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NHC-Ag/Pd Catalyzed Reductive Carboxylation of Terminal Alkyne with CO₂ and H₂, A Combined Experimental and Computational Study for Fine-Tuned Selectivity

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Abstract: Reductive carboxylation of terminal alkynes utilizing CO_2 and H_2 as reactants is an interesting and challenging transformation. Theoretical calculations indicated it would be kinetically possible to obtain cinnamic acid, the reductive carboxylation product, from phenylacetylene in a CO_2/H_2 system with *N*-heterocyclic carbene (NHC) supported Ag/Pd dual-metal catalysts *via* competitive carboxylation/hydrogenation cascade reactions in one step. These calculations have been verified experimentally with a poly-NHC-supported Ag/Pd catalyst. By tuning the catalyst composition and reaction temperature, phenylacetylene was selectively converted to cinnamic acid, hydrocinnamic acid or phenylpropiolic acid in excellent yields.

The use of carbon dioxide as an abundant, renewable and environmentally benign source of carbon in organic synthesis has seen great progress in the past decade.^[1] Among the many elegant examples using CO2 in organic synthesis, transition metal-catalyzed reductive carboxylation of alkynes with CO2 provides an efficient approach for the synthesis of synthetically attractive α,β -unsaturated alkenoic acid derivatives.^[2,3] Since Hoberg's seminal preparation of oxanickelacyclopentene derivatives from alkynes, CO₂ and nickel(0), the carbometalation of carbon-carbon triple bonds has been extended to enynes and diynes, affording a variety of conjugated alkenoic acids.^[4] In these early protocols, the carboxylic acid products were obtained by hydrolysis of oxanickelacyclopentenes, necessitating the use of stoichiometric quantities of Ni(0) Recent advances in the field of alkyne reagent. hydrocarboxylation incorporate Et₂Zn,^[5] Mn,^[6] or Zn ^[7] as reductants to regenerate Ni(0) from the oxametallocycle intermediate, enabling the reaction to be catalytic in nickel. However, these organometallic reagents and metal reductants are incompatible with terminal alkynes. Apart from nickel, copper-catalyzed alkyne hydrocarboxylations and boracarboxylations with CO2 and diboranes^[8] or hydrosilanes^[9] respectively have emerged, as well as cobalt-caltalyzed reductive carboxylations utilizing Zn powder as the external reductant.^[10] Mechanistically, the copper and cobalt catalytic cycles proceed by initial hydrometalation (or borametalation) of the alkyne, followed by CO₂-insertion at the carbon-metal bond.

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Scheme 1 Potential range of products from the Ag(Cu)/Pdcatalyzed reductive carboxylation of terminal alkynes with CO_2/H_2 mixtures.

From the environmental and economic points of view, using hydrogen gas as the reductant in the hydrocarboxylation of alkynes with carbon dioxide is much more attractive.^[11] However there is no existing system can directly convert alkynes to α,β unsaturated alkenoic acids with CO₂ and H₂ in one step. A dualmetal catalyst system could, in theory, realize this transformation under mild conditions. The reaction would proceed by initial carboxylation of the alkyne with CO₂ affording a propiolic acid which is subsequently reduced with H₂. Considering silver ^[12] and copper ^[13] are efficient catalysts for the conversion of terminal alkynes to propiolic acids with CO₂, while palladium is an established catalyst for the hydrogenation of unsaturated carbon-carbon bonds with H2,[14] there exists an opportunity to carry out terminal alkyne reductive carboxylation under a mixture of CO₂/H₂ gases with Ag(Cu)/Pd dual metal catalyst in a single system.

However, there are several competing reactions in this system each leading to a different product. As illustrated in Scheme 1, the alkyne could first undergo copper or silver-catalyzed carboxylation with CO₂ to form phenylpropiolic acid **A** (eq 1), upon which palladium-catalyzed semi-hydrogenation of acid **A** with H₂ would afford the desired alkenoic acid **B** (eq. 2). Further reduction of **B** would lead to saturated acid **C** (eq. 3). In addition, the terminal alkyne itself could be reduced by H₂ to form alkene **D** and alkane **E** (eq.s 4 and 5). Are there conditions that steer this system towards producing product **B** selectively? In the present work, we conducted theoretical computations using density functional theory (DFT) to provide a detailed understanding of the aforementioned competing reaction pathways. These findings guided experimental studies to identify conditions that lead to alkenoic acid **B** with exclusive selectivity.

We began by constructing energy profiles for three pertinent reaction pathways – carboxylation of the terminal alkyne (eq. 1), hydrogenation of alkynoic acid **A** (eq.s 2 and 3) and competitive semi-hydrogenation of the terminal alkyne (eq. 4). All species involved in the reaction, including reactants, products, minima, and transition states, were fully optimized by density functional theory using B3LYP ^[15] functional and DGDZVP ^[16] basis set as built in the Gaussian 09 package.^[17] All calculations are performed in DMF solvent using the Polarizable Continuum Model (PCM) ^[18,19], which using the integral equation formalism

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variant (so called IEFPCM) was initially devised by Tomasi and coworkers ^[18] and Pascual-Ahuir and coworkers.^[19] Poly-NHC ligands were selected for our study based on previous findings from one of our groups that these ligands promote copper and silver-catalyzed carboxylation of terminal alkynes with CO₂.^[12d, 13b, 20] The structure of poly-NHC and the simplified structure, i.e. NHC monomer used in calculations are shown in Figure 1a. A recent DFT study ^[21] on the pathways for C–H carboxylation of terminal alkynes determined that the reaction energy barrier is much lower when two NHCs are associated with the same copper center as a result of the second NHC increasing the electrophilicity of the metal center. In this study, we treated the NHC as a bidentate ligand.



Figure 1. (a) The structure of poly-NHC synthesized experimentally, and NHC monomer used in the calculations. (b) Reaction profile for the hydrogenation of phenylacetylene with a NHC-Pd catalyst. (c) Comparison of NHC-Cu and Ag-catalyzed carboxylation of phenylacetylene with CO₂. Full circle reaction profiles and stationary-point energies (Δ G). The bonding orbital of INT2 both in Cu- and Ag- catalyzed routes are shown, indicating Cu-C has stronger binding strength. In INT2_{Cu} Cu-C bond length is 1.99 Å and in INT2_{Ag} Ag-C bond length is 2.26 Å. TS stands for transition state. INT stands for intermediate.

The cationic pathway for phenylacetylene hydrogenation catalyzed by NHC-Pd catalyst was calculated (eq. 4, Scheme 1),^[22] as shown in Figure 1b. The initial migration of hydride to alkyne produces a vinyl palladium complex with a low energy barrier of 0.55 kcal/mol. For the reaction to proceed, an additional molecule of H₂ is added to the complex, forming coordination bonds with Pd. A second hydride migration to the vinyl ligand completes the overall addition of H₂ to phenylacetylene, generating styrene (**D**). The second step has

an energy barrier of 10.98 kcal/mol, which is the rate-limiting step for alkyne hydrogenation. Duckett et al.^[22] used a different Pd(dhpe) catalyst and calculated the barrier for two-step alkyne hydrogenation to be 1.24 and 9.18 kcal/mol respectively.

Continuing with phenylacetylene, we next studied its carboxylation reaction with CO2 using Cu and Ag catalysts (eq. 1, Scheme 1). The reactants were taken to be the NHC metal complex, CO₂, phenylacetylene (PhC≡CH) and inorganic base (K₂CO₃), and the products were PhC≡C–COOK and KHCO₃. The energy profiles of this reaction with NHC-complexed copper and silver catalysts are shown in Figure 1c, with the overall reaction being exergonic by 12.70 kcal/mol. In the presence of a base, the NHC complex reacts with phenylacetylene to form INT1 comprising metal acetylide complex (PhC=C-Cu/Ag-NHC) KHCO₃ and KI. On introducing CO₂ to the metal acetylide, the complex PhC≡C-Cu/Ag-NHC...CO₂ (INT2) is formed, in which the main donor-acceptor interaction is lone pair donation from the terminal carbon of the alkyne to the metal center as analyzed by Natural Bond Orbital method [21]. Both the orbital interaction and the stabilization energy E(2) indicate that Cu has stronger coordination ability than Ag (Figure 1c and Figure S3). Weaker binding between Ag and the acetylide, i.e. in INT2 Ag-C bond length is 2.26 Å vs. Cu-C bond length of 1.99 Å; Ag-C binding energy is 102.52 vs. Cu-C binding energy of 111.92 kcal/mol, would facilitate the next step of CO2 insertion.

The interatomic distance between C3(CO₂) and C1(alkyne) is 3.71 Å for INT2_{Cu} and 3.52 Å for INT2_{Ag} (Figure S2, SI). The transition state, TS, is formed as CO₂ continues to approach the metal-bound carbon of the acetylide (C1). The C1-C3 interatomic distance in TS_{Cu} is 2.10 Å, which compared to the C1-C3 interatomic distance in TS_{Aq} of 2.18 Å, corresponds to a change of 1.61 Å from INT2_{Cu}→TS_{Cu} versus 1.34 Å from $INT2_{Ag} \rightarrow TS_{Ag}$. Moreover, in the Cu-catalyzed route, the distance between the two phenyl side chains on the NHC ligand increases by 0.68 Å then decreases by 2.07 Å, whereas in the Ag-catalyzed route the Ph...Ph distance increases by 0.16 Å before decreasing by 1.44 Å. In all, the larger geometric change around the metal center throughout the Cu-catalyzed route compared to the Ag-catalyzed route also supports the higher reaction barrier for the reaction of CO2 with the NHC-Cu complex than the NHC-Ag complex. In TS, developing donoracceptor interactions between the terminal carbon of the alkyne and CO2 describes the partially formed C-C bond. Due to stronger electron donation from the terminal acetylide carbon to Cu than to Ag and the larger Ag ion, the terminal acetylide carbon will bear more negative charge when associated with NHC-Ag, facilitating attack at electrophilic C3(CO₂), thereby reducing the energy barrier for the Ag-catalyzed route. This unravels the electronic origins of the higher energy barrier associated with the Cu-catalyzed route.

Between the two metal systems, the reaction with NHC-Ag has a lower reaction barrier of 8.98 kcal/mol compared to the 13.61 kcal/mol energy barrier of the NHC-Cu route along this single reaction steps using the largest single activation barriers, and is expected to be more facile. The highest reaction barrier for phenylacetylene hydrogenation is 10.98 kcal/mol as presented in Figure 1b, which is higher than the reaction barrier

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for carboxylation catalyzed by Ag (8.98 kcal/mol) and lower than that of carboxylation catalyzed by Cu (13.61 kcal/mol). This suggests that for a mixture of phenylacetylene, CO₂ and H₂, an NHC-Ag/Pd catalyst promotes alkyne carboxylation while an NHC-Cu/Pd catalyst favors alkyne hydrogenation, considering the selectivity in reaction pathways is influenced by the interplay among the largest single activation barriers of competing pathways, esp. under kinetically controlled circumstances.



Figure 2. Reaction profile for the hydrogenation of phenylpropiolic acid to cinnamic acid (a) and the hydrogenation of cinnamic acid to hydrocinnamic acid (b) with a NHC-Pd catalyst.

Next, the cationic pathways for NHC-Pd-catalyzed hydrogenation of phenylpropiolic acid **A** to cinnamic acid **B** (eq. 2, Scheme 1) and subsequent hydrogenation of **B** to hydrocinnamic acid **C** (eq. 3) were calculated and are shown in Figure 2. The highest barrier for the hydrogenation of phenylpropiolic acid to generate cinnamic acid is 9.95 kcal/mol while the highest barrier for hydrogenation of cinnamic acid to hydrocinnamic acid is 14.17 kcal/mol. This result indicates that hydrogenation of phenylpropiolic acid to cinnamic acid is kinetically favored and it should thus be possible to realize high selectivity for the hydrocarboxylation product.

The DFT calculations suggested that the conversion of phenylacetylene to cinnamic acid with a mixture of CO_2/H_2 gases could be accomplished under Ag/Pd dual-metal catalyst. We then went on to verify these computational findings experimentally. Preliminary screening was carried out with a mixture of CO_2/H_2 gases and Cs_2CO_3 in dimethylformamide (DMF) (SI, Table S1).^[12,13] When Cu/Pd or Cu/Pt were used as catalysts, only hydrogenation products (styrene **D** and ethylbenzene **E**) were observed. There was no evidence for the formation of any carboxylation products. However, when a Ag/Pd catalyst mixture was employed, reductive carboxylation products **D** and **E**. When the Ag/Pd ratio and/or CO_2/H_2 ratio were increased, the ratio of carboxylation product increased. These encouraging preliminary results were found to be in

agreement with the DFT calculations described above.

We went on to fine-tune the reaction conditions with poly-NHC as the catalyst support. Poly-NHC ligands were synthesized as previously reported and combined with silver (I) and palladium (II) salts to afford mixed metal catalysts with the formula poly-(NHC-Ag)x(NHC-Pd)1-x. [12d,13b] As summarized in Table 1, increasing the Ag/Pd ratio from 1 to 5 caused the product distribution to shift from fully reduced hydrocinnamic acid C to semi-hydrogenated cinnamic acid B, to unreduced propiolic acid A at the highest ratio of Ag:Pd (entries 1-3). Extending the reaction time resulted in a greater proportion of fully reduced acid C (entries 2 and 4). When the reaction temperature was increased from 70 °C to 100 °C, only fully reduced hydrocinnamic acid C was observed (entry 5). By using a catalyst with the formula poly-(NHC)_{0.2}(NHC-Ag)_{0.6}(NHC-Pd)_{0.2} in which the overall metal content relative to NHC units was reduced, we were able to obtain the desired cinnamic acid product B with exclusive selectivity.

Having determined the ideal catalyst composition, other reaction conditions, such as base, solvent and temperature were further optimized. As shown in Table 1, Cs_2CO_3 and DMF represent the most suitable base and solvent combination for this reaction (entry 6 and 7). Under the optimized conditions of 85 °C over 16 h, reductive carboxylation product **B** was produced in near-quantitative yields. Increasing the reaction temperature to 100 °C affords fully reduced hydrocinnamic acid **C** exclusively, whereas lowering the temperature to 50 °C returns only phenylpropiolic acid **A**. This method can also be extended to other terminal alkynes, such as 1-hexyne (90% yield of substituted acrylic acid or heptanoic acid was achieved under similar conditions).

Table 1. Reaction conditions screening for hydrocarboxylation of phenylacetylene with CO_2/H_2 .^[a]



Entry	NHC/Ag/Pd	Base	T (°C)	t (h)	Product
2	molar ratio ^b				Ratio ^c
1 ^d	2:1:1	Cs ₂ CO ₃	70	15	B/C (1:1)
2^d	4:3:1	Cs_2CO_3	70	15	B/C (9:1)
3 ^d	6:5:1	Cs ₂ CO ₃	70	15	A/B (4:6)
4 ^d	4:3:1	Cs ₂ CO ₃	70	48	B/C (1:4)
5 ^d	2:1:1	Cs ₂ CO ₃	100	10	С
6	5:3:1	Cs ₂ CO ₃	85	16	B 99 (95)
7	5:3:1	K_2CO_3	85	16	B 80
8	5:3:1	Na ₂ CO ₃	85	16	B 30
9	5:3:1	Cs_2CO_3	95	16	B 99
10	5:3:1	Cs_2CO_3	50	16	A 95
11	5:3:1	Cs_2CO_3	120	16	C 99

^a Reaction conditions: phenylacetylene (1.0 mmol), CO₂ (50 psi), H₂ (50 psi), base (2.5 mmol), DMF (10 mL). Phenylacetylene was fully consumed at the end of the reaction. ^b Poly-NHC-Ag/Pd catalyst (5 mg), NHC/Ag/Pd refers to the molar ratio of total *N*-heterocyclic carbene, Ag and Pd. ^c Entries 1-5: Products were analyzed by GCMS and ¹H NMR spectroscopy, cinnamic acid **B** was observed with a *Z*:*E* ratio of 98:2 (Figure S3). Entries 6-11: Yields determined by ¹H NMR spectroscopy with isolated yield given in parentheses. ^d Phneylacetylene was fully converted to related products.

In conclusion, our theoretical calculations indicated that it is acid, kinetically possible to obtain cinnamic the hydrocarboxylation product, from phenylacetylene in a CO₂/H₂ system with NHC-supported Ag/Pd dual metal catalysts. The reaction barriers in the single reaction steps for Cu or Agcatalyzed alkyne carboxylation and Pd-catalyzed alkyne hydrogenation increase in the following order: Ag < Pd < Cu. This indicates the reaction pathway selectivity in the following order: Ag > Pd > Cu. The higher reaction barrier for NHCsupported Cu-catalyzed carboxylation, as opposed to Agcatalyzed carboxylation, could be rationalized from the relative stability of the metal acetylide complexes and different coordinating ability of phenylacetylide to the metal center. The reaction barriers for the Pd-catalyzed hydrogenation of unsaturated intermediates and substrate were found to be phenylpropiolic acid < phenylacetylene < cinnamic acid. Taken together, these calculations provided an important clue to the possibility of obtaining α,β -unsaturated alkenoic acids from terminal alkynes under a CO₂/H₂ atmosphere with a Ag/Pd dual catalyst system. These calculations have inspired and guided experimental endeavor for successful development a poly-NHC supported Ag/Pd catalyst for the carboxylation/hydrogenation cascade reaction of terminal alkyne with CO₂/H₂. By tuning the catalyst composition and reaction temperature, phenylacetylene was selectively converted to cinnamic acid, hydrocinnamic acid or phenyl propiolic acid in excellent yields.

Experimental Section

Poly-NHC-Ag/Pd catalyst synthesis Poly-NHC materials and Poly-NHC-Ag/Pd catalysts were synthesized based on literature.^[13b, 20] For P(NHC-Ag)_{0.5}(NHC-Pd)_{0.5}, AgNO₃ (42.5 mg, 0.25 mmol) and Pd(OAc)₂ (56 mg, 0.25 mmol) was added to a DMSO (10 ml) suspension of Poly-imidazolium¹ (250 mg, 0.5 mmol of imidazolium motif) in a reaction flask. The reaction mixture was stirred at 70 °C for 8 h. The solid product was filtered and dried to obtain a brown powder P(NHC-Ag)_{0.5}(NHC-Pd)_{0.5}. The catalyst is directly used for reaction.

General procedure for hydrocarboxylation of phenylacetylene Poly-(NHC)_{0.2}(NHC-Ag)_{0.6}(NHC-Pd)_{0.2} (5 mg), Cs_2CO_3 (2 mmol), phenylacetylene (1 mmol) were added to DMF (4 mL) in a pressure reactor (25 mL). The pressure reactor was flushed with CO₂ (balloon). The reactor was filled with CO₂ up to 50 psi and then H₂ up to 100 psi. The reaction mixture was stirred at 85 °C for 16 hours. After complete consumption of the starting material, the reaction mixture was cooled to room temperature added to an aqueous solution of potassium carbonate solution (2 N, 5 mL) and stirred for 30 mins. Then the mixture was extracted with dichloromethane (3 × 5 mL) and the aqueous layer was acidified with concentrated HCl to pH = 1 and extracted with diethyl ether (3 × 5 mL). The combined organic layers were dried with anhydrous Na_2SO_4 , filtered and concentrated *in vacuo* to give the cinnamic acid product. The *E/Z* selectivity was determined by ¹H NMR spectroscopy.

Calculation Methods All species involved in the reaction, including reactants, products, minima, and transition states, were fully optimized by density functional theory using B3LYP^[15] functional and DGDZVP^[16] basis set as built in Gaussian 09 package.[17] The convergence thresholds are 10⁻³ a.u. on the gradient, 10⁻³ a.u. on the displacement, and 10⁻⁶ a.u. on the energy. The harmonic vibrational frequencies and corresponding zero-point vibrational energies (ZPVE) are calculated at the same level for all the optimized geometries, no imaginary mode for minima and only one imaginary mode for transition states were confirmed The imaginary mode of each transition state was checked to correspond to the right reaction coordinate. For each transition-state structure, we calculated the intrinsic reaction coordinate (IRC) routes in both directions toward the corresponding minima. All the energies reported in the present study include the ZPVE and thermal correction. NBO analysis was performed for the reactant and transition state (TS) for both Cu- and Ag-catalyzed routes using NBO version 3.1.[23]

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Keywords: CO_2 utilization • H_2 reduction • reductive carboxylation • Ag/Pd catalyst • terminal alkyne

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Entry for the Table of Contents

Dingyi Yu,^{[a], #} Feng Zhou,^{[b], #} Diane S. A combined theoretical W. Lim,^[a] Haibin Su,^[b] and Yugen Zhang^{*[a]} соон calculation and experimental development for reductive 85 °C carboxylation of terminal NHC-Ag/Pd Catalyzed Reductive alkynes utilizing CO $_2$ and H $_2$ H₂ Carboxylation of Terminal Alkyne with CO_2 and H_2 , A Combined Experimental and Computational Cu/Pd as reactants. In the system соон with phenylacetylene, CO_2/H_2 CO₂ and NHC-supported Ag/Pd Study for Fine-Tuned Selectivity 100 °C dual-metal catalysts, cinnamic acid, hydrocinnamic acid or юон phenylpropiolic acid were selectively produced in excellent yields under a finetuned condition.