37.5 mmol), 35 °C, CO_2 (1 bar), 24 h. [b] Isolated yield. [c] 36 h.

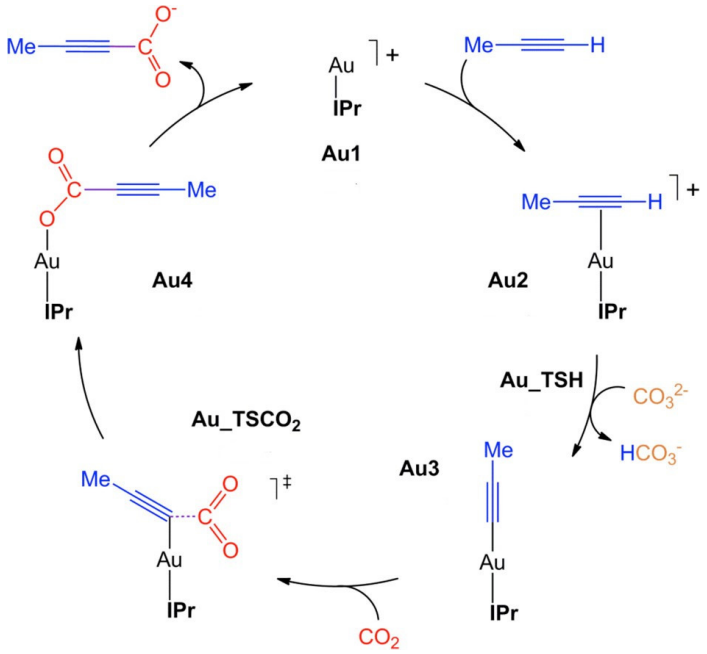
To the best of our knowledge, only Gooßen et al. [69] dealt with gold-catalyzed carboxylation reaction of terminal alkynes. They tested the complex **20** (Figure 20, shown in Figure 10 as well) in the reaction of carboxylation of 1-octyne, obtaining a 9% conversion.



20: (IPr)AuCl

Figure 20. NHC-Au(I) complex **20** employed by Gooßen and co-workers.

Using DFT simulations, Maseras and Jover [70] identified the mechanism of the gold-catalyzed carboxylation process. The authors have used complex **20** as a model and propyne as olefin for the calculations (Scheme 7).



Scheme 7. Mechanism for the gold-catalyzed carboxylation, including the free energies in (kcal/mol). ‡ Transition state. Reprinted, with permission, from [70]. Copyright 2014, American Chemical Society.

By the analysis of the mechanism, reported in Scheme 7, the σ-acetylide gold complex results as the species with the lowest free energy (–62.8 Kcal/mol). The energy barrier required for the carboxylation of the alkyne is 22.9 kcal/mol. The low conversion could be attributed to the high stability of the gold acetylide complex and the middle-high energy to overcome.

3.2. Carboxylation Cyclization

The addition of carbon dioxide to alcohols and amines are two equilibrium transformations. The main limitation for these reactions is the difficulty to isolate the corresponding carbonate/carbamate, after the quenching the reaction. In fact, until few years ago, the synthesis of these compounds was conducted using phosgene, due to its higher reactivity than CO_2, avoiding the equilibrium condition [71].

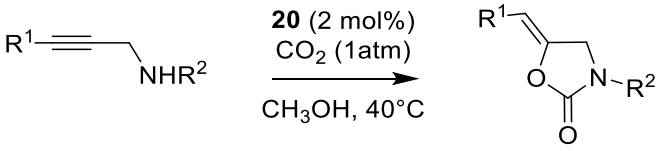
Transformation of unstable scaffolds into stable products, and development of efficient catalysts have been the solution of the problems due to equilibrium condition and use of hazardous chemicals in harsh condition reaction.

In the 2007, the discovery of the catalytic activity of silver salts in the cascade carboxylation and cyclization of propargyl alcohols was an important breakthrough in the transition metal catalyzed conversion of carbon dioxide [72].

3.2.1. Reaction of Carboxylative Cyclization Catalyzed by AuNHC

In 2013, Ikariya and collaborators [73] reported the synthesis of (*Z*)-5-alkylidene-1,3-oxazolidin-2-ones, by carboxylative cyclization with 2 mol% of **20** in methanol, under 1 atm of carbon dioxide. Table 26 reports all the obtained results. The authors did not observe the formation of any other by-products or isomers. Furthermore, by ^{1}H-NMR spectroscopy and X-ray crystallographic analysis, the authors outlined the *Z* configuration of the C-C double bond.

Table 26. Fixation of CO_2 catalyzed by **20**.

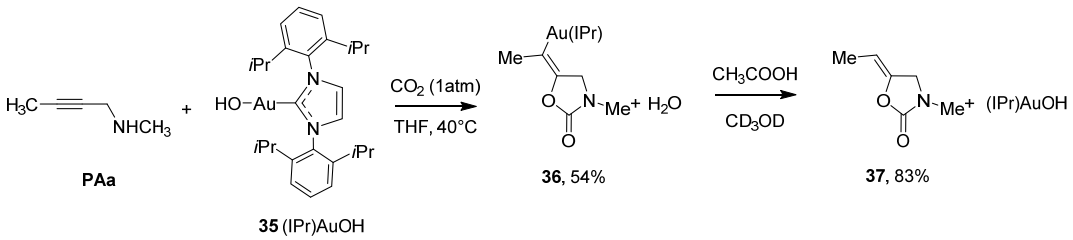


Entry [a]	Substrate	R^1	R^2	Time (h)	Yield (%) [b]
1	**PAa**	Me	Me	15	91
2	**PAb**	Et	Me	15	83
3	**PAc**	*i*Pr	Me	15	87
4	**PAd**	*t*Bu	Me	15	81
5	**PAe**	H	Me	15	16
6	**PAf**	Me	Et	48	85
7	**PAg**	Me	Prop	48	86
8	**PAh**	Me	Bn	15	83
9	**PAi**	Me	*i*Pr	66	27
10	**PAj**	Ph	Me	48	76
11	**Pak**	Ph	H	48	47

[a] Reaction condition: the reaction was carried out with 2.0 mmol of propargylamine substrates **PAa-k** and **20** (2 mol%) in MeOH (2.0 mL) under CO_2 (1 atm) at 40 °C. [b] The yields were determined by ^{1}H NMR.

The gold complex **20** converted various *N*-methylaminoalkynes into analogous urethanes with yields ranging from 81 to 91% (Table 26, Entries 1–4). The reaction between carbon dioxide and the terminal alkyne (*N*-methylpropargylamine) led to only 16% of the corresponding cyclic product (Entry 5). The authors associated the low yields with the formation of σ acetylide gold complex, less catalytically reactive. The conversion of the amine was reduced when the alkyl groups were replaced with aromatics, even with longer reaction times (Entries 10–11).

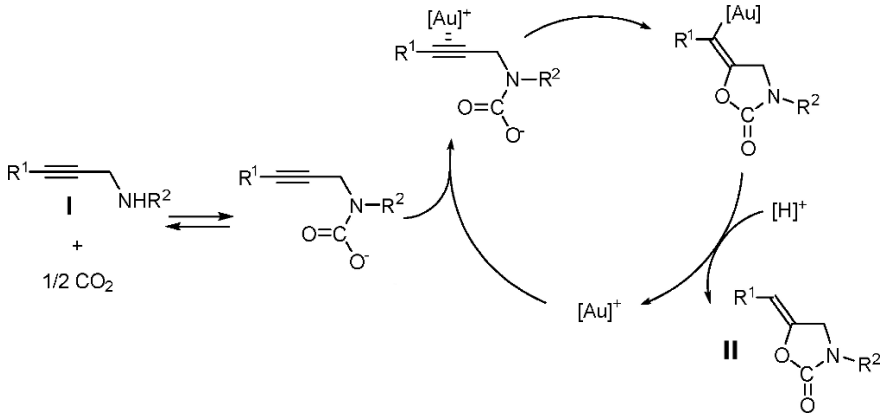
To gain mechanistic information, the authors evaluated the carboxylation reaction of the substrate 1-methylamin-2-butyne **PAa** (Table 26), using a stoichiometric amount of (IPr)AuOH **35** [74] in non-acid conditions, 1atm of CO_2, and in dehydrated THF at 40 °C. As shown in Scheme 8, they obtained the alkenylgold complex **36** in a 54% yield. The side product of the reaction is H_2O, which does not have sufficient acidity to damage the alkenylgold complex. The successive addition of an equimolar solution of acetic acid in CD_3OD to lead the urethane **37** with an 83% yield in 1 h.



Scheme 8. Synthesis of the alkenylgold complex.

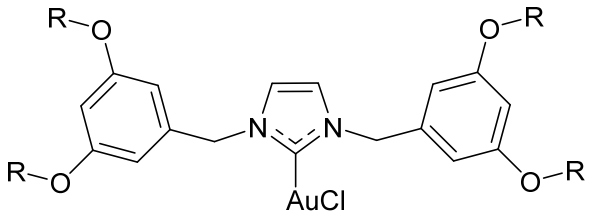
Given these experimental observations, the authors proposed a mechanism of cyclization reaction promoted by the NHC gold complexes [75] (Scheme 9). In a polar medium (methanol), the gold precursor forms the catalytic species by dissociation of the chloride, whereas the carboxylation of the amine moiety (**I**) produces the formation of a propargylic carbamate. The triple bond of the propargylic carbamate is activated by the cationic gold(I) centre, which undergoes the nucleophilic attack by the carbamate ion on the triple bond to generate the neutral gold alkenyl compound. The subsequent addition of a proton (protodeuration) leads to the urethane **II** and regenerates the catalytic gold cation. This mechanism was also investigated by Lin and coworkers through DFT calculations [76]. It

was found that polar protic solvents, such as CH_3OH, can stabilize the negative charge on the carboxylic moiety, promoting the catalytic reaction [76].



Scheme 9. Proposed mechanism of the carboxylation fixation of carbon dioxide by propargylamines, promoted by AuNHCX complexes. Adapted with permission from [75]. Copyright 2013, American Chemical Society.

Fujita et al. [77] conducted further studies, synthesizing a series of amphiphilic dendritic NHC gold complexes and evaluating the catalytic activity of carbon dioxide addition to propargylic amines in aqueous media. The main aim of this research was to introduce a hydrophilic group to a hydrophobic dendron in order to give the complexes amphiphilic. Tri(ethylene glycol) (TEG), penta(ethylene glycol) (PEG), and dodecyl(ethylene glycol) (DEG) were added to the dendron. The structures of such complexes are reported in Figure 21.

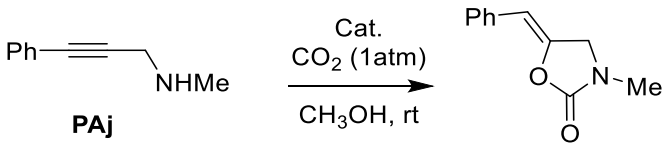


R=$(CH_2CH_2O)_3CH_3$ [TEG] **38**
$(CH_2CH_2O)_5CH_3$ [PEG] **39**
$(CH_2CH_2O)_{12}CH_3$ [DEG] **40**

Figure 21. Structure of amphiphilic gold NHC complexes **38**–**40**.

The authors of the paper examined the catalytic activity of the amphiphilic gold complexes in the reaction of carbon dioxide fixation to *N*-methyl-3-phenylprop-2-yn-1-amine (substrate **PAj**, Table 27), which lead in 15–24 h to the corresponding 2-oxazolidinone in aqueous solution at room temperature. As shown in Table 27, all the complexes are catalytically active. The NHC gold complex **39** showed the highest production of oxazolidinone (Entries 3–5). A good yield was obtained using 1% mol of the catalyst (Entries 4 and 5). A dramatical decrease in yield was recorded lowering the catalyst loading to 0.5% (Entry 6).

Table 27. Carboxylation of propargylamine in an aqueous solution catalyzed by dendritic NHC gold complexes **38**–**40**.

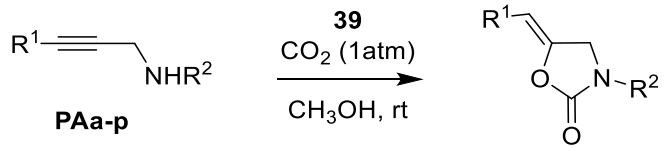


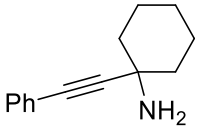
Entry [a]	Complex	Au(%mol)	Time (h)	Yield (%) [b]
1	**38**	2	24	85
2	**38**	1	24	60
3	**39**	2	24	87
4	**39**	1	24	82
5	**39**	1	15	72
6	**39**	0.5	24	17
7	**40**	2	24	84
8	**40**	1	24	77
9	**40**	1	15	61

[a] Reaction conditions: **PAj** (0.8 mmol), MeOH (1 M) under CO_2 (1 atm) at rt. [b] The yields were determined by ^{1}H NMR.

Furthermore, Fujita and collaborators [78] tested the catalytic activity of **39** in the carboxylation of various propargyl amines in aqueous media. The results are listed in Table 28. The reaction of carbon dioxide fixation was carried out for 48 h, except for the propargylamine **PAj**, using 1%mol of gold complex, to give the corresponding 2-oxazolidinone in acceptable to good yields. Despite the use of 2 mol% of gold complex, the reaction with terminal alkynes (Table 28, Entries 1 and 7) gave low chemical yields. However, terminal amines did not react with the carbon dioxide (Entry 8).

Table 28. Carboxylation of propargylamines catalyzed by complex **39**.



Entry [a]	Substrate	R^1	R^2	Au (%mol)	Time (h)	Yield (%) [b]
1	**PAe**	H	Me	2	72	49
2	**PAi**	CH_3	iPr	1	48	63
3	**PAj**	Me	Ph	1	48	82
4	**PAl**	4-Me C_6H_4	Me	1	48	87
5	**PAm**	Me	Bn	1	48	74
6	**PAn**	Et	Bn	1	48	72
7	**PAo**	H	Bn	2	48	20
8	**Pap**			2	72	n.d.

[a] Reaction conditions: **PA** (0.8 mmol), MeOH (1 M) under CO_2 (1 atm) at rt. [b] The yields were determined by ^{1}H NMR. n.d. Not detected.

In 2020, Nolan and collaborators synthesized and characterized eight dinuclear gold(I) complexes (**41**–**48**, Figure 22), evaluating their catalytic activity in the fixation reaction of carbon dioxide to *N*-benzylbut-2-yn-1-amine (substrate **PAh**) [79]. All the eight complexes were active toward the cyclization of carbon dioxide at room temperature in MeOH. Table 29 reports the catalytic activity of these complexes. The complexes **41**–**44** (Table 29, Entries

1–4) bearing a 2,6-diisopropylphenyl group on the *N*-heterocyclic ligand, showed better catalytic activity than the mononuclear analogues (Table 29, Entry 9). A counter anion influence in terms of catalytic activity was not noticed. At the same time, a little drop in activity when the linker length on the NHC ligand is shortened was observed.

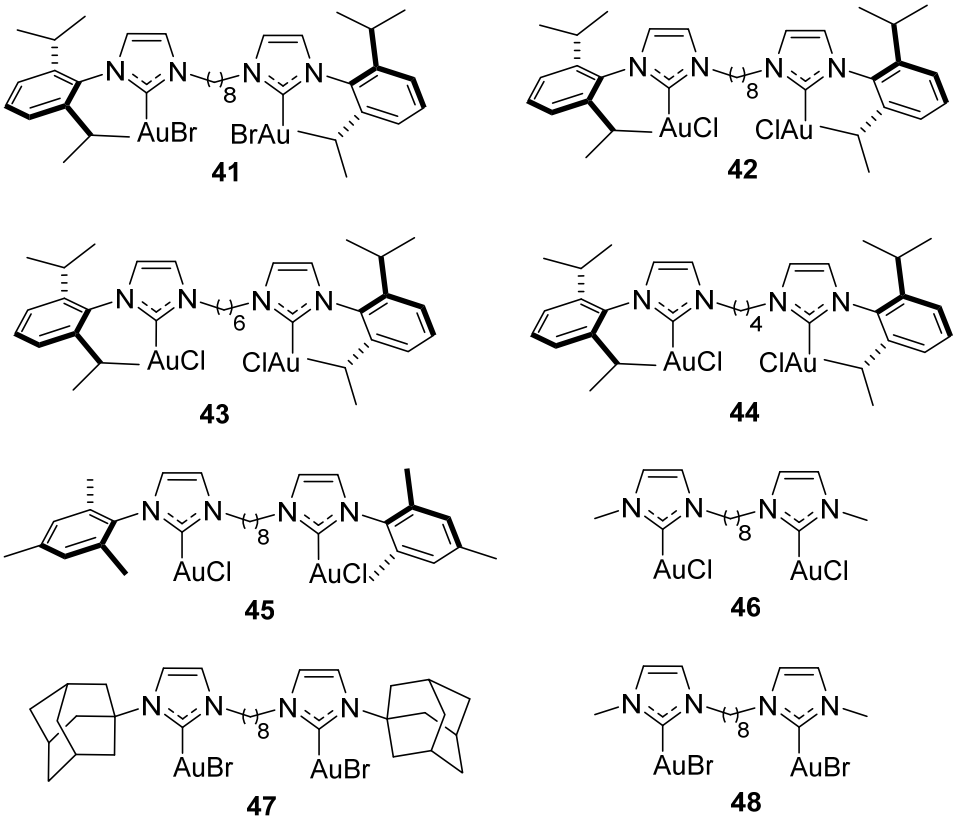
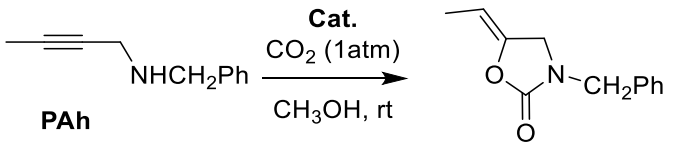


Figure 22. Structure of dinuclear complexes **41**–**48** tested by Nolan et al. [79].

Table 29. Carboxylative cyclization of **PAh**, catalyzed by dinuclear complexes **41**–**48**.

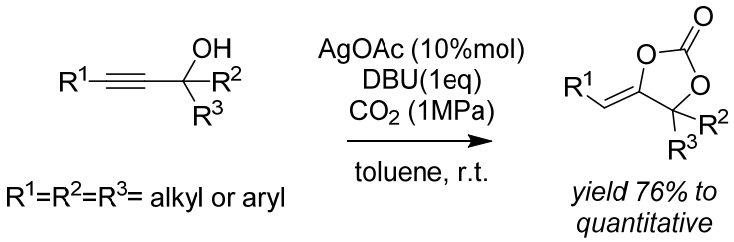


Entry [a]	Catalyst	Yield (%) [b]
1	**41**	87
2	**42**	87
3	**43**	79
4	**44**	76
5	**45**	47
6	**46**	47
7	**47**	62
8	**48**	47
9	**20**	63

[a] Reaction conditions: **PAh** (0.5 mmol) and dinuclear gold NHC complex (1% mol) in MeOH (0.4 mL) under CO_2 (1 atm) at room temperature for 15 h. [b] The yields were determined by ^{1}H NMR using 1,3,5-trimetoxybenzene as the internal standard.

3.2.2. Reaction of Carboxylative Cyclization Catalyzed by AgNHC

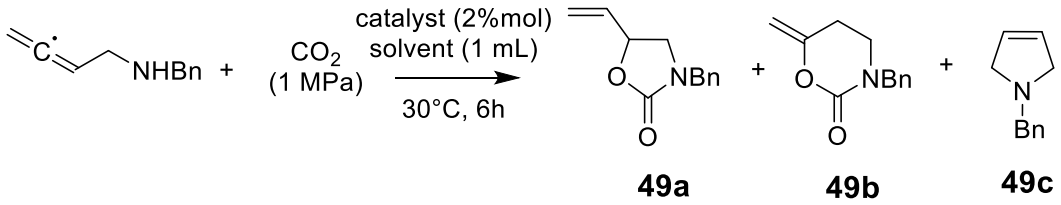
The carbon dioxide cycloaddition to propargylic alcohol, to achieve cyclic carbamates, mediated by silver salts, has gained more and more attention in the last years. In 2007, Yamada and collaborators reported for the first time silver catalyzed cycloaddition of carbon dioxide to propargyl alcohols (Scheme 10) [72]. They evaluated the catalytic activity of several inorganic silver salts (AgCN, AgOTf, Ag_2CO_3, AgOAc, $AgBF_4$, AgF, $AgSbF_6$, $AgClO_4$, AgOMs). AgOAc showed the best catalytic activity at room temperature in the incorporation of carbon dioxide, using a stochiometric amount of DBU as a base to reach cycloadduct yields ranging from good to quantitative. Other metal salts such as $Rh(acac)_3$, $Hg(OTf)_2$, $PtCl_2$, $Pd(OAc)_2$, CuCl, and AuCl were not effective in this transformation.



Scheme 10. Propargyl alchol cyclization catalyzed by AgOAc.

In 2015, Takao Ikariya et al. [80] reported, for the first time, the catalytic activity of NHC silver complexes in the carbon dioxide cycloaddition to the allenyl moiety. Initially, they tested a series of complexes of Group 11. Complex **5d** (infra Figure 2) showed better catalytic activity (Table 30, Entry 1) than the gold and copper analogues (Table 30, Entries 2–3). Moreover, the silver NHC complex bearing the benzoate ion did not exhibit improved catalytic activity, and when the acetate ion moiety was replaced with the chloride ligand, it was found that conversion dramatically worsened (Entries 4 and 5). These findings imply that the carboxylation process depends critically on the production of active cationic species. Remarkably, the NHC ligand influences the selectivity of the reaction. In fact, the use of silver acetate has led to the formation of the carboxylated compound in 71% yield and the byproduct **49b** in 26% yield (Entry 6). Other acetate silver complexes showed a reduced activity for carboxylation (Entries 8 and 9). As shown in Table 30 (Entries 10–16), the nature of the solvent plays an important role in the reaction rate and in the selectivity of cyclization. Aprotic solvents, such as toluene, THF, and CH_2Cl_2, compared to 2-propanol, produced low conversions of 1-benzylamino-2,3-butadiene (Entries 10–12). In MeOH and CF_3CH_2OH it was observed the formation of hydroamination product **49c** (Entries 13 and 15). The authors asserted that the more acidity of these alcohol makes the allenyl moiety more susceptible to the amine group. Despite the low catalytic loading (0.1 mol%, Entry 16) the reaction of carboxylation continued in 2-propanol to give the urethane product a 77% yield with a long reaction time.

Table 30. Carboxylation of 1-(benzylamino)-2,3-butadiene.



49a **49b** **49c**

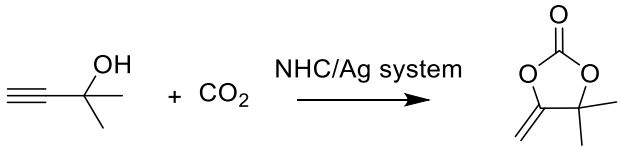
Entry [a]	Catalyst	Solvent	Yield (%) [b]		
			49a	**49b**	**49c**
1	**5d**	2-propanol	86	6	7
2	**(IPr)Au(OAc)**	2-propanol	n.d.	n.d.	n.d.
3	**(IPr)Cu(OAc)**	2-propanol	3	n.d.	n.d.
4	**(IPr)AgOBz**	2-propanol	85	6	7
5	**5a**	2-propanol	7	n.d.	n.d.
6	**AgOAc**	2-propanol	71	1	26
7 [c]	**(I^{t}Bu)Ag(OAc)**	2-propanol	69	2	26
8	**(PPh_3)Ag(OAc)**	2-propanol	3	n.d.	3
9 [d]	**[(*S*)-BINAP]Ag(OAc)**	2-propanol	3	n.d.	3
10	**5d**	toluene	2	n.d.	2
11	**5d**	THF	5	n.d.	4
12	**5d**	CH_2Cl_2	50	3	4
13	**5d**	CH_3OH	61	4	31
14	**5d**	*t*-BuOH	71	6	4
15	**5d**	CF_3CH_2OH	31	2	36
16 [e]	**5d**	2-propanol	77	5	7

[a] The reaction was carried out with 1-(benzylamino)-2,3-butadiene (1.0 mmol) and the catalyst (2% mol) in solvent (1.0 mL) under CO_2 (1 MPa) at 30°C for 6 h. [b] The yields were determined by ^{1}H NMR using durene as internal standard. [c] 40 °C, 7.0 MPa, 15 h. [d] 5 MPa. [e] 0.1 mol% of the catalyst for 96 h. BINAP: 2,2′-Bis(diphenylphosphino)-1,1′-binaphthalene. n.d. Not detected.

Verpoort et al. [81] tested the catalytic precursors represented in Figure 19 (infra Page 30) in the cycloaddition of carbon dioxide to propargyl alcohols, gaining the corresponding α-alkylidene cyclic carbamates, under atmospheric CO_2 pressure; the results are listed in Table 31. The authors tested Ag_2O, KI and NHC precursor as catalyst individually, observing no formation of the desirable product (Entries 1–3, Table 31). The addition of AgI to Ag_2O or the use of the only AgI ware found to be ineffective to catalyze the cycloaddition to propargyl alcohol (Entries 4–5, Table 31). Yet, the Ag_2O/KI system was able to catalyze that reaction when NHC precursor was added (Entries 6–9). The imidazolium salt with the greatest catalytic activity was **P-L3**. The authors have looked at the impacts of the silver salt and halide, in order to determine the ideal reaction conditions. The best catalytic system, as demonstrated in Entries 8 through 13 was composed of Ag_2O, KI, and **P-L3**. The catalytic system was also examined in several solvents (DMF, DMSO, CH_3CN, CH_2Cl_2, CH_3OH). The system AgI/**P-L3**/KI has showed excellent activity in both polar and aprotic solvents. The solvent basicity, which is likely capable of activating the hydroxyl group of substrates, is the cause of the somewhat greater activity in DMF.

The catalytic system was tested in the reaction of carboxylation with other substrates under 1 bar of CO_2, to lead the α-alkylidene cyclic carbamates. It was observed that the steric hindrance of the substituted group has influenced the catalytic activity. Less sterically hindered propargyl alcohols exhibited better tendency to undergo the reaction of cyclization (Table 32).

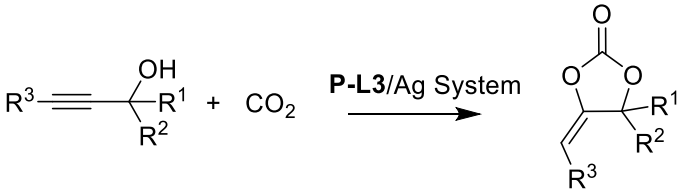
Table 31. Optimization of reaction conditions.

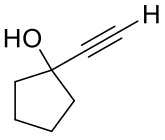
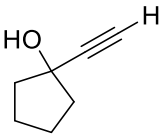


Entry [a]	Catalyst	Solvent	Yield (%) [b]
1	Ag_2O	DMF	n.d.
2	KI	DMF	n.d.
3	**P-L1**	DMF	n.d.
4	AgI	DMF	n.d.
5	Ag_2O + KI	DMF	n.d.
6	Ag_2O + KI + **P-L1**	DMF	59
7	Ag_2O + KI + **P-L2**	DMF	60
8	Ag_2O + KI + **P-L3**	DMF	65
9	Ag_2O + KI + **P-L4**	DMF	62
10	Ag_2CO_3 + KI + **P-L1**	DMF	10
11	Ag_2WO_4 + KI + **P-L1**	DMF	n.d.
12	Ag_2O + KBr + **P-L1**	DMF	40
13	Ag_2O + KCl + **P-L1**	DMF	38
14	Ag_2O + KI + **P-L1**	DMSO	41
15	Ag_2O + KI + **P-L1**	CH_3CN	n.d.
16	Ag_2O + KI + **P-L1**	CH_2Cl_2	n.d.
17	Ag_2O + KI + **P-L1**	CH_3OH	n.d.
18 [c]	Ag_2O + KI + **P-L1**	DMF	94

[a] The reaction was carried out with Ag salts (1 mol%), KX (2% mol), NHC (2% mol), in 10 mL of solvent, at 65 °C for 3 h. 2-methylbut-3-yn-2-ol (5 mmol) was then added and reacted for 12 h at 1 bar of CO_2. [b] Yield determined by NMR, using 1,1,2,2-tetrachloroethane as internal standard. [c] Ag_2O (2 mol%), KI (4% mol), NHC (4% mol), in 10 mL DMF, at 65 °C, for 24 h. 2-methylbut-3-yn-2-ol (2.5 mmol) was then added and reacted for 24 h at 1 bar of CO_2. n.d. Not detected.

Table 32. Cyclization of propargyl alcohols catalyzed by NHC proligands/Ag system **P-L3**.

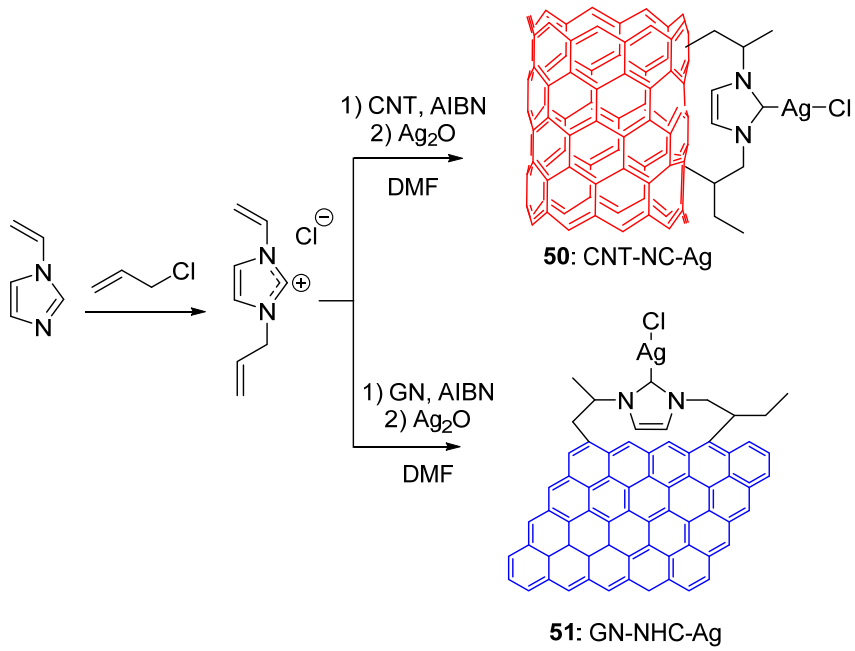


Entry [a]	R^1	R^2	R^3	Yield (%) [b]
1	Me	Me	H	94 (90)
2	Me	Et	H	90 (87)
3	Et	Et	H	93 (90)
4	Me	*i*-Pr	H	87 (85)
5 [c]				99 (95)
6 [d]				80 (77)
7 [c]	Ph	Me	H	25 (20)
8 [c]	Me	Me	Ph	25 (21)

[a] The reaction was carried out with Ag_2O (2 mol%), KI (4mol%), **P-L3** (4 mol%), in DMF 10 mL of solvent at 65 °C, substrate (2.5 mmol), 1 bar of CO_2. [b] Yields determined by ^1H NMR using 1,1,2,2-tetrachloroethane as internal standard. The isolated yields were shown in parenthesis. [c] 48 h. [d] 36 h.

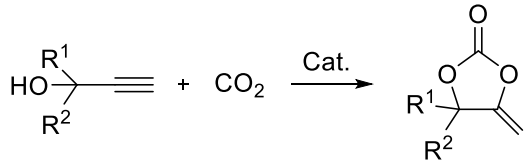
In 2018, an interesting paper by Chen [82] and collaborators was published, in which they synthesized carbon nanotube (CNT) and graphene (GN) grafted NHC-Ag complexes as heterogenous catalysts for the cycloaddition of CO_2 to propargyl alcohol.

In Scheme 11, the synthesis of these heterogenous catalysts is represented. The composite materials were synthesized by reaction of polymerization of 3-allyl-1-vinylimidazolium chloride in presence of CNT or GN suspension. The heterogenous catalysts (Scheme 11, catalysts **50** and **51**) were synthesized by reaction of corresponding materials with Ag_2O. These heterogenous complexes were tested in the cycloaddition of carbon dioxide to terminal propargyl alcohols showing an interesting activity in the formation of carbonate. As shown in Table 33, the reaction doesn't occur in absence of the catalyst. Silver salts, like Ag_2O, Ag_2CO_3, AgOTf, AgOAc were inactive toward the transformation (Entries 1–6).



Scheme 11. Synthesis of the heterogenous catalysts **50**–**51**.

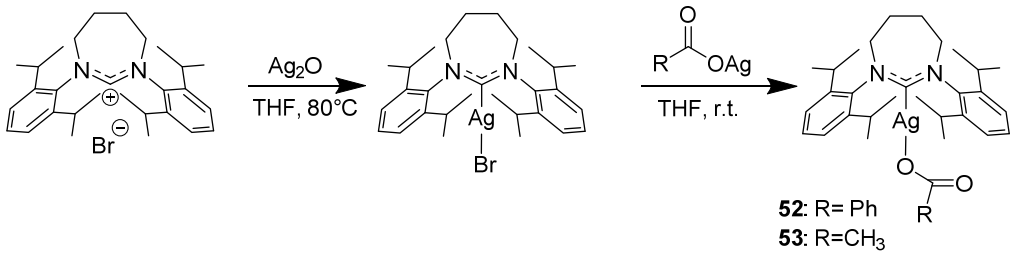
Table 33. Formation of carbonate by cycloaddition of CO_2 to terminal propargyl alcohols using heterogenous catalysts.



Entry [a]	R^1	R^2	R^3	Catalyst	Yield (%) [b]
1	H	Me	Me	CNT-IL	n.d.
2[c]	H	Me	Me	Ag_2O	2
3[c]	H	Me	Me	Ag_2CO_3	2
4[c]	H	Me	Me	AgOTf	1
5[c]	H	Me	Me	AgOAc	n.d.
6[c]	H	Me	Me	**50**	99
7[c]	H	Me	Me	**51**	99
8[c]	H	Me	Et	**50**	99
9	H	Me	Et	**51**	99
10	H	Me	*i*-Pr	**50**	97
11	H	Me	*i*-Pr	**51**	95

[a] The reaction was carried out with propargylic alcohol (0.53 mmol); catalyst (80 mg); PCO_2 (3.0 MPa); T 80 °C; t 24 h. [b] Isolated yields based on propargylic alcohols. [c] Ag species (0.073 mmol) in the Ag catalysts are used on equimolar amount of Ag sites in the CNT-NHC-Ag. n.d. Not detected.

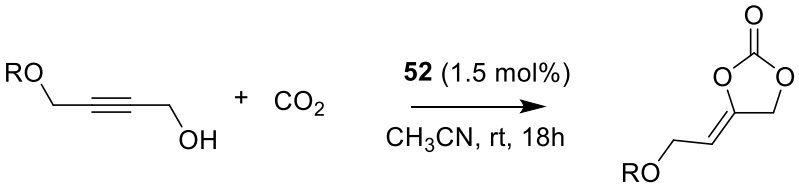
Very recently Hashimi and co-workers [83] reported the synthesis, the characterization, and the catalytic application of new silver carboxylate carbene complexes, in the carbon dioxide cycloaddition to propargyl alcohols and propargylic amines. The synthesis of the silver carboxylate complexes is reported in Scheme 12. As shown, the carboxylate complexes were synthesized by the preparation in the first instance, of the silver bromide complexes, followed by ion exchange to gain the silver carboxylate salts (acetate, benzoate).



Scheme 12. Synthesis of carboxylate silver carbene complexes.

Complex **52** showed the best catalytic activity. Under the optimized reaction conditions, a variety of propargylic alcohols were converted to the corresponding carbamates. In Table 34 the yields obtained using the complex **52** are reported. By the analysis of the yields, the authors observed that the presence of alkyl or aryl group on the Ph ring contributed to a slightly better yield than the ones bearing electron withdrawing group (Entries 1–8 vs. 13).

Table 34. Cyclization of various alcohols catalyzed by complex **52**.



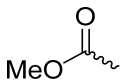
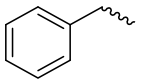
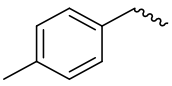
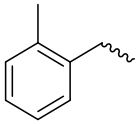
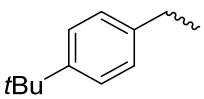
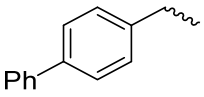
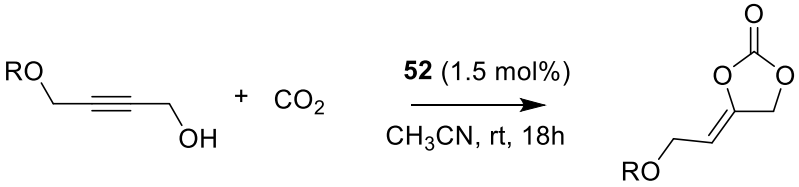
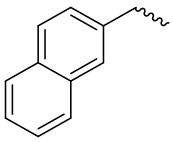
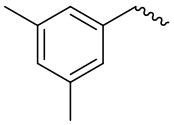
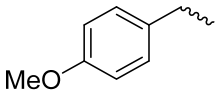
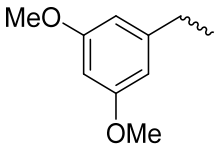
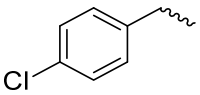
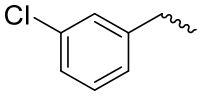
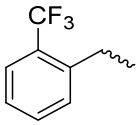
Entry [a]	R	Yield (%) [b]
1		87
2		89
3		90
4		83
5		85
6		84

Table 34. *Cont.*



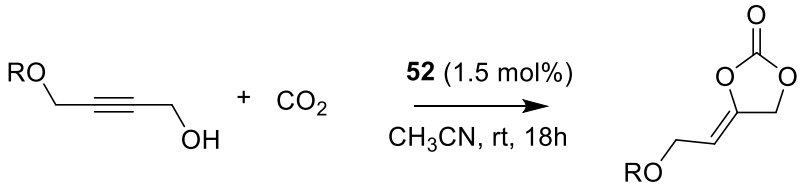
Entry [a]	R	Yield (%) [b]
7		82
8		90
9		91
10		93
11		84
12		81
13		72

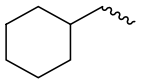
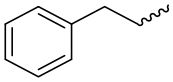
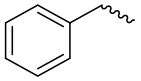
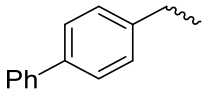
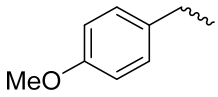
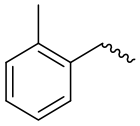
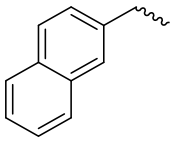
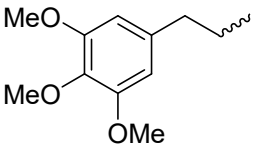
[a] The reaction was carried out with propargylic alcohol (0.5 mmol); CH_3CN (0.5 mL); P CO_2 (2.0 bar); **52** (1.5%mol); r.t.. [b] Isolated compounds.

Instead, the silver NHC acetate complex **53** showed better catalytic activity in the synthesis of 2-oxazolidinones by cyclization of propargylic amines than complex **52**. As listed in Table 35, all the examined reactions give good yields. The reaction times vary from 1.5 to 16 h.

Another important aspect, evaluated by the authors, was the recyclability of the catalysts. The complexes synthesized were insoluble in organic polar solvent, whereas the cyclic carbonate was soluble in solvent such as CH_3CN and AcOEt. This immiscibility has allowed for the easy recyclability of the complexes by filtration. In fact, decomposition of the silver complexes was not recorded, and the catalytic activity was up 96% yield after the 7th cycle.

Table 35. Cyclization of various amines catalyzed by **53**.



Entry [a]	R^1	Yield (%)
1	Me	94
2 [b]	*n*Bu	92
3 [b]	Cy	90
4 [b]		95
5 [c]		86
6 [c]		92
7 [c]		89
8 [c]		93
9 [d]		85
10 [c]		91
11 [c]		95

[a] The reaction was carried out with propargylic alcohol (1 mmol); CH_2Cl_2 (0.5 mL); P CO_2 (balloon); **53** (0.01 mol%); r.t, 6 h. [b] 8 h. [c] 12 h. [d] 16 h.

4. Conclusions

The plethora of efficient one-pot reactions catalyzed by NHC metal complexes has expanded greatly in the past couple of decades, since the first isolation of an N-heterocyclic carbene by Arduengo. NHC complexes of silver(I) and gold(I) have received a great deal of attention thanks to their easy handling, compared to the parent coinage metal copper. This advantage, together with the wide applicability, has made possible an exponential growth of published papers. This review article focused on two particularly interesting multicomponent reactions involving alkynes, i.e.,: A^3-coupling and CO_2 fixation, having

as main aim to furnish an up-to-date comprehensive overview of the application of such complexes in these processes. Multicomponent reactions outcome can be strictly controlled employing a late-transition metal catalyst. Particularly, in the presence of a NHC metal complex, for the A^3 coupling, reaction conditions can be easily adjusted towards a greener process, while maintaining good yields, when compared to the metallic inorganic salt. As far as carboxylation is concerned, the presence of such catalysts allows the reduction of the reaction temperatures and CO_2 pressure, making for a straightforward synthetic procedure. The undiscussed versatility of the heterocyclic ring, both from the electronic and steric point of view, together with the multitude of the counteranions available, produces a platform of tunable catalytic systems whose metal complexes' characteristics may be tailored to the chemist's imagination and have yet to be fully explored.

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