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Catalytic Behavior of NHC–Silver Complexes in the Carboxylation of Terminal Alkynes with CO₂

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Abstract: A number of N-heterocyclic carbene–silver compounds (NHCs)AgX were tested in the direct carboxylation of terminal alkynes using carbon dioxide as the C1 carbon feedstock. The reactions proceed at a pressure of 1 atm of CO₂ at room temperature, in the presence of Cs₂CO₃, and using silver–NHC complexes as catalysts. Thus, phenylacetylene and several alkynes are converted to the corresponding propiolic acids in good to high conversions. The activity of the catalysts is strongly influenced by the substituents on the NHC backbone and the nature of the counterion. Specifically, the most active compound exhibits iodide as the counterion and is stabilized by a benzimidazole derivative. After 24 h of reaction, a quantitative conversion is obtained utilizing DMF as the solvent and phenylacetylene as the substrate.

Keywords: carboxylation; terminal alkynes; CO₂; propiolic acids; NHC silver complexes



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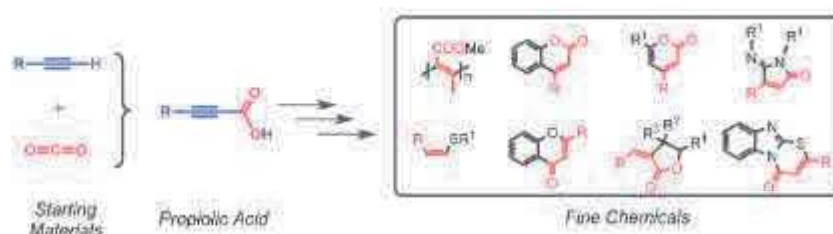
1. Introduction

The widespread use of fossil fuels has resulted in a considerable increase in CO₂ levels in the atmosphere, hence enhancing the greenhouse effect. Carbon dioxide is currently one of the most fascinating reagents for organic chemistry because it is inexpensive and non-toxic. It is thermodynamically stable and chemically inert, so the activation of this molecule to use it as a reagent requires the use of specific catalysts or particularly drastic reaction conditions, generally high pressures, temperatures higher than room temperatures, or completely anhydrous conditions [1–3]. In recent years, research has achieved significant results, also from the point of view of sustainable chemistry, in the exploitation of this important raw material with catalytic transformation into chemical substances with high added value, e.g., the reaction of CO₂ with epoxides to obtain cyclic carbonates [4–6] or polycarbonates [7,8], the carboxylation of ethylene and methyl iodide to form acrylates [9–12], and that of alkynes to give carboxylic acids or esters [13,14]. Among the several reactions that activate CO₂, the carboxylation of terminal alkynes has shown to be particularly noteworthy since it yields propiolic acids. They are essential intermediates for the production of fine chemicals, medicines, bioactive compounds, synthetic fibers, and conductive polymers [13,15–21], as well as substrates for other reactions such as hydroarylations, decarboxylative couplings, and cycloadditions [18–28] (Scheme 1). The latter can give heterocycles such as butyrolactones, flavonoids, furanone, and pyranone [29–33].

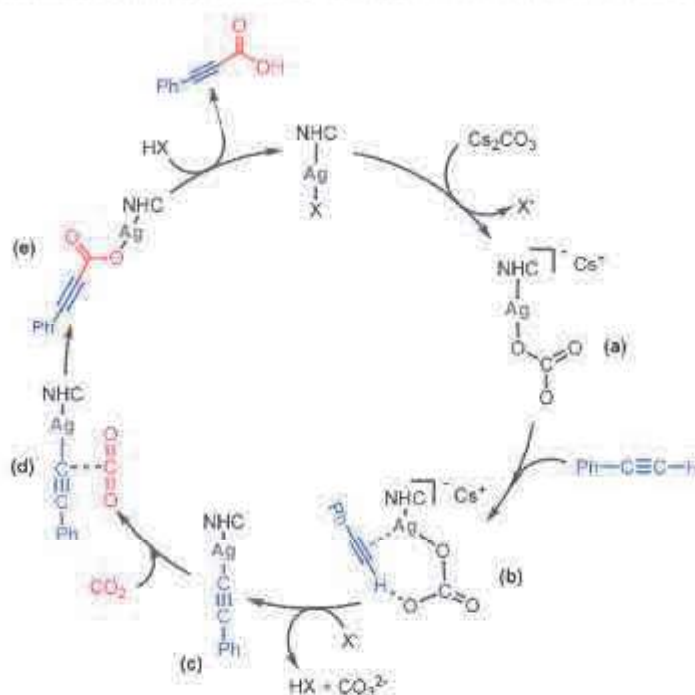
Significant contributions in the carboxylation of terminal alkynes have been made by many research groups [34–49].

This reaction can happen in the absence of catalysts and at a high temperature [50]. In the presence of copper(I) and silver(I) halide complexes that have shown good activity in catalyzing the carboxylation of various alkynes in the presence of a strong base [51–54], it can occur under mild conditions. The mechanism of this reaction, as proposed by C. Liu et al. [55] or J. Jover et al. [56], who corroborated their findings with DFT calculations,

involves the reaction of CsCO_3^- with $(\text{NHC})\text{AgX}$ to form the anionic complex (a), which represents the catalytically active species (see Scheme 2). Coordination of the alkyne to the metal center (b), followed by its deprotonation, assisted by the cesium carbonate as a base, produces silver acetylide (c). Then, the interaction of CO_2 with the $\text{C}(sp)\text{-Ag}$ (d) and its subsequent insertion into the C-metal bond (e) after acidification with CsHCO_3 produces the propiolic acid (see Scheme 2) [56,57].



Scheme 1. Examples of conversion reactions of propiolic acids in organic synthesis.



Scheme 2. Hypothesized mechanism for the silver-NHC catalyzed carboxylation of terminal alkynes.

The reactivity of group 11 metals in low oxidation states (0 or 1) in this type of reaction is attributed to their tendency to act as carbophilic Lewis acids, allowing them to interact with triple C-C bonds. The π -complexation produces the activation of both the C-C and the $\text{C}(sp)\text{-H}$ bonds, facilitating the coupling [58–61]. Among the many copper(I)- or silver(I)-based complexes employed in this catalytic process, N-heterocyclic carbenes showed great activity and good stability [36,37,62–65]. Zhang et al. [36,62] reported the carboxylation of terminal alkynes with CO_2 (1 atm) using poly-NHC-Cu(I) or poly-NHC-Ag(I) catalysts, which showed high activity and stability, yielding functionalized propiolic acids effectively under ambient conditions with Cs_2CO_3 . Similarly, Fang et al. [63] described the synthesis and catalytic activity of *N*-benzyl-substituted NHC-Ag complexes in the same reaction, also achieving high activity and stability with good to excellent yields (up to 83%—TOF 519 h^{-1}) under similar experimental conditions. Verpoort et al. [37,64] documented excellent data on isolated and in situ-generated silver-based catalysts with sulfonated NHC ligands for the direct carboxylation of terminal alkynes under mild conditions with high yields. It is worth noting that gold(I) complexes display lower activity than silver analogs due to the different electronegativities of the two metals: 1.9 for silver and 2.4 for gold. This difference

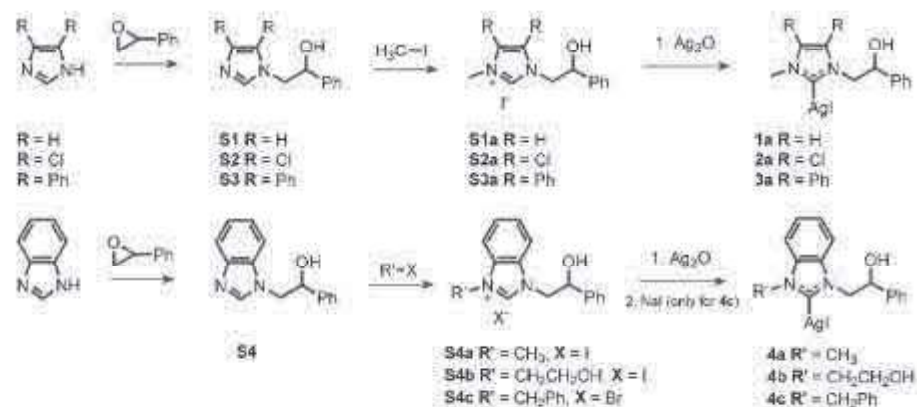
makes the M-C≡C-R bond more stable and, consequently, the carbon that must interact with the CO₂ less nucleophilic.

Recently, some of us developed and characterized several novel silver and gold complexes stabilized by asymmetrically nitrogen-substituted N-heterocyclic carbene ligands, such as N-(2-hydroxyethyl)-N'-(2-hydroxy-2-phenylethyl)ethyl-2-ylidene. In this study, various silver complexes were investigated in the carboxylation reaction with CO₂ of numerous terminal alkynes to produce propiolic acids. A kinetic study was carried out to assess the effects of the following: (i) different substituents on the backbone of the imidazole ring; (ii) different metal counterions, and (iii) different reaction solvents.

2. Results

2.1. Synthesis and Characterization of Complexes

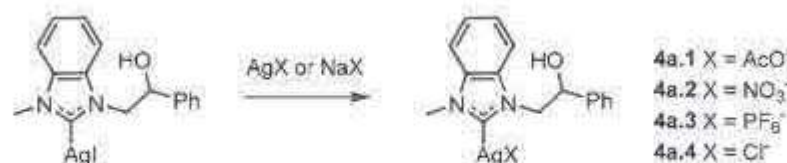
The NHC metal complexes **1a** [66], **2a**, **3a** [67], and **4a** [68] were synthesized as reported in the literature. Complexes **4b** and **4c** were synthesized by slightly modifying the literature procedure (Scheme 3). The first step is the synthesis of N-2-phenyl-2-hydroxyethyl-benzimidazole (**S4**), which was obtained by the reaction of benzimidazole with styrene oxide. The opening of the epoxide generates a hydroxyl group, which was introduced in order to increase the solubility of the catalyst in a polar reaction media. **S4b** and **S4c** were obtained with the reaction of **S4** with 2-iodoethanol or benzyl bromide (see Scheme 3). Complex **4b** was synthesized by mixing a solution of imidazolium salt **S4b** with 0.6 eq. of Ag₂O at room temperature and in the dark. The reaction of imidazolium salt **S4c** with Ag₂O leads to the formation of the (NHC)AgBr complex. Complex **4c** was obtained by a counterion metathesis reaction of (NHC)AgBr with sodium iodide (see Supplementary Materials).



Scheme 3. Synthesis of NHC-silver(I) complexes **1–3a** and **4a–c**.

The iodide complexes were characterized by means of ¹H- and ¹³C-NMR spectroscopy, mass spectrometry (MALDI), and the elemental analysis technique. Influences of the imidazole's backbone on the σ-donation properties of the ligand were evaluated, according to Nolan and Huynh [69,70], for proligands **S1a**, **S2a**, and **S4a**, measuring one-bond CH J-coupling (DMSO-d₆, 150 MHz). ¹J_{C–H} were coherent with increasing σ-donation in the order **S2a** < **S1a** < **S4a** (229.92 Hz, 222.84 Hz, 221.56 Hz).

The iodide counterion of complex **4a** undergoes exchange when it reacts with the appropriate silver or sodium salt due to the precipitation of silver iodide. Thus, **4a.1**, **4a.2**, and **4a.3** were obtained using silver acetate, silver hexafluorophosphate, and silver nitrate, respectively (Scheme 4). Chloride complex **4a.4** was obtained by the reaction of **4a** with an excess of NaCl. The main evidence of the counterion exchange is due to the shift of the carbenic carbon in the ¹³C NMR spectra of **4a.1**, **4a.2**, **4a.3**, and **4a.4**, whereas the rest of the spectra remain mostly unaltered. Table 1 shows the chemical shifts of these carbon atoms, which are at lower ppm (upfield shifted), as the σ-donor capacity of the NHC decreases [71].



Scheme 4. Synthetic routes for the exchange of the counterion.

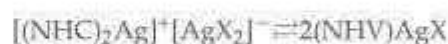
Table 1. Chemical Shift of carbenic carbon of silver–NHC complexes **4a** (NHC)AgX.

| Complex | X | δ_C (DMSO- <i>d</i> ₆) Ag-C (ppm) |
|-------------|------------------------------|---------------------------------------------------------|
| 4a | I ⁻ | 191.1 |
| 4a.1 | AcO ⁻ | 188.4 |
| 4a.2 | NO ₃ ⁻ | 189.9 |
| 4a.3 | PF ₆ ⁻ | 191.4–188.3 |
| 4a.4 | Cl ⁻ | 184.6 |

As can be noticed by observing the data in Table 1, the σ donation of the carbene ligand follows the order **4a** > **4a.2** > **4a.1** > **4a.3** > **4a.4**, i.e., to NHC-AgX complexes with X equal to I⁻, NO₃⁻, OAc⁻, PF₆⁻, and Cl⁻, respectively [69,72,73].

The main evidence of the counterion exchange is due to the shift of the carbenic carbon in the ¹³C NMR spectra of **4a.1**, **4a.2**, **4a.3**, and **4a.4**, whereas the rest of the spectra remain mostly unaltered.

The two signals attributable to the carbenic carbon of the complex with PF₆⁻ may be due to two species present in the solution. In fact, as frequently observed both by diffractometric and by mass spectrometry analysis of similar compounds [74–77], silver complexes with N-heterocyclic carbenic ligands give rise to two possible species due to the silver following equilibrium in solution:



Thus, while for X = I⁻, NO₃⁻, OAc⁻, and Cl⁻, the equilibrium is more shifted towards the formation of the neutral species and is faster than the NMR time scale, for the PF₆⁻ ion the equilibrium is probably slower, and, therefore, two carbenic signals are visible, i.e., at 191.4 and 188.3 ppm due to carbenic carbon of [(NHC)₂Ag]⁺ and (NHC)AgPF₆, respectively. Alternatively, the presence of a doublet attributable to C_{carbene} in the spectrum of the silver complex with PF₆⁻ could be due to the coupling constant of C_{carbene} and Ag, whose two natural isotopes have both nuclear spin 1/2, and therefore they are NMR active, with a narrow coupling constant of 55 Hz.

It is worth recalling that it is known from the literature that the pattern of carbene carbons bonded to silver (C_{carbene}-Ag) can present itself in three distinct ways, i.e., (i) no splitting (sharp or broad singlet), (ii) doublet of doublets (coupling constants with each silver isotope ¹⁰⁷Ag and ¹⁰⁹Ag), and (iii) no peak attributable to the carbene carbon [76].

2.2. Catalytic Carboxylation of Alkynes with CO₂

The catalytic activity of silver complexes (1% mol) was evaluated in the coupling reaction of phenylacetylene and CO₂ at atmospheric pressure, carrying out the reactions at room temperature in DMSO for 16 h in the presence of cesium carbonate [64].

For the catalysis conditions, we were inspired by the work of Fang et al. [63]. In this work, the carboxylation of terminal alkynes with CO₂ (1 atm) with NHC–Ag complexes was tested using different bases (Cs₂CO₃, DBU, K₂CO₃, KO^tBu, NaO^tBu, NaOH) and solvents (DMF, DMSO, CH₂Cl₂, CH₃CN, THF).

The best catalysis conditions were found using Cs₂CO₃ as a base and DMF as a solvent.

Table 2 reports the obtained results. It is worth noting that the silver complexes are needed to obtain propiolic acid [63]. In fact, a reaction carried out under our experimental

conditions (run 18) using the imidazolium salt **S4a** (1.0 mmol), Cs_2CO_3 (1.2 mmol), and phenylacetylene (100 mmol) under the pressure of 1.0 atm of CO_2 did not produce the carboxylic acid. Comparing the data from runs 1–4 reveals that the substituents on the backbone of the imidazole ring have a considerable influence on the catalyst's activity. Indeed, these complexes differ only for these substituents, with **4a** being the most active, having a condensed arene ring, and the least active having two chlorine atoms in positions 4 and 5 of the ring. This suggests that the inductive effect of the substituents is important; clearly, those that give electron density to the carbenic carbon and, consequently, to the metal center favor the formation of the acetylide and make the C bonded to the metal center more nucleophilic, thus more reactive towards CO_2 carbonilic carbon. The choice of dry DMSO as the reaction solvent was made on the basis of the results reported by Velázquez [64], and since then, high conversions in the carboxylation of alkynes with CO_2 with catalysts based on silver–NHC complexes were obtained by Zhang [78] in dry DMF as the solvent, whereby complex **2a** and **4a**, the least and most active, respectively, were tested in DMF as well (see Table 2, runs 5 and 6). Furthermore, complex **4a** was tested with a series of solvents of different polarity (see Table 2, runs 7–11). As is evident from the data in Table 2, solvents with low dipole moments (dioxane, THF, and CH_2Cl_2) give very low conversions (0–15%), those with high dipole moments and weakly acids (DMSO and DMF) give very high conversions ($\approx 90\%$), while those with high dipole moments and weakly basic (CH_3CN) or with intermediate polarity (CH_3COOEt) give more modest conversions (≈ 30 – 40%). The best solvent for carrying out the carboxylation reaction of phenylacetylene with these catalytic systems was dimethylformamide.

Table 2. Carboxylation reaction of phenylacetylene.

| Run [a] | Catalyst | Solvent | Conversion (%) [b] | TOF (h^{-1}) |
|---------|-------------|--------------------------|--------------------|-------------------------|
| 1 | 1a | DMSO | 75 | 469 |
| 2 | 2a | DMSO | 54 | 338 |
| 3 | 3a | DMSO | 82 | 513 |
| 4 | 4a | DMSO | 87 | 544 |
| 5 | 2a | DMF | 75 | 469 |
| 6 | 4a | DMF | 92 | 575 |
| 7 | 4a | CH_3CN | 30 | 188 |
| 8 | 4a | THF | - | - |
| 9 | 4a | Dioxane | 7 | 44 |
| 10 | 4a | CH_2Cl_2 | 15 | 94 |
| 11 | 4a | Ethylacetate | 40 | 250 |
| 12 | 4b | DMF | 52 | 325 |
| 13 | 4c | DMF | 63 | 394 |
| 14 | 4a.1 | DMF | 75 | 469 |
| 15 | 4a.2 | DMF | 40 | 250 |
| 16 | 4a.3 | DMF | 37 | 231 |
| 17 | 4a.4 | DMF | 25 | 156 |
| 18 | S4a | DMF | - | - |

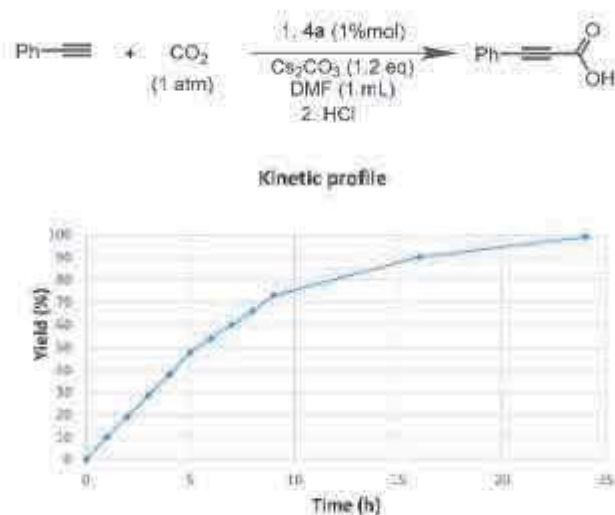
[a] Reaction conditions: phenylacetylene 1.0 mmol, CO_2 (1 atm), Cs_2CO_3 1.2 mmol; dry solvent—1 mL, 16 h, room temperature. [b] Conversions: calculated using $^1\text{H-NMR}$ spectroscopy with the integration of the signals of aromatic protons with respect to CH the signal of residual phenylacetylene ($\delta = 3.14$ ppm in CD_2Cl_2).

Thus, by performing runs 6, 12, and 13 in DMF, we confirmed that having higher electron density on the carbenic carbon makes the silver complexes more catalytically active. The catalysts used in these tests differ in only one substituent on nitrogen, i.e., methyl for **4a**, 2-hydroxyethyl for **4b**, and benzyl for **4c**. Complex **4a** has the greatest activity, while the one with the least activity is complex **4b**, the latter having the most

electron-withdrawing substituent. Having established that the best ancillary ligand of tested complexes is *N*-2-phenyl-2-hydroxyethyl-*N'*-methyl-benzimidazole-2-ylidene, we tried to determine the possible effect of the ancillary ligand. In runs 6 and 14–17, the activities of the Ag(I) complexes with the just-mentioned NHC ligand and iodide, acetate, nitrate, hexafluoro phosphate, and chloride are compared. The catalyst showing the highest activity is **4a** (run 6), while the one with the lowest is **4a.4** (run 17). Complex **4a.4** has chloride as the counterion and has the carbene with the lowest σ -donating capacity, while complex **4a** has iodide as the counterion and has the carbene with the highest σ -donating capacity, as demonstrated by the ^{13}C NMR resonances of the carbene ligands (see above). This causes the silver iodide bond to be weaker than the silver chloride bond and, thus, more likely to leave the coordination site free for the alkyne.

It is worth noting that the reaction is highly selective since no by-product is obtained, and the whole reaction contains only the propiolic acid and the unreacted alkyne.

The catalytic activity of complex **4a** was evaluated by monitoring the carboxylation reaction of phenylacetylene carried out at room temperature in DMF under a CO_2 atmosphere. The kinetic data are reported, and the corresponding kinetic profile is shown in Scheme 5. The conversions/time curve was determined with ^1H -NMR spectroscopy using the integration of the signals of the aromatic protons and that of the alkynyl proton of the residual phenylacetylene at δ 3.14 ppm.



Scheme 5. Kinetic profile of **4a** in the reaction.

As seen in the kinetic plot, catalyst **4a** is extremely efficient, achieving approximately 50% conversion in 5 h and allowing for the quantitative reaction of phenylacetylene with CO_2 in 24 h.






Thus, because our catalytic system is particularly effective, we decided to investigate various alkynes in this reaction with both alkyl and aryl substituents. Table 3 reports the results obtained performing the reaction at room temperature in the presence of 1% mol of complex **4a** and 1.2% mol of Cs_2CO_3 under an atmosphere of CO_2 , using DMF as solvent.

All products were isolated and characterized by ^1H and ^{13}C -NMR, elemental analysis (See Supplementary Materials), and GC-MS, obtaining a correspondence between conversion (obtained through ^1H NMR) and yield of the isolated product very close to each other. The differences found were less than 4%.

Table 3. Alkynes scope in the carboxylation reaction with **4a**.

$$\text{R}-\text{C}\equiv\text{C} + \text{CO}_2 \xrightarrow[\text{2. HCl}]{\text{1. 4a (1\% mol), Cs}_2\text{CO}_3 \text{ (1.2 eq), DMF (1 mL)}} \text{Ph}-\text{C}\equiv\text{C}-\text{C}(=\text{O})\text{OH}$$

(1 atm)

| Run [a] | R | Conversion (%) [b] |
|---------|------------------------------------------------------------------------------------|--------------------|
| 1 | $n\text{-C}_4\text{H}_9$ | 99 |
| 2 | $t\text{-C}_4\text{H}_9$ | 90 |
| 3 | CH_2Ph | 70 |
| 4 |  | 70 |
| 5 |  | 70 |
| 6 |  | 68 |
| 7 |  | 65 |
| 8 |  | 55 |

[a] Reaction conditions: alkyne 1.0 mmol; CO_2 (1 atm); Cs_2CO_3 1.2 mmol; dry DMF—1 mL, 16 h, room temperature. [b] Conversions: calculated using $^1\text{H-NMR}$ spectroscopy with the integration of the signals of aromatic protons with respect to the CH signal of residual alkyne.

Alkylacetylenes are more reactive than arylacetylenes, e.g., *n*-butyl- and *tert*-butyl-acetylene give conversion higher than 90% in 16 h. Instead, the arylacetylenes have a conversion between 55 and 70% in 16 h. This is easily understood given that alkyls have a higher electron-donating capacity than aryls, which means they have a better coordinating ability to the metal center. It is worth noting that the different para substituents on the aryl acetylenes have little impact on the reactivity, probably because of their contrasting effect, i.e., (i) electron-withdrawing groups increase the acidity of the alkyne but make the C(sp) less nucleophilic and thus less reactive towards the CO_2 carbon; and (ii) electron donating groups decrease the acidity of the alkyne and thus make it less reactive towards the metal center to give the acetylide, which, however, has the more nucleophilic C(sp) and therefore is more reactive towards the carbon of the CO_2 .

3. Materials and Methods

3.1. Synthesis of Catalysts **1-4a-c** and **4a.1-4a.4**

Detailed information regarding the synthesis and characterization of metal complexes **1-4a-c** and **4a.1-4a.4** is reported in the Supplementary Materials.

3.2. General Procedure for Carboxylation of Alkynes

Catalyst (1.0 mol%), Cs_2CO_3 (390 mg, 1.2 mmol), and freshly dried solvent (1.0 mL) were added to a 10 mL Schlenk tube under an inert atmosphere. The tube was evacuated and filled with CO_2 . The alkyne (1.0 mmol) was added under a stream of carbon dioxide, and the resulting mixture was stirred at room temperature and ambient pressure. After 16 h, the mixture was quenched using 1.0 mL of CH_2Cl_2 , and then it was treated with 10 mL of solution 2N of K_2CO_3 and stirred for 30 min. The mixture was extracted with dichloromethane (3×10 mL). The aqueous portion was acidified with HCl until $\text{pH} = 1$ and extracted with diethyl ether (3×10 mL). The two organic portions were dried with MgSO_4 . The corresponding carboxylic compound was obtained with filtration and removal of the solvent in vacuo.

A characterization of the product carboxylic acids is reported in the Supplementary Materials.

4. Conclusions

The catalytic behavior of silver–NHC complexes in the selective carboxylation process between carbon dioxide and phenylacetylene and other terminal alkynes was investigated in this work. The catalyst structure affects the phenylacetylene carboxylation conversion. The most active complex is stabilized by an NHC benzimidazole derivative, while the least performing is an NHC derivative of 4,5-dichloroimidazole. On the other hand, the substitution of one of the nitrogen atoms with a methyl group rather than a (2-hydroxyethyl) moiety provides a more performing catalyst. This shows that complexes with electron-donating groups on the nitrogen and backbone of NHC ligands provide a higher electron density on the carbenic carbon and, as a result, on the metal center, increasing the catalyst's activity. This is because the increased electron density on the metal center causes the carbon bonded to the metal center to become more nucleophilic, which in turn increases its reactivity with the carbon of CO₂. Catalysis tests were conducted with **4a** in different solvents, and the highest conversion was obtained when DMF was used, becoming quantitative after 24 h. Furthermore, we evaluated the function of the counterion under optimal catalytic circumstances. Tested under solvent-optimized circumstances, the combination containing the iodide ion proved to be the most active. Lastly, compound **4a** exhibited good to high conversions of activity in the carboxylation of various terminal alkynes.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/inorganics12110283/s1>. In the Supplementary materials are reported the synthesis and characterization (¹H-NMR, ¹³C-NMR, mass spectrometry and elemental analysis) of the new salts and metal complexes. The characterization of propiolic acids obtained in catalysis tests is also reported. The authors have cited additional references within the Supplementary Materials [79–81].

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Data Availability Statement: The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

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