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Water-initiated hydrocarboxylation of terminal alkynes with CO₂ and hydrosilane[†]

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This work discloses a Cu(II)-Ni(II) catalyzed tandem hydrocarboxylation of alkynes with polysilylformate formed from CO₂ and polymethylhydrosiloxane that affords α , β -unsaturated carboxylic acids with up to 93% yield. Mechanistic studies indicate that polysilylformate functions as a source of CO and polysilanol. Besides, a catalytic amount of water is found to be critical to the reaction, which hydrolyzes polysilylformate to formic acid that induces the formation of Ni-H active species, thereby initiating the catalytic cycle.

Hydrocarboxylation of alkynes¹⁻⁴ is one of the effective approaches to synthesize α,β -unsaturated carboxylic acids which are important structural motifs in a myriad of pharmaceuticals. To realize the transformation of alkynes to α,β unsaturated carboxylic acids, sources of "H" and "COOH" moieties are formally required. Recent years have witnessed an endeavour to use CO₂ for the straightforward incorporation of the "COOH" moiety into substrates.⁵⁻⁸ In this context, several preeminent catalytic hydrocarboxylation processes of alkynes using CO₂ were developed. With different "H" sources and/or reductants, a variety of alkynes were smoothly transformed into α , β -unsaturated carboxylic acids (Scheme 1a).⁹⁻¹⁶ However, terminal alkynes are not suitable substrates for most of the CO₂-involving hydrocarboxylation reactions, possibly due to their hydrogenation propensity in such reductive environments.9-15

In addition, palladium or nickel catalyzed carbonylation reactions offered an alternative approach to achieve the hydrocarboxylation of alkynes, where the combination of CO and acids or formic acid and acid anhydrides was employed (Scheme 1b).^{17–21} Considering that CO_2 can be transformed into CO or its surrogates *in situ* with suitable reductants, a

series of CO-involving processes using CO₂ as a substrate have been developed, providing carboxylic acids, aldehydes, alcohols and carboxylic acid derivatives as products.²²⁻³² Hydrosilanes, especially PMHS (polymethylhydrosiloxane), as a kind of effective reductant, can reduce CO₂ to silvl formate under mild conditions.³³ Silyl formate has been reported as an ideal carbonyl source for carbonylative transformations.^{28-30,32} Moreover, as a kind of formate, silvl formate has similar properties to methyl formate and phenyl formate,³⁴⁻³⁷ which can be decomposed into CO and a nucleophile. Recently, our group reported the carboxylation of aryl/vinyl halides with silyl formate formed from CO₂ and PMHS.³² It is confirmed that the reaction proceeds in a silyloxycarbonylation manner and the corresponding silanol plays a vital role as a nucleophilic reagent. As part of our continuous work of utilizing CO₂, we report the hydrocarboxylation of alkynes with polysilylformate in situ formed from CO2 and PMHS under neutral conditions (Scheme 1c). As far as we know, there is no report on the use of silvl formate to realize the hydrocarboxylation of alkynes.

We have demonstrated that silvl formate can work as a carboxylation reagent to introduce a "COOH" moiety into aryl/vinyl halides.³² Here, we envisage the possibility of silvl formate serving as an "H" source like phenyl formate, which has been employed for the hydroesterification of alkynes or alkenes without an additional "H" source.^{34–37} We carried out the hydrocarboxylation reaction in a one-pot manner, where polysilylformate (PMS-formate) was generated *in situ* from CO₂ and PMHS catalyzed by a Cu(OAc)₂–dppbz (1,2-bis(diphenylphosphino)benzene) system through the hydrosilylation reaction in dry 1,4-dioxane and then



Scheme 1 Metal-catalyzed hydrocarboxylation of alkynes.

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Table 1 Optimization of the hydrocarboxylation reaction conditions^a



Table 2	Hvdrocarbox	vlation of	different	alkvnes
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$\begin{array}{c} \text{CO}_2 + \text{PMHS} \\ & \downarrow \text{Step 1} \\ \text{R}^1 R^2 + \left[\text{PMS-formate} \right] \\ 1 \end{array}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	D₂H
R^1/R^2	Yield of 2 and 3^{b} (%)	2/3 ^c
Ph/H (1a)	86	4.7/1
$4 - MeC_6H_4/H$ (1b)	93	8.8/1
$3-MeC_6H_4/H(1c)$	80	16.7:1
$2 - MeC_6H_4/H(1d)$	71	25.0/1
4-MeOC ₆ H ₄ /H (1e)	90	9.2/1
$4 - FC_6 H_4 / H (1f)$	$53^{d}(66)^{e}$	3.4/1(4.1/1)
$4 - ClC_6H_4/H(1g)$	$51(74)^{f}$	9.5/1(9.3/1)
4-PhenylC ₆ H ₄ /H (1h)	50 ^g	8.2:1
<i>n</i> Bu/H (1i)	52^g	12.5/1
Ph/TMS(1j)	62^{gh}	6.8/1
Ph/Me(1k)	22	0.8/1
Ph/Et (11)	26^g	1.8/1
Ph/Ph (1m)	$< 10^{g}$	/
	$\begin{array}{c} & \begin{array}{c} & \begin{array}{c} & & \\ & & \\ & & \\ & & \\ & \\ & \\ R^{1} - = -R^{2} + \left[\begin{array}{c} PMS \text{-} formate \right] \\ & 1 \end{array} \right] \\ \hline \\ & 1 \end{array}$ $\begin{array}{c} R^{1}/R^{2} \end{array}$ $\begin{array}{c} Ph/H (1a) \\ 4 \text{-}MeC_{6}H_{4}/H (1b) \\ 3 \text{-}MeC_{6}H_{4}/H (1c) \\ 2 \text{-}MeC_{6}H_{4}/H (1c) \\ 2 \text{-}MeC_{6}H_{4}/H (1c) \\ 4 \text{-}NeOC_{6}H_{4}/H (1c) \\ 4 $	$\begin{array}{c c} & \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & CO_2 + \text{PMHS} \\ & & \begin{array}{c} & \begin{array}{c} & \text{Step 1} \end{array} \end{array} \end{array} \\ \hline & \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \text{Step 2} \end{array} \end{array} \end{array} \end{array} \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & R^2 \\ & & \end{array} \end{array} \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & R^2 \\ & & \end{array} \end{array} \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & R^2 \\ & & \end{array} \end{array} \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & R^2 \\ & & \end{array} \end{array} \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & R^2 \\ & & \end{array} \end{array} \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & R^2 \\ & & \end{array} \end{array} \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & R^2 \\ & & \end{array} \end{array} \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & R^2 \\ & & \end{array} \end{array} \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & R^2 \\ & & \end{array} \end{array} \begin{array}{c} & \begin{array}{c} & \end{array} \end{array} \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & R^2 \\ & \end{array} \end{array} \begin{array}{c} & \begin{array}{c} & \end{array} \end{array} \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & R^2 \\ & \end{array} \end{array} \begin{array}{c} & \begin{array}{c} & \end{array} \end{array} \begin{array}{c} & \begin{array}{c} & R^2 \\ & \end{array} \end{array} \begin{array}{c} & \begin{array}{c} & \end{array} \end{array} \begin{array}{c} & \end{array} \end{array} \begin{array}{c} & \begin{array}{c} & \end{array} \end{array} \begin{array}{c} & \end{array} \end{array} \begin{array}{c} & \begin{array}{c} & \end{array} \end{array} \begin{array}{c} & \end{array} \end{array} \begin{array}{c} & \end{array} \end{array} \begin{array}{c} & \begin{array}{c} & \end{array} \end{array} \end{array} \begin{array}{c} & \begin{array}{c} & \end{array} \end{array} \end{array} \begin{array}{c} & \end{array} \end{array} \end{array} \begin{array}{c} & \end{array} \end{array} \end{array} \begin{array}{c} & \begin{array}{c} & \end{array} \end{array} \end{array} \end{array} \begin{array}{c} & \begin{array}{c} & \end{array} \end{array} \end{array} \end{array} \begin{array}{c} & \end{array} $

^a Reaction conditions: step 1: Cu(OAc)₂·H₂O (1.0 mol%), dppbz (1.5 mol%), PMHS (0.165 g, Si-H, 2.5 mmol), CO2 (balloon), 1,4dioxane (2 mL), 65 °C, 30 min; step 2:1a (1.0 mmol), Ni[acac]₂ (5 mol%), dppbz (10 mol%), solvent (8 mL), 100 °C, 24 h.^{*b*} Total isolated yield of 2a and 3a based on 1a. ^c Isomer ratio (b:l) determined by ¹H NMR. ^d Step 1: Cu(OAc)₂ (1.0 mol%), dry 1,4-dioxane (2 mL); step 2: dry toluene (8 mL) and 10 mol% water; other conditions remain unchanged. THF = tetrahydrofuran; DMF = N,N-dimethylformamide.

^a Reaction conditions: step 1: the same as that in Table 1; step 2:1 (1.0 mmol), Ni(acac)₂ (5 mol%), dppbz (10 mol%), solvent (8 mL), 100 °C, 24 h; for entries 1, 2 and 11, THF was used as a solvent. All the others used anisole as a solvent. ^b Total isolated yield of 2 and 3 based on 1. ^c Determined by ¹H NMR. ^d 120 °C. ^e 120 °C, 48 h. ^f 58 h. ^g 48 h. ^h TMS group was removed.

dry toluene, phenylacetylene (1a) and Ni(acac)₂/dppbz were added. After the reaction was conducted at 100 °C for 24 hours, no desired product was obtained. Screening of the reaction conditions remained unsuccessful, which implies that polysilylformate presumably could not provide the "H" source itself and an additional active "H" source is indispensable. Fortunately, when 10 mol% of water was added in dry toluene, α , β -unsaturated carboxylic acids 2a and 3a were obtained in a total yield of 53% (Table 1, parentheses in entry 1). Taking into account the facile hydrolysis tendency of silyl formate, we deduce that the added catalytic amount of water is to hydrolyze the polysilylformate into formic acid which provides the "H" source to initiate the reaction.³⁸ Also, we find that the reaction can afford the products with 45% yield in normal 1,4-dioxane and toluene (solvents for step 1 and step 2) (Table 1, entry 1). For convenience, the following reaction conditions were optimized with the normal solvents.

The effect of ligands on the reaction shows that the reactivity markedly depends on the nature of the ligands (Table S1, ESI,† entries 1-5). Among all the screened mono- and bidentate ligands, the biphosphine ligand dppbz appears to be the optimal ligand for the reaction. The reaction results of other nickel precursors Ni(OAc)₂, Ni(PPh₃)₂Br₂ and Ni(PPh₃)₂Cl₂ are inferior to that of $Ni(acac)_2$ (Table S1, ESI,[†] entries 6–8). The solvent effect indicates that ether solvents (Table 1, entries 2-6), including 1,4-dioxane, diphenyl ether, ⁿbutyl ether, anisole and THF are all effective for the reaction and THF is the most striking one to deliver products in 86% yield (Table 1, entry 6). Besides, acetonitrile is also an excellent solvent for the reaction (Table 1, entry 7). However, DMF can hardly afford the desired products (Table 1, entry 8). Through the analysis of the relationship between the yield and the b:l ratio, it can be basically concluded that as the yield of the reaction increases, the corresponding b:l ratio decreases. The reactivity of the tandem reaction is also affected by the ratio and the amount of two solvents (Table S2, ESI†). The reactivity at 80 °C, 100 °C, and 120 °C indicates that 100 °C is an optimal temperature for the reaction (Table S3, ESI[†]). When the reaction is conducted in a one-time addition manner, no product is obtained, which confirms that the tandem method is essential for the hydrocarboxylation of phenylacetylene (Table S4, ESI[†]).

Having optimized the reaction conditions, we began to investigate the scope of the phenylacetylene derivatives (Table 2). For various terminal phenylacetylenes, the corresponding phenylacrylic acid products are obtained with the dominant product being a branched α -phenylacrylic acid. Phenylacetylenes bearing an electron-donating substituent on the phenyl ring afford the hydrocarboxylation products in good to excellent yields (entries 2–5). The position of the substituent on the phenyl ring has some effect on the reaction and the hydrocarboxylation of para-methyl phenylacetylene 1b provides a higher yield of 93% (entry 2) than that of the ortho- or meta-methyl substituted phenylacetylene (entries 3 and 4). In addition, the position of the substituent on the phenyl ring affects the b:l ratio of the product (entries 2-4). The reaction with ortho-methyl substituted phenylacetylene affords the highest b:l ratio (25.0/1, entry 4), which indicates that the steric effect controls the regioselectivity. Substrate 1e with a 4methoxyl group on the phenyl ring performs quite well affording a yield of 90% (entry 5). When 1f and 1g bearing a fluoro or chloro group on the phenyl ring are hydrocarboxylated under the same conditions, lower yields of 53% and 51% are achieved, respectively (entries 6 and 7), indicating that the electronwithdrawing substituent on the phenyl ring has a negative effect on the reactivity. When anisole is used as a solvent

instead of THF, the reactions with 1f and 1g afford slightly higher yields of 66% and 74%, respectively, at a higher temperature or with a longer reaction time (parentheses in entries 6 and 7). For the substrate 1h with a phenyl substituent, a moderate yield of 50% is achieved (entry 8). This catalyst system is also effective for aliphatic 1-hexyne 1i, affording the product in a moderate yield with high branched-selectivity (entry 9). It is worth noting that terminal alkynes are not favourable substrates for most of the CO2-involving direct hydrocarboxylation.9-15 Our strategy making use of polysilylformate generated in situ from CO₂ and PMHS provides an alternative route for the hydrocarboxylation of terminal alkynes. When internal alkynes 1j bearing the TMS group at one end of the alkyne react with polysilylformate, the TMS group is removed during the reaction, leaving α -phenylacrylic acid and *trans*cinnamic acid as the products (entry 10).^{39,40} However, this catalyst system is inefficient for the hydrocarboxylation of internal alkynes such as 1k, 1l, and 1m (entries 11-13). For these substrates, low yields of 22%, 26%, and <10% are obtained even after prolonging the reaction time or by increasing the reaction temperature in anisole.

To understand the catalytic reaction mechanism, several control experiments were performed. Firstly, through monitoring the amount of CO simultaneously under the reaction conditions with (Fig. S1, ESI,[†] condition **A**) or without phenylacetylene **1a** (Fig. S1, ESI,[†] condition **B**), we found that: (1) the amount of CO under both conditions **A** and **B** increased as the reaction proceeded; (2) the amount of CO under condition **B** was a multiple of that under condition **A** at the same measuring time. These results indicate that CO is produced rapidly and a large proportion of it is further consumed during the reaction, which implies that polysilylformate is decomposed into CO and a carbonylation process is involved. (For more details see Fig. S2 in the ESI,[†])

As mentioned in the former part, a catalytic amount of water is essential in this system. It is proposed that the role of water is to hydrolyze polysilylformate to formic acid, which provides an active "H" source to initiate the catalytic cycle. If it is so, a catalytic amount of formic acid should promote the reaction similarly. To confirm this assumption, we performed the reaction with 10 mol% water or 10 mol% formic acid using dry 1,4-dioxane and dry anisole as solvents. As expected, a similar result was obtained providing the product with 71% or 81% yield, which is in agreement with our assumption.

To figure out the optimized amount of water for the reaction, a series of experiments with different amounts of water in a dry solvent were implemented and the results are summarized in Fig. 1a. As shown in Fig. 1a, the conversion of phenylacetylene increases with the increase of water, and 15 mol% or more water achieves complete conversion of phenylacetylene. However, with the increase of the amount of water added, a side reaction of phenylacetylene hydrogenation to styrene begins to emerge and it becomes more serious when the amount of water increases further. Strikingly, when the amount of water added reaches 50 mol%, the yield of styrene becomes as high as 45%. As a result, 15–20 mol% of water seems to be a favourable range for



Fig. 1 (a) Effect of water on the reaction; (b) the effect of formic acid on the reaction. Reaction conditions: For (a): step 1: the same as that in Table 1, only Cu(OAc)₂ and dry 1,4-dioxane were used; step 2: **1a** (1.0 mmol), Ni(acac)₂ (5 mol%), dppbz (10 mol%), dry anisole (8 mL), and water (0–100 mol%) were added, 100 °C, 24 h. For (b): the same as that in (a), only formic acid (0–100 mol%) was added instead of water. PA = phenylacetylene; acids = α -phenylacrylic acid and *trans*-cinnamic acid; ST = styrene.

the hydrocarboxylation of phenylacetylene. The effect of the formic acid amount on the reaction was also investigated and is shown in Fig. 1b. According to Fig. 1b, the reaction conversion increases with the increase of formic acid added and 10 mol% or more formic acid achieves complete conversion of phenylacetylene while styrene increases continually. When formic acid addition reaches 50 mol%, the yield of styrene also becomes very high. A similar trend to that of the effect of water on the reaction is observed, and the suitable amount of formic acid for the reaction is found to be in the range of 10–20 mol%. Obviously, the catalytic amount of formic acid present in the actual reaction system is enough for the reaction.

Based on the above results, a possible reaction mechanism is proposed as shown in Scheme 2. In the presence of a catalytic amount of water, the catalytic amount of polysilylformate is hydrolyzed to formic acid and the remaining polysilylformate was decomposed into CO and the corresponding polysilanol. Then, Ni(acac)₂ reacts with formic acid and produces $[L_n(HCOO)Ni-H]$ (L = dppbz) species **A** accompanied by the release of CO₂ and acetylacetone. Insertion of **A** into the phenylacetylene produces intermediate **B**. Polysilanol as a nucleophile that existed in the reaction system attacks **B** and replaces the formate on **B** to form intermediate **C**. Subsequently, CO inserts into the Ni–C bond of **C**, forming the acyl nickel species **D**, and



Scheme 2 Possible catalytic cycle for the hydrocarboxylation of alkynes.

then reductive elimination of **D** affords the desired silyl ester of α , β -unsaturated carboxylic acid **F** and Ni(0) complex **E**. Oxidative addition of formic acid to **E** regenerates Ni(II) complex **A**.²¹ And, **F** is hydrolyzed to free acid. This mechanism can explain well the effect of the electronic properties of the substrate on the reactivity. The electron-withdrawing substituent on the phenyl ring will reduce the electron cloud density of the triple bond of alkyne, which is unfavorable for the electrophilic addition of [L_n(HCOO)Ni–H] (L = dppbz) species **A** to the triple bond. Therefore, the electron-withdrawing substituent on the phenyl ring has a negative effect on the reactivity. On the contrary, the electron-donating substituent on the phenyl ring has a positive effect on the reactivity.

In this catalytic cycle, the polysilylformate decomposition product polysilanol participates as a nucleophile in the nucleophilic substitution step to replace the formate on complex **B**. The nucleophilic substitution of formate by polysilanol is very critical because it inhibits the occurrence of styrene to a certain extent.¹⁸ Although CO and formic acid exist simultaneously in our system, based on the fact that the nucleophilicity of silanol is stronger than that of formic acid, and on the experimental result that the side reaction becomes dominant when the amount of formic acid is more than 0.5 equivalents, we virtually rule out the reaction mechanism of stoichiometric formic acid participating in the formation of formic acrylic anhydride mentioned in the literature.^{18–21}

In conclusion, we have discovered a Cu(π)–Ni(π) catalyzed hydrocarboxylation reaction of terminal alkynes with CO₂ and PMHS *via* a tandem reaction in a one-pot manner, which affords a series of α , β -unsaturated carboxylic acids in good to excellent yields with high branched-selectivity. The reaction proceeds through a hydro-silyloxycarbonylation pathway under neutral conditions in which polysilylformate provides the source of CO and nucleophilic polysilanol, and a catalytic amount of water (formic acid) provides the "H" source. Further application of this strategy to other carbonylation reactions is underway.

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Conflicts of interest

There are no conflicts to declare.

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