Catal Lett
DOI 10.1007/s10562-016-1920-5

Inserting CO_2 into Terminal Alkynes via Bis-(NHC)-Metal Complexes

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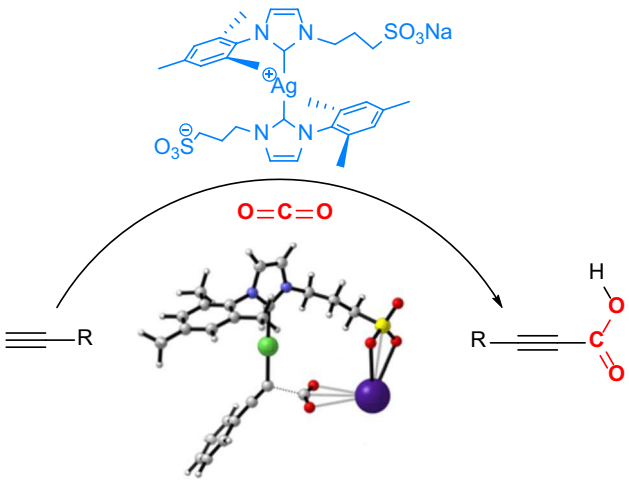
Received: 13 September 2016 / Accepted: 12 November 2016

Abstract The direct interaction between CO_2 and terminal alkynes in the presence of bis-(NHC)-metal catalysts at ambient conditions was studied. Two Cu and Ag-based bis-*N*-heterocyclic carbene Transition Metal catalysts were synthesized. The $(NHC)_2$-Ag complex showed a better catalytic performance towards the carboxylation of terminal alkynes in comparison with the copper analogue even for the conversion of acetylene gas. The optimized conditions for the carboxylation are: the use of Cs_2CO_3 as additive, one atmosphere CO_2 and room temperature using 1% mol catalyst. Mechanistic insight into the reaction mechanism is obtained by means of state-of-the-art first principles calculations.

Graphical Abstract



Keywords Carboxylation · Terminal alkyne · *N*-Heterocyclic carbene · Homogeneous catalysis · DFT

Electronic supplementary material The online version of this article (doi:10.1007/s10562-016-1920-5) contains supplementary material, which is available to authorized users.

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1 Introduction

As an abundant, economical and renewable carbon source, carbon dioxide is of great interest and has attracted much attention for its efficient utilization, which has become a long-term target and research hotspot [1–9]. At present, the conversion of carbon dioxide into useful fine chemicals receives extensive attention and motivates scientists' interest [10]. In the field of carbon dioxide fixation, one of the most promising catalytic reactions is the direct reaction from carbon dioxide with other organic compounds to carboxylic acids and related derivatives [11]. Though organolithium and Grignard reagents can react with carbon dioxide easily, it is impossible to synthesize functionalized carboxylic acid compounds using these complexes [12]. On the contrary, transition-metal-catalyzed carboxylation of less reactive terminal alkynes or alkenes [13–15] and other nucleophiles [16–26], such as organozinc, organoboron, and organosilicone, with CO_2 provide an efficient approach to diverse functionalized carboxylic acids and derivatives [27–33].

In numerous CO_2 transformations, the direct insertion has become the main field due to easy C–H bond activation of terminal alkynes [34–36]. In 2010, Yu and Zhang [37] applied a copper *N*-heterocyclic carbene system combined with a base, and immobilized this on a polymer generating a Poly[$(NHC)_{0.5}(NHC\text{-}Cu)_{0.5}$] species for the direct carboxylation of terminal alkynes. Later on, he reported on a new approach applying a silver nano-polymeric heterocyclic carbene as catalyst realizing the reaction between CO_2 molecules and terminal alkynes and the recycling of the catalyst [38]. In 2011, apart from complicated systems, Lu's group worked out the carboxylation of terminal alkynes in CO_2 atmosphere while utilizing AgI as catalyst in combination with Cs_2CO_3 as basic additive (50–60 °C, 2 atm) [39]. In 2012, Gooßen and co-workers similarly studied the CO_2 inserting in terminal alkynes catalyzed by silver tetrafluoroborate instead of silver iodide [40]. One of the major drawbacks of the Ag-based catalyst systems is their high ambient and light sensitivity, which makes their manipulation highly complicated, besides the elevated cost of the silver precursors or ligands utilized and the use of the environmentally toxic DMF as reaction solvent [41]. Despite the present achievements for the catalytic CO_2 insertion into terminal alkynes, several drawbacks need to be optimized for the carboxylation process. Due to the inherent chemical thermodynamic and kinetic stabilities, rigorous catalytic conditions such as high temperature and pressure are usually required to offer the energy for the endothermic carboxylation. Additionally, the suitable catalysts for the reaction are usually made from expensive ligands or metal sources, which hinder the industrial development of the direct carboxylation of CO_2 and terminal alkynes [40]. Since the utilization of thegases CO_2 and acetylene gas can lead to the generation of the important medical intermediate propiolic acid, the research of simple and efficient catalytic system used for direct carboxylation in mild conditions is urgently required [42].

In 2006, Saughnessy and co-workers reported the synthetic strategy for the ligand 1-(2,4,6-trimethylphenyl)-3-(3-sulfo-propyl)-imidazole, which was used to generate the silver bis *N*-heterocyclic carbene catalysts **2** (Fig. 1) [43]. Verpoort and co-workers used the same ligand to synthesize catalyst **1** in Click reactions [44], Both complexes exhibit high ambient stability and robustness. Herein, based on earlier investigations in this field, we present unprecedented notable activities for two metal bis *N*-heterocyclic carbene complexes **1** and **2** (Fig. 1) for the terminal alkyne C–H bond activation. The catalytic performance for the direct carboxylation using CO_2 was investigated as well as the suitable catalytic conditions and substrate adaptability (Fig. 1). This work represents,

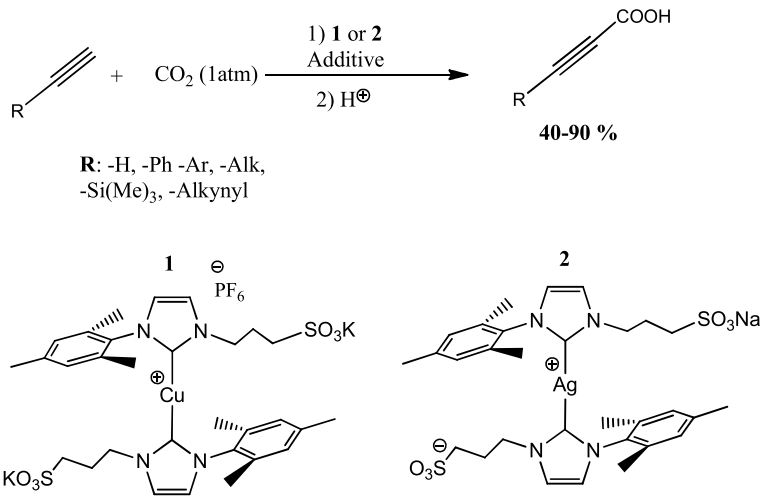


Fig. 1 Carboxylation of terminal alkynes by catalysts **1** and **2**

at the best of our knowledge, the first documented case of the use of bis-(NHC)-metal complexes for the carboxylation of terminal alkynes.

2 Experimental

2.1 Materials and Instrumentation

All reagents were used as received, Cu(I) sources were stored under argon in a glove box. Solvents were dried using standard procedures. 1-(2,4,6-Trimethylphenyl)-3-(3-sulfonato-propyl)-imidazolium and bis(1-mesityl-3-(3-sulfonatopropyl)imidazol-2-ylidene) silver sodium salt were synthesized according to literature procedures [43]. NMR characterizations were carried out using a Bruker Advance 500 MHz spectrometer, chemical shifts (δ) are reported in parts per million (ppm) referenced to tetramethylsilane (^{1}H) or the internal (NMR) solvent signals (^{13}C). Terminal alkynes were purchased and used without further purification. Carboxylation experiments were carried out under dry conditions. 1-(2,4,6-Trimethylphenyl)-imidazole [45], 1-(2,4,6-trimethylphenyl)-3-(3-sulfonato-propyl)-imidazolium, bis[1-(4-sodiumsulfonatebutyl)-3-(2,4,6-trimethyl-phenyl)-4,5-imidazolyl-3-ylidine] copper(I) hexafluorophosphate (**1**) [44] and bis(1-mesityl-3-(3-sulfonatopropyl)imidazol-2-ylidene) silver sodium salt (**2**) were prepared according to literature procedures [43].

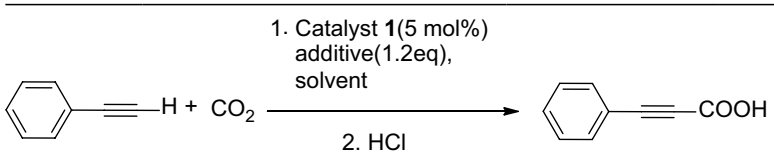
2.2 General Procedure for the Carboxylation Reaction of Terminal Alkynes with Carbon Dioxide

A suitable catalytic loading of complex **1** or **2** was dissolved in 1 ml of dried DMSO in a 10 ml Schlenk flask along with 1.2 eq Cs_2CO_3 (391 mg) and 1 mmol terminal alkyne under inert atmosphere. Then CO_2 gas was bubbled continuously through the reaction mixture under continuous stirring for 16 h at room temperature. After the reaction time, diluted HCl acid was added to the mixture until pH = 1. Thereafter, extraction with ethyl acetate separated the product from the solution, after which anhydrous magnesium sulfate was added to dry organic phase. Finally, after filtration the solvent was removed under reduced pressure, giving the pure product, which was characterized by ^{1}H and ^{13}C-NMR.

2.3 Computational Methods

The proposed catalytic cycles for catalyst **1** and **2** (Cu, and Ag, respectively) were studied by means of Density Functional Theory (DFT). All intermediates and transition states were fully optimized at the DFT level of theory using the B3LYP hybrid functional ([46] and references therein) as implemented in Gaussian09 [47]. The double-zeta Pople

Table 1 Different conditions applied for the optimization of the carboxylation of phenyl acetylene with catalyst **1**



Entry	Solvent	Additive	Pressure (bar)	Temperature (°C)	Yield (%)[a]
1	DMF	K_2CO_3	1	R.T.	45
2	DMF	Cs_2CO_3	1	R.T.	50
3	DMSO	K_2CO_3	1	R.T.	25
4	DMSO	Cs_2CO_3	1	R.T.	80
5	DMSO	Cs_2CO_3	1	50	20
6	DMSO	Cs_2CO_3	35	R.T.	50
7	DMF-H_2O	Cs_2CO_3	35	R.T.	15
8	DMF-H_2O	Cs_2CO_3	35	50	~5
9	DMSO-H_2O	Cs_2CO_3	35	R.T.	20
10	DMSO-H_2O	Cs_2CO_3	35	50	15

Reaction conditions: (1) phenyl acetylene (1 mmol) at CO_2 atmosphere, catalyst **1** (0.05 mmol, 5 mol%), 1.2 eq additive, 16 h; (2) HCl 2N was used to acidify the reaction mixture

[a]Catalytic yields were calculated using ^{1}H-NMR integration using 1,4-ethynylbenzene as internal standard

basis set 6–311G(3df,2p) was used for all the atoms except for Cu and Ag, for which the LANL2DZ effective core potential and basis set was applied [48]. The frequencies were calculated at the same level of theory as the geometry optimizations and confirmed that all structures were either local minima on the potential energy surface or transition states. Furthermore, also the van der Waals corrections as developed by Grimme were included [49]. More specifically, the dispersion corrections are calculated according to the third version of Grimme [50]. The calculation procedures for the activation free energy barriers and reaction free energies were performed with the software module TAMKIN [51].

3 Results and Discussion

3.1 Optimizing Reaction Conditions

The effects of catalytic loading, solvent, base, pressure and temperature play a significant role in the direct carboxylation of terminal alkynes. Here, phenyl acetylene was selected as standard substrate to test the catalytic performance using a variety of base additives and solvents along with 5 mol% copper catalyst **1** under carbon dioxide atmosphere for 16 h. The different reaction conditions (solvent, base, pressure and temperature) together with the %-yields are given in Table 1.

The results indicate that the utilization of DMF or DMSO as solvent made little difference with respect to the yield (entry 1–4, Table 1). Aiming to take advantage of the high water solubility of the catalyst due to the presence of sulphate groups on the NHC ligand, mixed solvents of DMF-H_2O and DMSO-H_2O were selected as reaction media, (entry 7–10), which disclosed that water has a deleterious effect on the catalytic performance. Experiments carried out with phenyl acetylene in aqueous conditions confirmed the inhibition of the carboxylation (Table S1, Supporting Information). Therefore, dried organic solvents such as DMF or DMSO are the preferred solvents for catalysis. The addition of Cs_2CO_3 (1.2 eq) as base additive resulted in higher yields than adding K_2CO_3, suggesting that the use of a stronger base is beneficial for the catalytic process. Moreover, the sharp increase of pressure from 1 bar (entry 4) to 35 bar (entry 6) gave rise to a notable drop of the yield from 80 to 50%, although this is not necessarily a clear indicative of a harmful effect of the positive pressure. In this case, a very high concentration of CO_2 was applied, thus hindering the dissociation of the catalytically active mono-(NHC)-Cu species. In case of entries 4–5, 7–8, and 9–10, the temperature was increased from room temperature to 50 °C, contrarily the catalytic yields decreased, revealing that room temperature was

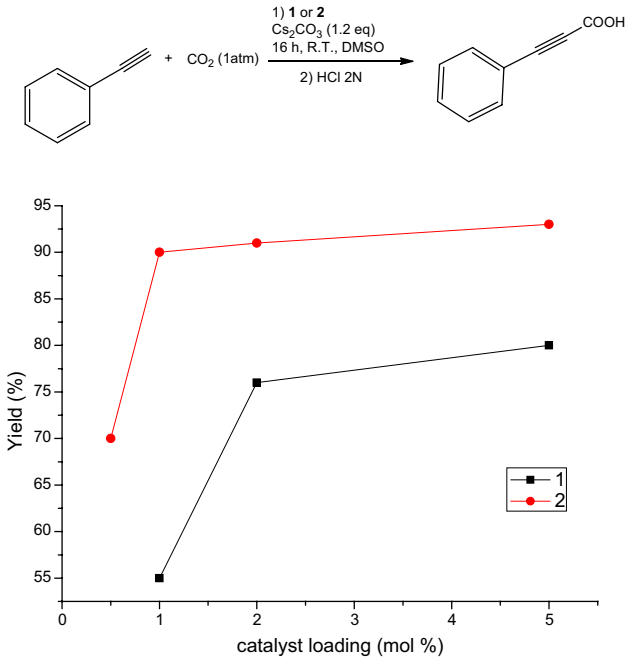


Fig. 2 Comparison of catalytic yields between catalysts **1** and **2** for the carboxylation of terminal alkynes. (Catalytic yields were determined via ^{1}H-NMR integration.)

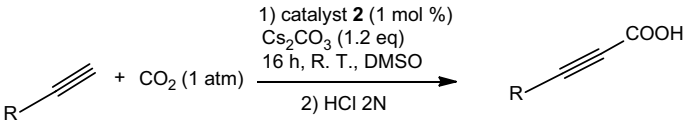
considered to be beneficial for the catalytic system while elevated temperatures had a deleterious effect on the catalytic performance. Some experiments carried out at temperatures higher than 50 °C have shown a clear decrease on the yield, ascribed to the instability of the metal-propiolate intermediate formed mainly due to the reversibility of this initial step, taking this process towards the initial reactants condition. Furthermore, it is well known that Cu catalysts can activate decarboxylation of propiolic acids efficiently at 60 °C [37, 52, 53]. Based on the analysis above, we optimized the reaction conditions for following carboxylation experiments: DMSO as solvent, 1.2 eq Cs_2CO_3 as base additive, atmospheric pressure and ambient temperature using our Cu and Ag-based catalyst systems.

3.2 Activity of Bis-(NHC)-Cu vs. Bis-(NHC)-Ag Catalysts

For the study of the catalyst performance of both complexes **1** and **2** (Fig. 1), 1 equivalent of phenyl acetylene and 1.2 equivalents Cs_2CO_3 were added in DMSO under 1 atm of CO_2 at room temperature for 16 h, followed by acidification of the crude product. A comparison was made in order to determine which catalyst demonstrated the best catalytic performance for the carboxylation (Fig. 2).

From the graph displayed in Fig. 2, it is apparent that the Ag-NHC complex outperformed the Cu-based one for the carboxylation reaction. At all catalyst loadings, higher

Table 2 Bis-(NHC)-Ag catalyzed carboxylation of alkynes



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

Reaction conditions: (1) 1 bar of CO_2 atmosphere, room temperature, catalyst 2 (0.01 mmol, 1 mol %), 1.2 eq Cs_2CO_3, 16 h; (2) HCl 2N to acidify the mixture

[a]Catalytic yields are obtained by ^{1}H-NMR integration

[b]2.4 eq of Cs_2CO_3

activities under the same conditions were obtained for catalyst **2** in comparison with catalyst **1**. When the catalyst loading of **2** were 1 mol% or higher, only slight changes in the catalytic yield was observed, reaching values from 90 to 93%. On the contrary, when the catalytic loading was decreased to 0.5 mol%, a notable drop in yield to 70% was noticed. According to these results, aimed for optimized catalytic conditions, we selected 1 mol% catalyst **2** as the suitable catalytic loading for carboxylation of terminal alkynes.

3.3 Substrate Scope of Catalysts

Due to the higher catalytic activity of **2** we explored the substrate scope of **2** using the optimized conditions (Table 2). The results obtained with a series of terminal alkynes reveal that the reactivity of the bis-(NHC)-Ag complex towards the used alkynes is variable, probably due to the difference in acidity of the alkyne proton. As clearly depicted in Table 2, in entry 1–3, when using aromatic terminal alkynes as substrates, which are the most acidic amongst the substrates applied, the catalytic yields could be over 85%, showing higher reactivity towards carboxylation than the rest of the substrates investigated. In the contrary, among entry 4–7, the highest yield from aliphatic terminal alkynes was not higher than 77% (entry 4), thus indicating that the presence of a benzene ring is beneficial for the high conversion of terminal alkynes with CO_2. We consider this is attributed to the conjugative effect of the benzene ring, lowering thereby the electron density of the alkynyl group which moves toward the benzene ring to reach a more steady structure. Hence, the C–H bond of the alkynyl group is much easier to be activated, and thus causing a facile carboxylation reaction. However, it is expected that the behavior of complex **2** towards substrates containing electron-withdrawing groups (e.g. R = *para*-NO_2, NC, CHO-Ph,) may not be so efficient for carboxylation, since such groups lower the electron density on the Pi-bonds of the alkyne, producing a weaker NHC-M-acetylide bond. Such trend was already experimentally observed by Zhang [37].

In entry 3 and 4, diynes were selected as substrates on account of the hypothesis that a dicarboxylic acid may be obtained. But unexpectedly, according NMR spectra of the products (Supporting Information), diynes were not fully carboxylated since complex **2** could only catalyze the conversion of the dyines into mono propiolic acids instead of the double carboxylated analogs even when increasing the amount of base up to ten equivalents. Unfortunately, a reason for this unexpected behavior remains unknown.

3.4 Mechanism of Catalyzed Carboxylation of Terminal Alkynes Using Bis-(NHC)-M (M=Cu, Ag)

There was no experimental approach to determine what the real active species is, however, with DFT calculations on bis-(NHC)-complexes, we could not find any possible reaction pathway for the CO_2-addition due to the steric effects of the ligands. Therefore, bis-NHC complexes were eliminated as possible candidates to catalyze the CO_2 addition and mono-NHC-complexes were used for further study [44, 54]. ^{1}H-NMR experiments made by Nolan et al. for bis-(NHC)-Cu(I) complexes in Azide-Alkyne Cycloaddition reactions further confirmed the existence of a mono-NHC-complex as the real active species [54]. In order to obtain a full mechanistic understanding of the catalyst, we decided

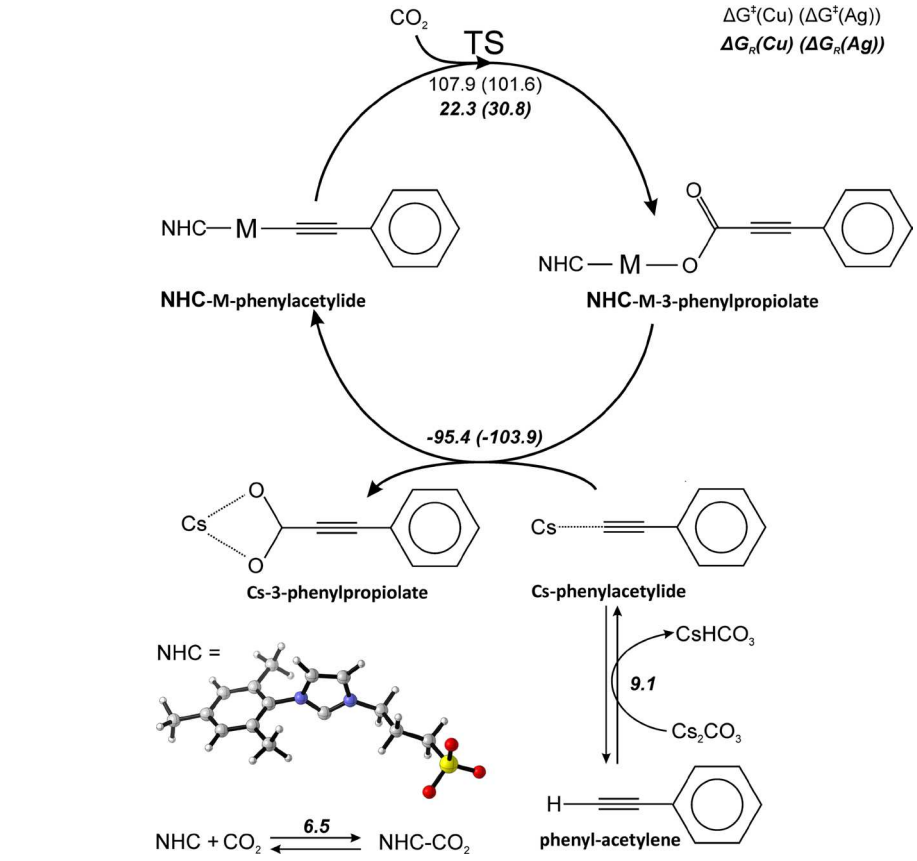


Fig. 3 Calculated catalytic mechanism of carboxylation between phenyl acetylene and CO_2. Reaction free energy barriers $\Delta G^{\ddagger}$ and reaction free energies ΔG_R are given in kJ/mol at 298 K for catalyst **1** and in *brackets* for catalyst **2**. The results were obtained at the B3LYP/6-311g (3df,2p)-D3 level of theory

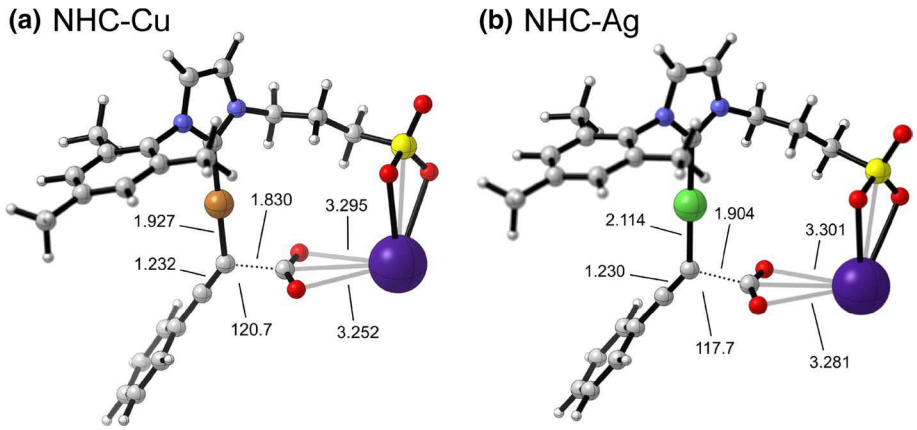


Fig. 4 Overview of difference in TS geometry between catalyst **1** (NHC-Cu) and catalyst **2** (NHC-Ag)

to investigate the feasibility of the described reaction mechanism with state of the art first principle calculations assuming gas phase conditions (Fig. 3). More specifically, the carboxylation of phenyl acetylene and CO_2 was studied for catalysts **1** and **2** (Fig. 1) employing the B3LYP/6-311g(3df,2p) level of theory (see above for a detailed description of the computational methodology, Sect. 2.3). Note first that in the active mono-metal-NHC catalysts, we considered Cs coordination to the $–SO_3^-$ group of the NHC ligand (Fig. 4). Whenever an NHC-M-phenylacetylide is formed in the catalytic cycle, it can react with CO_2 to form an NHC-M-3-phenylpropiolate. For conciseness, we present the elimination of NHC-M-3-phenylpropiolate as well as the creation of NHC-M-phenylacetylide as an equilibrium reaction from Cs-phenylacetylide, rather than showing all separate steps (Fig. 4). The activation free energy for the rate determining CO_2 addition step in the catalytic cycle is about 6 kJ/mol higher for NHC-Cu (catalyst **1**) with respect to NHC-Ag (catalyst **2**). A difference in 6 kJ/mol, should be visible in an a least approximately ten times faster initial

reaction rate, which compares favorably with the observed activity difference between both catalysts (Fig. 2). The geometric comparison between both transition states shows a larger C–C coupling distance for NHC-Ag, which points to a more early transition state. Moreover, for NHC-Ag the Metal phenylacetylide distance is larger, which explains its faster activation (or lower free energy barrier). For both catalysts, the generation of the NHC-M-phenylacetylide is modeled as an exergonic equilibrium step where Cs-phenylacetylide and NHC-M-3-phenylpropiolate are consumed and Cs-3-phenylpropiolate is produced. Remark that this scheme represents just one possible reaction route. Another route could be CO_2 addition via a CO_2-carbene adduct rather than a CO_2 molecule, as was also investigated by Yang et al. [55]. However, this type of addition could not compete with regular CO_2 addition and was therefore omitted for further investigation (a comparison is shown in Figure S.1, see supporting information). Other CO_2 addition routes have been postulated by Liu et al. for anionic Ag complexes [56], yet the transition states found here, happen in a similar fashion compared to the anionic complexes.

With a reaction free energy difference of only 6.5 kJ/mol, CO_2 can be activated by a free NHC [37], forming a NHC-CO_2 adduct, which can act as a temporarily CO_2 storage in the solvent phase.

According to the experimental results, there is a strong relationship between the acidity of the terminal alkyne hydrogen and the total conversion to propionic acid, therefore, the driving force of the reaction must be the proton withdrawal from the alkyne by the cesium carbonate and concomitant formation of the cesium-acetylide intermediate (Fig. 4). This also explains why the use of Cs_2CO_3 as a stronger base gives better results than K_2CO_3 (see Table 1). With a modeled reaction free energy of 9.1 kJ/mol, the formation of Cs-phenylacetylide from Cs_2CO_3can indeed be regarded as feasible. For completeness, free energy differences and their respective enthalpy and entropy contributions for all catalytic pathways in this paper are summarized in Table S.2 (supplementary information). The influence of the free NHC is supported by the works of Zhang et al. where the application of a polymer supported-free NHC mixed with metal-NHC complexes of Cu and Ag (I) dramatically increased the yield of the carboxylation reactions of a wide variety of substrates [38]. After the formation of the NHC-M-3-phenylpropiolate, intermolecular ion exchange to form the corresponding cesium phenylpropiolate takes place with the concomitant release of the mono NHC-M species. Finally, this cesium phenylpropiolate salt is converted to the acid after the addition of HCl. A decrease in catalytic activity when a high CO_2 pressure is applied (Table 1) might come from the high concentration of CO_2 in the reaction media, affecting the equilibrium between the bis- and mono-metal-(NHC) species, and hence hindering the formation of the last species. This is also an indication that there is no coordination of DMSO with the Ag(I), which accounts for the catalytic activity when Ag(I) salts are used, as was suggested by Gooβen [57].

4 Conclusion

In this report, we successfully applied a Cu(I) and a Ag(I)-based sulfonated-bis(*N*-heterocyclic carbene) complexes in the carboxylation reaction of a series of terminal alkynes with carbon dioxide. The feasibility of the carboxylation reaction and suitable reaction conditions for both complexes were studied in depth. From this analysis, it turned out that the Ag-bis(NHC) complex showed a higher conversion at lower catalyst load than the Cu-based analog, and that our optimal reaction conditions were attained when using a dry DMSO solution of terminal alkyne and CO_2 at 1 atm along with 1 mol% of bis-(NHC)-Ag catalyst, using 1.2 eq of base Cs_2CO_3 at room temperature. These conditions can lead to yields higher than 90% within 16 h. Furthermore, the acidity of the proton at the terminal alkyne mostly determined the yield of the carboxylation, as indicated by the high yields obtained when using aromatic alkynes as substrates, given by their higher acidity compared to the rest of the substrates applied. Based on these results, we computationally modeled a reaction mechanism where the active site of the complex is on a metal-mono-NHC species. The comparison of free energy barriers quantitatively confirmed that the Mono-Ag-(NHC) is more active than the Mono-Cu-(NHC), which is in good agreement with the experiments and an extra validation of the postulated reaction mechanism.

Acknowledgements F.V. acknowledges the Chinese Central Government for an "Expert of the State" position in the program of Thousand talents. H. D. V. acknowledges funding from the research funds of the Mexican Petroleum institute for a postdoctoral fellowship No. 90903. M.V. acknowledges funding from the Scientific Research-Foundation Flanders (FWO) for a postdoctoral fellowship. The computational resources and services used in this work were provided by VSC (Flemish Supercomputer Center), funded by the Hercules foundation and the Flemish Government—Department EWI. The authors would like to express their deep appreciation for financial support from the Natural Science Foundation of China (No. 21172027), the Fundamental Research Funds for the Central Universities (WUT: 2014-IV-099) and Independent Innovation Foundation of Wuhan University of Technology (No. 444-20510039).

References

1. Louie J (2005) Transition metal catalyzed reactions of carbon dioxide and other heterocumulenes. Curr Org Chem 9:605

2. Mori M (2007) Regio- and stereoselective synthesis of tri- and tetrasubstituted alkenes by introduction of CO_2 and alkylzinc reagents into alkynes. Eur J Org Chem 2007:4981–4993. doi:10.1002/ejoc.200700196
3. Sakakura T, Choi J-C, Yasuda H (2007) Transformation of carbon dioxide. Chem Rev 107:2365–2387. doi:10.1021/cr068357u
4. Aresta M, Dibenedetto A, Mathisen A, et al (2007) Utilisation of CO_2 as a chemical feedstock: opportunities and challenges. Dalt Trans 17:2975. doi:10.1039/b700658f
5. Riduan SN, Zhang Y (2010) Recent developments in carbon dioxide utilization under mild conditions. Dalt Trans 39:3347. doi:10.1039/b920163g
6. Correa A, Martín R (2009) Metal-catalyzed carboxylation of organometallic reagents with carbon dioxide. Angew Chem Int Ed 48:6201–6204. doi:10.1002/anie.200900667
7. Federsel C, Jackstell R, Beller M (2010) State-of-the-art catalysts for hydrogenation of carbon dioxide. Angew Chem Int Ed 49:6254–6257. doi:10.1002/anie.201000533
8. Huang K, Sun C-L, Shi Z-J et al (2011) Transition-metal-catalyzed C–C bond formation through the fixation of carbon dioxide. Chem Soc Rev 40:2435. doi:10.1039/c0cs00129e
9. Liu Q, Wu L, Jackstell R, Beller M (2015) Using carbon dioxide as a building block in organic synthesis. Nat Commun 6:5933. doi:10.1038/ncomms6933
10. Aresta M, Dibenedetto A, Quaranta E (2016) State of the art and perspectives in catalytic processes for CO_2 conversion into chemicals and fuels: the distinctive contribution of chemical catalysis and biotechnology. J Catal. doi:10.1016/j.jcat.2016.04.003
11. Liu A-H, Yu B, He L-N (2015) Catalytic conversion of carbon dioxide to carboxylic acid derivatives. Greenh Gases Sci Technol 5:17–33. doi:10.1002/ghg.1461
12. Kim SH, Kim KH, Hong SH (2014) Carbon dioxide capture and use: organic synthesis using carbon dioxide from exhaust gas. Angew Chem Int Ed 53:771–774. doi:10.1002/anie.201308341
13. Ukai K, Aoki M, Takaya J, Iwasawa N (2006) Rhodium(I)-Catalyzed Carboxylation of Aryl- and Alkenylboronic Esters with CO_2. J Am Chem Soc 128:8706–8707. doi:10.1021/ja061232m
14. Takaya J, Tadami S, Ukai K, Iwasawa N (2008) Copper(I)-catalyzed carboxylation of aryl- and alkenylboronic esters. Org Lett 10:2697–2700. doi:10.1021/ol800829q
15. Ohmiya H, Tanabe M, Sawamura M (2011) Copper-catalyzed carboxylation of alkylboranes with carbon dioxide: formal reductive carboxylation of terminal alkenes. Org Lett 13:1086–1088. doi:10.1021/ol103128x
16. Greco GE, Gleason BL, Lowery TA et al (2007) Palladium-catalyzed [3+2] cycloaddition of carbon dioxide and trimethylenemethane under mild conditions. Org Lett 9:3817–3820. doi:10.1021/ol7017246
17. Aoki M, Izumi S, Kaneko M et al (2007) Ni(0)-promoted hydroxycarboxylation of 1,2-dienes by reaction with CO_2 and O_2. Org Lett 9:1251–1253. doi:10.1021/ol070038h
18. Takaya J, Iwasawa N (2008) Hydrocarboxylation of allenes with CO_2 catalyzed by silyl pincer-type palladium complex. J Am Chem Soc 130:15254–15255. doi:10.1021/ja806677w
19. Correa A, Martín R (2009) Palladium-catalyzed direct carboxylation of aryl bromides with carbon dioxide. J Am Chem Soc 131:15974–15975. doi:10.1021/ja905264a
20. Louie J, Gibby JE, Farnworth MV, Tekavec TN (2002) Efficient nickel-catalyzed [2+2+2] cycloaddition of CO_2 and diynes. J Am Chem Soc 124:15188–15189. doi:10.1021/ja027438e
21. Takimoto M, Nakamura Y, Kimura K, Mori M (2004) Highly enantioselective catalytic carbon dioxide incorporation reaction: nickel-catalyzed asymmetric carboxylative cyclization of bis-1,3-dienes. J Am Chem Soc 126:5956–5957. doi:10.1021/ja049506y
22. Fujihara T, Xu T, Semba K et al (2011) Copper-catalyzed hydrocarboxylation of alkynes using carbon dioxide and hydrosilanes. Angew Chem Int Ed 50:523–527. doi:10.1002/anie.201006292
23. Yoo W, Li C (2008) Copper-catalyzed four-component coupling between aldehydes, amines, alkynes, and carbon dioxide. Adv Synth Catal 350:1503–1506. doi:10.1002/adsc.200800232
24. Zhang X, Jia Y-B, Lu X-B et al (2008) Intramolecularly two-centered cooperation catalysis for the synthesis of cyclic carbonates from CO_2 and epoxides. Tetrahedron Lett. doi:10.1016/j.tetlet.2008.09.035
25. Darensbourg DJ, Moncada AI (2010) Tuning the selectivity of the oxetane and CO_2 coupling process catalyzed by (Salen)CrCl/n-Bu_4 NX: cyclic carbonate formation vs aliphatic polycarbonate production. Macromolecules 43:5996–6003. doi:10.1021/ma100896x
26. Ebert GW, Juda WL, Kosakowski RH et al (2005) Carboxylation and esterification of functionalized arylcopper reagents §. J Org Chem 70:4314–4317. doi:10.1021/jo047731s
27. Yoshida H, Fukushima H, Ohshita J, Kunai A (2006) CO_2 incorporation reaction using arynes: straightforward access to benzoxazinone. J Am Chem Soc 128:11040–11041. doi:10.1021/ja064157o
28. Yoshida H, Morishita T, Ohshita J (2008) Direct access to anthranilic acid derivatives via CO_2 Incorporation reaction using arynes. Org Lett 10:3845–3847. doi:10.1021/ol801588s
29. Tan M, Zhang Y, Ying JY (2009) Hydrosilylation of ketone and imine over poly-*N*-heterocyclic carbene particles. Adv Synth Catal 351:1390–1394. doi:10.1002/adsc.200800815
30. Chen G, Fu C, Ma S (2009) A novel synthesis of 1,3-oxazine-2,4-diones via a simple and efficient reaction of CO_2 with 2,3-allenamides. Org Lett 11:2900–2903. doi:10.1021/ol9009046
31. Chen G, Fu C, Ma S et al (2011) A novel synthesis of oxazolidine-2,4-diones via an efficient fixation of CO_2 with 3-aryl-2-alkynamides. Org Biomol Chem 9:105–110. doi:10.1039/C0OB00550A
32. Vechorkin O, Hirt N, Hu X (2010) Carbon dioxide as the C1 source for direct C–H functionalization of aromatic heterocycles. Org Lett 12:3567–3569. doi:10.1021/ol101450u
33. Peterson SL, Stucka SM, Dinsmore CJ (2010) Parallel synthesis of ureas and carbamates from amines and CO_2 under mild conditions. Org Lett 12:1340–1343. doi:10.1021/ol100259j
34. Boogaerts IIF, Nolan SP (2010) Carboxylation of C–H bonds using *N*-heterocyclic carbene gold(I) complexes. J Am Chem Soc 132:8858–8859. doi:10.1021/ja103429q
35. Boogaerts IIF, Nolan SP, Riduan SN et al (2011) Direct C–H carboxylation with complexes of the coinage metals. Chem Commun 47:3021–3024. doi:10.1039/C0CC03890C
36. Sasano K, Takaya J, Iwasawa N (2013) Palladium(II)-catalyzed direct carboxylation of alkenyl C–H bonds with CO_2. J Am Chem Soc 135:10954–10957. doi:10.1021/ja405503y
37. Yu D, Zhang Y (2010) Copper- and copper-*N*-heterocyclic carbene-catalyzed C–H activating carboxylation of terminal alkynes with CO_2 at ambient conditions. Proc Natl Acad Sci 107:20184–20189. doi:10.1073/pnas.1010962107
38. Yu D, Tan MX, Zhang Y (2012) Carboxylation of terminal alkynes with carbon dioxide catalyzed by poly(*N*-heterocyclic carbene)-supported silver nanoparticles. Adv Synth Catal 354:969–974. doi:10.1002/adsc.201100934
39. Zhang X, Zhang W-Z, Ren X et al (2011) Ligand-free Ag(I)-catalyzed carboxylation of terminal alkynes with CO_2. Org Lett 13:2402–2405. doi:10.1021/ol200638z
40. Manjolinho F, Arndt M, Gooßen K, Gooßen LJ (2012) Catalytic C–H carboxylation of terminal alkynes with carbon dioxide. ACS Catal 2:2014–2021. doi:10.1021/cs300448v

41. Guo C-X, Yu B, Xie J-N et al (2015) Silver tungstate: a single-component bifunctional catalyst for carboxylation of terminal alkynes with CO_2 in ambient conditions. Green Chem 17:474–479. doi:10.1039/C4GC01638F
42. Maeda K, Goto H, Yashima E (2001) Stereospecific polymerization of propiolic acid with rhodium complexes in the presence of bases and helix induction on the polymer in water. Macromolecules 34:1160–1164. doi:10.1021/ma001651i
43. Moore LR, Cooks SM, Anderson MS et al (2006) Synthesis and characterization of water-soluble silver and palladium imidazol-2-ylidene complexes with noncoordinating anionic substituents. Organometallics 25:5151–5158. doi:10.1021/om060552b
44. Díaz Velázquez H, Ruiz García Y, Vandichel M et al (2014) Water-soluble NHC-Cu catalysts: applications in click chemistry, bioconjugation and mechanistic analysis. Org Biomol Chem 12:9350–9356. doi:10.1039/C4OB01350F
45. Liu J, Chen J, Zhao J et al (2003) A modified procedure for the synthesis of 1-arylimidazoles. Synthesis 2003:2661–2666. doi:10.1055/s-2003-42444
46. Becke AD (1993) Density-functional thermochemistry. III. The role of exact exchange. J Chem Phys 98:5648. doi:10.1063/1.464913
47. Gaussian 09 citation http://www.gaussian.com/g_tech/g_ur/m_citation.htm
48. Hay PJ, Wadt WR (1985) Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. J Chem Phys 82:270. doi:10.1063/1.448799
49. Grimme S (2004) Accurate description of van der Waals complexes by density functional theory including empirical corrections. J Comput Chem 25:1463–1473. doi:10.1002/jcc.20078
50. Ghysels A, Verstraelen T, Hemelsoet K et al (2010) TAMkin: a versatile package for vibrational analysis and chemical kinetics. J Chem Inf Model 50:1736–1750. doi:10.1021/ci100099g
51. Verstraelen T, Van Houteghem M, Van Speybroeck V, Waroquier M (2008) MD-TRACKS: a productive solution for the advanced analysis of molecular dynamics and Monte Carlo simulations. J Chem Inf Model 48:2414–2424. doi:10.1021/ci800233y
52. Kolarovič A, Fáberová Z (2009) Catalytic decarboxylation of 2-alkynoic acids. J Org Chem 74:7199–7202. doi:10.1021/jo901377b
53. Park K, Palani T, Pyo A, Lee S (2012) Synthesis of aryl alkynyl carboxylic acids and aryl alkynes from propiolic acid and aryl halides by site selective coupling and decarboxylation. Tetrahedron Lett. doi:10.1016/j.tetlet.2011.11.117
54. Díez-González S, Nolan SP (2008) $[(NHC)_2Cu]X$ complexes as efficient catalysts for azide-alkyne click chemistry at low catalyst loadings. Angew Chem Int Ed 47:8881–8884. doi:10.1002/anie.200803289
55. Yang L, Yuan Y, Wang H et al (2014) Theoretical insights into copper(i)–NHC-catalyzed C–H carboxylation of terminal alkynes with CO_2: the reaction mechanisms and the roles of NHC. RSC Adv 4:32457. doi:10.1039/C4RA00254G
56. Liu C, Luo Y, Zhang W et al (2014) DFT Studies on the silver-catalyzed carboxylation of terminal alkynes with CO_2: an insight into the catalytically active species. Organometallics 33:2984–2989. doi:10.1021/om500086u
57. Arndt M, Risto E, Krause T, Gooßen LJ (2012) C–H carboxylation of terminal alkynes catalyzed by low loadings of silver(I)/DMSO at ambient CO_2 pressure. ChemCatChem 4:484–487. doi:10.1002/cctc.201200047