Carboxyzincation Employing Carbon Dioxide and Zinc Powder: Cobalt-Catalyzed Multicomponent Coupling Reactions with Alkynes
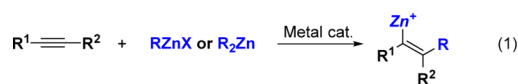
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S *Supporting Information*

ABSTRACT: Cobalt-catalyzed carboxyzincation reactions employing carbon dioxide and zinc metal powder are developed. By using alkynes as substrates, regio- and stereodefined (Z)-β-zincated acrylates are provided. The corresponding alkenylzinc moiety can be converted to various substituents, affording multisubstituted acrylic acids. Furthermore, by adding electron-deficient alkene to the reaction system, the four-component coupling reactions of alkyne, alkene, CO_2, and the Zn atom proceed via carboxyzincation.

Organozinc compounds are versatile organometallic reagents in organic synthesis because of their good reactivity and high compatibility with a broad range of functional groups.[1] Conventionally, organozinc compounds were prepared[1a] through the reactions of organic halides with Zn metal, alkyl iodides with Et_2Zn, and Grignard (or organolithium) reagents with ZnX_2. More recently, the *carbozincation*[2,3] of carbon–carbon multiple bonds in the presence of a transition metal catalyst proved an efficient method. The carbozincation of alkynes is a particularly useful and direct method. Various organozinc reagents (RZnX and R_2Zn: R = aryl, alkyl, alkenyl, alkynyl, allyl, and benzyl groups) react with alkynes to provide stereodefined alkenylzinc compounds (eq 1).

$$R^1 \!=\! R^2 \;+\; \text{RZnX or } R_2\text{Zn} \quad \xrightarrow{\text{Metal cat.}} \quad \underset{R^2}{\overset{R^1}{\diagdown}} \!=\!\!<\!\!\underset{}{\overset{Zn^+}{\diagup}}R \qquad (1)$$

On the other hand, *carboxyzincation*, in which both carboxyl functionality and the Zn atom are simultaneously incorporated across unsaturated bonds, was not realized, although it affords a new class of useful organozinc reagents. In the present study, we describe the first carboxyzincation reaction, employing alkynes **1**, carbon dioxide[4] (1 atm), and Zn metal powder in the presence of a cobalt complex, which acts as a catalyst (Scheme 1a). Both carboxyl and zinc functionalities are successfully incorporated[5] into the C–C triple bond with high regio- and stereoselectivity, affording (Z)-β-zincated acrylates **2**. Moreover, by adding an electron-deficient alkene (**3**) to the catalytic system, a four-component coupling reaction of **1**, **3**, CO_2, and Zn highly selectively gave the carboxyzincation product **4** (Scheme 1b).

First, the carboxyzincation of alkyne (Scheme 1a) was examined with 5-decyne (**1a**), CO_2 (1 atm), and Zn metal powder (1.5 equiv) in the presence of $CoI_2(dppf)$ (10 mol%, dppf =1,1′-bis(diphenylphosphino)ferrocene), $Zn(OAc)_2$ (10

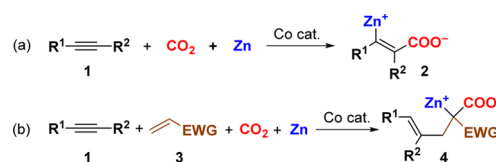## Scheme 1. Carboxyzincation Employing CO_2 and Zn Powder

Table 1. Cobalt-Catalyzed Carboxyzincation of 1a[a]

entry	changes from standard condition	yield of **2a-D** (%)[b]
1	none	80 (73)[c]
2	CoI_2 and dppf in place of $CoI_2(dppf)$	74
3	without $Zn(OAc)_2$	53
4	without Et_4NI	43
5	without $CoI_2(dppf)$	0
6	$CoI_2(dppe)$ in place of $CoI_2(dppf)$	<5
7	$CoI_2(bpy)$ in place of $CoI_2(dppf)$	0
8	$NiCl_2(dppf)$ in place of $CoI_2(dppf)$	0

[a]Reaction conditions: alkyne **1a** (0.25 mmol), $CoI_2(dppf)$ (10 mol%), Zn powder (1.5 equiv), $Zn(OAc)_2$ (10 mol%), Et_4NI (10 mol%), under CO_2 (1 atm) in CH_3CN/DMF (0.55 mL, 10/1 v/v) at 40 °C for 20 h. [b]Determined by ^1H NMR analysis. [c]Isolated yield.

mol%), and Et_4NI (10 mol%) in a mixture of CH_3CN and DMF (10/1 v/v) at 40 °C (Table 1). Treatment of the reaction mixture with D_2O (>99% D) afforded a deuterated product **2a-D** in 73% isolated yield with excellent deuterium incorporation (94%) at the β-position and perfect stereoselectivity (entry 1).[6] The catalyst generated *in situ* from CoI_2 and dppf was also effective and afforded the product in 74% yield (entry 2). Even the use of 1.1 equiv of Zn powder provided the product in 70% yield. As additives, $Zn(OAc)_2$ and Et_4NI were not indispensable in the catalytic system because **2a-D** was obtained in moderate yields even without these additives (entries 3 and 4). Et_4NI may facilitate the electron transfer from Zn metal to Co center.[7] No reactions occurred in the absence of the Co catalyst (entry 5). Particularly, dppf proved a suitable ligand, whereas other phosphine ligands such as 1,2-bis(diphenylphosphino)ethane (dppe) and 2,2′-bipyridine (bpy) were not effective at all (entries

6 and 7). Although Ni catalysts were active in several carboxylation reactions with CO_2,[5a−f,8] $NiCl_2(dppf)$ did not show any catalytic activity (entry 8).

Under optimal reaction conditions, the carboxyzincation of various alkynes **1** to **2** was performed, followed by *in situ* reactions with various electrophiles. The results are shown in Table 2. 4-Octyne (**1b**) successfully afforded **2b** with perfect stereoselectivity, which subsequently reacted with D_2O and provided **2b-D** in good yield (entry 1). By the reaction of **2b** wih I_2 and $(PhSe)_2$,[9] **2b-I** and **2b-Se** were afforded, respectively, in good yields (entries 2 and 3). Pd-catalyzed Negishi coupling of **2b** with aryl bromide[9] furnished the corresponding tetra-substituted alkene **2b-Ar** in 56% overall isolated yield in the two-step reaction (entry 4). Cu-catalyzed allylation of allyl bromide[9] and Negishi coupling with benzyl chloride afforded **2b-allyl** and **2b-Bn**, respectively, in good overall yields (entries 5 and 6). 1-(1-Naphthyl)-1-hexyne (**1c**) afforded **2c-D**[10] via **2c** with excellent regioselectivity (>20/1) in 82% yield (entry 7). Reaction of **2c** with I_2 afforded **2c-I** in 73% yield (entry 8). Similarly, thienyl-substituted alkynes **1d** and **1e** selectively furnished **2d-D**, **2d-allyl**, and **2e-D** (entries 9−11). Unsymmetrical alkynes bearing $4-Me_2N-$ and $4-MeOC_6H_4$ moieties, **1f** and **1g**, regioselectively gave **2f-D**[11] and **2g-Ar** by the reaction with D_2O and aryl iodide, respectively (entries 12 and 13). On the other hand, 1-phenyl-1-hexyne (**1h**) furnished regioisomers with fair regioselectivity (**2h-D/2h′-D** = 84/16) in total 82% NMR yield (entry 14). The major isomer **2h-D** was isolated in 66% yield (with >98% isomeric purity) by silica gel chromatography (entry 14). In contrast, diphenylacetylene (**1i**) was virtually not converted, giving only a trace amount of product (entry 15; vide infra). In all the entries in Table 2, only a trace amount of alkenes was detected by GC-MS analysis.[12]

Carbon−carbon bond formation between **1** and CO_2 (Scheme 1a, Tables 1 and 2) might proceed via cobaltacycle **A**[13] (Scheme 2) derived from Co species, **1**, and CO_2. In contrast, electron-deficient alkenes **3** and alkynes **1** are known to form cobaltacycle **B** (Scheme 2).[14,15] Thus, electron-deficient alkenes **3**, such as acrylates, can be employed as substrates for the multicomponent coupling reaction involving **B** as a key intermediate.

Scheme 2. Two Possible Cobaltacycle Intermediates
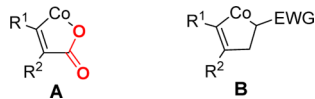
Gratifyingly, the four-component coupling reactions of **1**, **3**, CO_2, and Zn metal proceeded smoothly and afforded the carboxyzincation products **4** (Scheme 1b). The results are shown in Table 3. Diphenylacetylene (**1i**) reacted with butyl acrylate ($CH_2=CHCOOBu$, **3a**), CO_2, and Zn to afford **4a-H**, **4a-Me**, and **4a-allyl** via **4a** after reactions with H_2O, MeI, and allyl bromide, respectively (entries 1−3).[9,16] As shown above (entry 15, Table 2), in the absence of **3a**, **1i** was not converted in the carboxyzincation of the C−C triple bond. The intermediacy of **B** (consisting of **1i** and **3a**) appeared to facilitate the four-component coupling reaction. The reaction of unsymmetrical 1-phenyl-1-hexyne (**1h**) with **3a** gave **4b-H** and **4b-Et** with *perfect* regioselectivity (entries 4 and 5), whereas **1h** without **3a** gave a mixture of regioisomers (**2h** and **2h′**, entry 14, Table 2). Selective formation of **B** from **1h** and **3a** was responsible for the regioselective formation of **4b**. Chloro (**1j**: Ar−C≡C−Ar, Ar = $4-ClC_6H_4$) and trifluoromethyl (**1k**: Ar−C≡C−Ar, Ar = 3-

Table 2. Cobalt-Catalyzed Carboxyzincation of Alkynes and Subsequent Reactions with Electrophiles[a]

[a]Reaction conditions: alkyne **1**, $CoI_2(dppf)$ (10 mol%), Zn powder (1.5 equiv), $Zn(OAc)_2$ (10 mol%), Et_4NI (10 mol%), under CO_2 (1 atm) in CH_3CN/DMF (10/1 v/v) at 40 °C for 20 h. [b]Isolated yield. [c]$CoBr_2(dppf)$ (10 mol%) as a catalyst. [d]The corresponding halide (1.2 equiv or 1.5 equiv), $Pd(PPh_3)_4$ (2.0 mol%) at 70 °C for 20 h. [e]An allyl bromide (2.0 equiv), $CuCN·2LiCl$ (20 mol%), − 20 °C to RT for 20 h. [f]CH_3CN/DMF (1/4 v/v). [g]At 25 °C. [h]CH_3CN/DMF (1/1 v/v), at 50 °C. [i]An aryl iodide (1.5 equiv), $PdCl_2(PPh_3)_2$ (2.0 mol%) at 70 °C for 20 h. [j]By ^{1}H NMR.

$CF_3C_6H_4$) functionalities were well tolerated under reaction conditions (entries 6 and 7). Thienyl-substituted alkyne **1d** also regioselectively afforded **4e-Me** after methylation with MeI

Table 3. Cobalt-Catalyzed Four-Component Coupling Reaction of Alkyne, Electron-Deficient Alkene, CO_2, and Zn Powder[a]

entry	1[b]	3[c]	electrophile	4-E, yield[d]
1	1i	3a	H_2O	E = H, **4a-H**: 85%
2	1i	3a	MeI	E = Me, **4a-Me**: 88%
3	1i	3a	allyl—Br	**4a-allyl**: 74%
4	1h	3a	H_2O	E = H, **4b-H**: 70%
5	1h	3a	EtI	E = Et, **4b-Et**: 55%
6	1j	3a	MeI	Ar=4-ClC$_6$H$_4$, **4c-Me**: 55%
7	1k	3a	MeI	Ar=3-CF$_3$C$_6$H$_4$, **4d-Me**: 57%
8	1d	3a	MeI	**4e-Me**: 50%
9	1l	3a	MeI	**4f-Me**: 65%
10	1i	3b	MeI	R = Me, **4g-Me**: 47%
11	1i	3c	MeI	R = Et, **4h-Me**: 62%
12	1i	3d	MeI	R = tBu, **4i-Me**: 74%
13	1i	3e	H_2O	**4j-H**: 63%

[a]Reaction conditions: alkyne **1** (0.30 mmol), electron-deficient alkene **3** (0.25 mmol), CoI$_2$(dppf) (10 mol%), Zn powder (1.5 equiv), Zn(OAc)$_2$ (20 mol%), Bu$_4$NI (20 mol%), under CO_2 (1 atm) in CH$_3$CN (0.50 mL) at 25 °C for 20 h. [b]**1j**: Ar−C≡C−Ar, Ar = 4-ClC$_6$H$_4$; **1k**: Ar−C≡C−Ar, Ar = 3-CF$_3$C$_6$H$_4$; **1l**: MeOOC−C≡C−C$_5$H$_{11}$. [c]**3a**: butyl acrylate; **3b**: methyl acrylate; **3c**: ethyl acrylate; **3d**: tert-butyl acrylate; **3e**: dimethyl acrylamide. [d]Isolated yield.

(entry 8). Alkynoate **1l** (MeOOC−C≡C−C$_5$H$_{11}$) also afforded **4f-Me** in good yield (entry 9). Other acrylates, such as methyl, ethyl, and tert-butyl acrylates **3b**, **3c**, and **3d** provided corresponding products (entries 10−12). By employing N,N-dimethylacrylamide (**3e**) as an electron-deficient alkene, **4j-H**[11] was isolated in 63% yield (entry 13).

As shown in Scheme 3, **4a-Me** furnished 1-tetralone derivative **6** in 87% yield by the 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP)-promoted intramolecular Friedel−Crafts acylation[17] of the corresponding acid chloride **5**.

Possible mechanisms for both carboxyzincation reactions (Scheme 1) are depicted in Scheme 4. First, Co(II) precursors are reduced to Co(I) with Zn metal.[18] For the carboxyzincation of the C−C triple bond (Scheme 1a), oxidative cyclization of Co(I) with **1** and CO_2 affords cobaltacycle **A**[13] (step a). Then, transmetalation of **A** with Zn(II) species gives alkenylzinc species

Scheme 3. Intramolecular Cyclization Employing 4a-Me
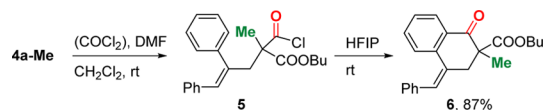
Scheme 4. Plausible Reaction Mechanism
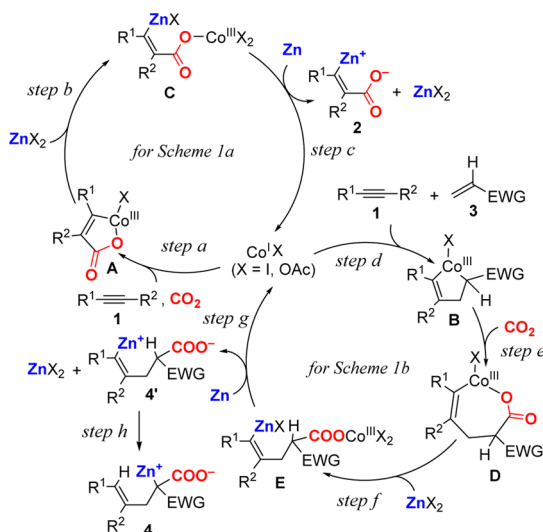
C (step b).[19] Finally, the two-electron reduction of Co(III) to Co(I) with Zn powder provides the carboxyzincation product **2** and Zn(II) species (step c), and the catalytic cycle is closed. As for the four-component coupling reaction (Scheme 1b), oxidative cyclization of Co(I) with **1** and **3** occurs in a highly regioselective manner, giving cobaltacycle **B** (step d).[14,15a−d] Then, CO_2 insertion into the Co−C(sp^3) bond furnishes seven-membered cobaltacycle **D** (step e).[20] Transmetalation of **D** with Zn(II) species affords alkenylzinc species **E** (step f).[19] Subsequently, the two-electron reduction with the Zn metal gives **4'** and Zn(II) species, and Co(I) is regenerated (step g). Finally, the carboxyzincation product **4** is furnished through 1,4-Zn migration (step h). Actually, when α-deuterated butyl acrylate (**3a-α-d**; 72% D) was employed as the substrate (entry 2, Table 3), **4a-Me-δ-d** was provided in 70% yield with excellent deuterium incorporation at the δ-position (eq 2) via putative 1,4-Zn migration (step h, Scheme 4).[21]
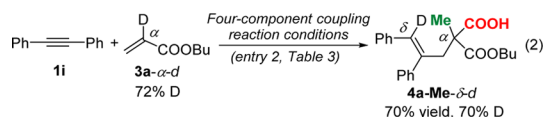
In conclusion, carboxyzincation reactions with CO_2 and Zn metal powder are realized via a Co catalyst. Using alkynes as the substrate, the reaction affords regio- and stereodefined (Z)-β-zincated acrylates. Successive transformation of the corresponding alkenylzinc moiety with diverse electrophiles furnishes multisubstituted acrylic acids without the loss of stereochemistry. Furthermore, by adding an electron-deficient alkene, the four-component coupling reactions of alkyne, alkene, CO_2, and Zn progress smoothly, affording carboxyzincation products with perfect regio- and stereoselectivity. Further experiments, especially exploring the use of different substrates, as well as mechanistic investigations are now in progress.

■ ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b02961.

Experimental details and characterization data (PDF)
Crystallographic data of **2c-D** (CIF)

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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(9) For the detailed reaction conditions of carboxyzincation products (**2** or **4**) with electrophiles, see Supporting Information.

(10) Structure of **2c-D** was confirmed by NMR and X-ray crystallographic analysis. See Supporting Information for details. In **2c-D**, **2d-D**, **2f-D**, and **2h-D**, the carboxylic acid functionality is located distal to the aromatic rings. This regioselectivity differs from our previous Cu-catalyzed hydrocarboxylation of alkynes employing CO_2 and hydrosilanes,[10a] while regioselectivity similar to that of **2** was observed in Ni-catalyzed hydrocarboxylation of alkynes with CO_2 and alcohols:[10b] (a) Fujihara, T.; Xu, T.; Semba, K.; Terao, J.; Tsuji, Y. *Angew. Chem., Int. Ed.* **2011**, *50*, 523. (b) Wang, X.; Nakajima, M.; Martin, R. *J. Am. Chem. Soc.* **2015**, *137*, 8924.

(11) To facilitate the isolation process, obtained carboxylic acid was further derivatized into the corresponding methyl ester by esterification with trimethylsilyldiazomethane.

(12) To examine the functional group compatibility, we carried out the reaction of **1a** in the presence of added acetophenone or benzaldehyde (1 equiv) under the standard reaction conditions (Table 1, entry 1). Acetophenone did not affect the reaction, but benzaldehyde suppressed the formation of **2a-D**. As for terminal alkynes, the corresponding products were not obtained due to oligomerization of alkynes.

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(16) When the reaction in Table 3, entry 1, was carried out with D_2O in place of H_2O, the corresponding **4a-D** was obtained as expected. However, the incorporated D was lost considerably due to rapid H/D exchange during the isolation process.

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(21) When the reaction in eq 2 was carried out employing a mixture of **3a-α-d** and **3c**, intermolecular H/D scramble between the corresponding products was observed by GC-MS analysis.