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# Cobalt-catalyzed carboxylation of propargyl acetates with carbon dioxide<sup>†</sup>

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Keisuke Nogi, Tetsuaki Fujihara,\* Jun Terao and Yasushi Tsuji\*

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The cobalt-catalyzed carboxylation of propargyl acetates with  $CO_2$  (1 atm) is described. The reaction proceeds at room temperature in the presence of Mn powder as a reducing reagent. Various propargyl acetates are converted to the corresponding carboxylic acids in good to high yields.

Carbon dioxide (CO<sub>2</sub>) is an environmentally friendly raw material and its utilization as a sustainable carbon source is one of the most important challenges in homogeneous transition-metal catalysis.<sup>1</sup> In particular, C-C bond forming reactions using CO<sub>2</sub> are the most promising.1a Reactions using highly reactive Grignard and organolithium reagents with CO<sub>2</sub> are fundamental for the C-C bond formation, but chemoselectivity with these reagents is very poor. In contrast, less reactive arylboronic esters<sup>2a-c</sup> and arylzinc compounds<sup>2d,e</sup> were found to react with CO<sub>2</sub> with good chemoselectivity in the presence of a transition-metal catalyst. However, all these organometallic compounds are mainly synthesized from the corresponding aryl halides. Thus, the direct carboxylation of aryl halides is more straightforward and efficient. We recently reported the nickel-catalyzed direct carboxylation of aryl and vinyl chlorides with  $CO_2$  (1 atm) at room temperature, <sup>3a,b</sup> while carboxylations of more reactive aryl bromides<sup>3c</sup> and benzyl chlorides<sup>3d</sup> as well as inert C-O bonds<sup>3e</sup> have also been reported.<sup>4</sup>

Reactions of allylic and propargylic compounds with CO<sub>2</sub> afford a variety of unsaturated carboxylic acids. These transformations consume a stoichiometric amount of the corresponding Grignard, organolithium, or other metal reagents.<sup>5</sup> These reactions also have problems in regioselectivity and chemoselectivity.

Therefore, the development of a new selective methodology is highly desirable. Allyl and propargyl esters (typically, acetates or carbonates) are well known as efficient *electrophiles* in transitionmetal-catalyzed C–C bond forming reactions.<sup>6</sup> In order to utilize these electrophiles with CO<sub>2</sub>, umpolung<sup>7</sup> reactivity of these esters is crucial. Actually, the reactions of *allyl* esters with  $CO_2$  were carried out under electrochemical conditions in the presence of Pd or Ni catalysts;<sup>8</sup> however, the yields and regioselectivities were low. Furthermore, there is no precedent for the carboxylation of *propargyl* esters with  $CO_2$ .<sup>9</sup> Herein, we report the Co-catalyzed carboxylation of propargyl acetates with  $CO_2$  utilizing Mn powder as a reducing agent. Various propargyl acetates were converted to the corresponding carboxylic acids under 1 atm  $CO_2$  at room temperature.

The carboxylation of propargyl acetate **1a** was carried out under  $CO_2$  (1 atm) at room temperature in the presence of  $CoI_2$ (phen)<sup>10</sup> (phen = 1,10-phenanthroline) and Mn powder (3.0 equiv.) in DMA (*N*,*N*-dimethylacetamide) (Table 1). The yield of the corresponding carboxylic acid (**2a**) was determined by gas chromatographic (GC) analysis after derivatization to the corresponding methyl ester (**2a-Me**). Under the standard conditions, **2a-Me** was obtained in 83% yield (entry 1). Compound **2a** was isolated from the reaction mixture in 82% yield. Without  $CoI_2$ (phen), **2a-Me** was not obtained (entry 2). In the absence of phen (*i.e.*,  $CoI_2$  as the catalyst), **1a** was

Table 1	Reaction	optimization
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			•			
	 1a	Me 	CO <sub>2</sub> (1 atm, closed) Col <sub>2</sub> (phen) (5.0 mol %)	1) HCl aq.	THE ME	
TMS			Mn (3.0 equiv) DMA, rt, 20 h	2) TMSCHN <sub>2</sub> Et <sub>2</sub> O/MeOH	COOMe 2a-Me	
Entry		Ca sta	ntalyst system: chan andard conditions	ge from the	Yield of $2\mathbf{a}$ - $\mathbf{Me}^{b}$ (%)	
1		No	one		83 (82) <sup>c</sup>	
2		Without CoI <sub>2</sub> (phen)			0	
3		Co	$I_2$ in place of $CoI_2$	0		
4		W	ithout Mn powder		0	
5		Μ	n powder (0.60 mm	ol, 1.2 equiv.)	74	
6		Co	Br <sub>2</sub> (phen) in place	of CoI <sub>2</sub> (phen)	80	
7		Co	$I_2(bpy)$ in place of	CoI <sub>2</sub> (phen)	76	
8		$CoI_2(PPh_3)_2$ in place of $CoI_2(phen)$			23	
9	CoI <sub>2</sub> (dppe) in place of CoI <sub>2</sub> (phen)			0		
10	Zn in place of Mn				41	
11	Mg in place of Mn				57	
$12^d$		Ni	7			

<sup>*a*</sup> Reaction conditions; **1a** (0.50 mmol),  $CoI_2$ (phen) (0.025 mmol, 5.0 mol%), Mn powder (1.5 mmol, 3.0 equiv.),  $CO_2$  (1 atm), in DMA (0.50 mL), at room temperature for 20 h. <sup>*b*</sup> Determined by GC analysis. <sup>*c*</sup> Isolated yield of **2a**. <sup>*d*</sup> With Et<sub>4</sub>NI (0.05 mmol, 10 mol%).

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan. E-mail: ytsuji@scl.kyoto-u.ac.jp; Tel: +81-75-383-2514

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not converted (entry 3). Without the addition of Mn powder, the carboxylation did not proceed at all (entry 4). When the amount of Mn powder was reduced to 1.2 equiv., the yield of 2a-Me was decreased to 74% (entry 5). CoBr<sub>2</sub>(phen) was also a good catalyst and afforded 2a-Me in 80% yield (entry 6). By employing CoI<sub>2</sub>(bpy) (bpy = 2,2'-bipyridine) as a catalyst, **2a-Me** was obtained in 76% yield (entry 7). Thus, phen and bpy show comparable efficiency as the ligand. In contrast,  $CoI_2(PPh_3)_2$  and  $CoI_2(dppe)$  (dppe = 1,2-diphenylphosphinoethane) suppressed the carboxylation considerably (entries 8 and 9). Other reducing agents such as Zn powder and Mg turnings gave 2a-Me in only moderate yields (entries 10 and 11).  $NiCl_2(PPh_3)_2$ , which was an efficient catalyst for the carboxylation of aryl chlorides,<sup>3a</sup> did not show good catalytic activity (entry 12). Other nickel catalysts such as NiBr<sub>2</sub>(bpy) and Nil<sub>2</sub>(phen) were not efficient. With regard to the choice of solvent, 1,3-dimethyl-2-imidazolidinone (DMI) and DMF were also suitable, while reactions in THF and toluene afforded 2a-Me in 26% and 0% yields, respectively (Table S1, ESI<sup>+</sup>).<sup>11</sup>

The carboxylation of various propargyl acetates was carried out in the presence of  $CoI_2$ (phen) or  $CoI_2$ (bpy) as a catalyst (Table 2). The carboxylation reaction of acetates of secondary alcohols (1b-h) bearing TMS in the R<sup>1</sup> position proceeded smoothly and afforded the corresponding carboxylic acids (2b-h) in high isolated yields (entries 1-7). It is noteworthy that ester (1e), chloro (1f), terminal alkene (1g), and furan (1h) functionalities were compatible in the reaction (entries 4-7). When the carboxylation of acetates derived from tertiary alcohols was examined with CoI2(phen), conversion of the starting material remained low. In this case, CoI<sub>2</sub>(bpy) was found to be a good catalyst and provided the carboxylated products (2i-l) in good to high yields (entries 8-11). Amide functionality (11) was also tolerated in the reaction (entry 11). The acetate of a primary propargylic alcohol (1m) also provided the corresponding carboxylic acid (2m) in moderate yield (entry 12). A substituent on the alkyne carbon of 1 (R<sup>1</sup>, Table 2) affects the carboxylation considerably. As the substituent R<sup>1</sup> became less bulky, the yields of the carboxylated products (2) decreased;  $1n (R^1 = TBS, TBS = tert$ butyldimethylsilyl), 10 ( $R^1 = CMe_2(OTBS)$ ), 1p ( $R^1 = t$ -Bu), and 1q  $(\mathbf{R}^1 = \mathbf{C}\mathbf{y})$  afforded the corresponding products  $(2\mathbf{n}-\mathbf{q})$  in 88%, 55%, 57%, and 26% yields, respectively (entries 13-16). Propargyl acetates having a phenyl ring (1:  $R^1 = Ph$ ,  $R^2 = Me$ ,  $R^3 = H$ ) afforded the product in 9% yield. Substrates bearing a terminal alkyne moiety (1:  $R^1 = H$ ,  $R^2 = Me$ ,  $R^3 = H$ ) did not provide the carboxylated product.12

The TMS group of the products shown in Table 2 could easily be removed *via* protodesilylation<sup>13</sup> in the presence of a suitable base. In the case of  $\alpha, \alpha$ -disubstituted carboxylic acids such as **2a**, reaction with tetrabutylammonium fluoride (TBAF, 1.0 M in THF) provided the corresponding carboxylic acid **2r** in 78% yield (Scheme 1a). In contrast, when **2a** or **2d** was treated with KOH (crushed), carboxylic acids bearing an allenyl moiety (**2s** and **2t**) were selectively obtained in 80% and 65% yields, respectively (Scheme 1b). A similar reaction of **2a** with K<sub>2</sub>CO<sub>3</sub> resulted in the formation of a mixture of **2r** and **2s** (**2r**/**2s** = 1/3). On the other hand,  $\alpha, \alpha, \alpha$ -trisubstituted carboxylic acids such as **2i** and **2j** reacted with K<sub>2</sub>CO<sub>3</sub> to give **2u** and **2v** in 98% and 79% yields, respectively (Scheme 1c). Aryl and alkenyl carbons were

Table 2 Cobalt-catalyzed carboxylation of various propargyl acetates<sup>a</sup>

	$R^{1} = \begin{bmatrix} R^{2} \\ R^{3} \\ Color \\ Color \\ Mn (3.0 \text{ equiv}) \end{bmatrix}$	sed) mol %) HCl aq. R <sup>1</sup> ────────────────────────────────────	2 ~R <sup>3</sup>
	1 DAC DMÀ, rt, 20 h	2	
Entry	Substrate 1	Product 2	Yield <sup>5</sup> (%)
1	TMS — Bu OAc 1b	TMS-= COOH 2b	80
2	(CH <sub>2</sub> ) <sub>2</sub> µn TMS- <del></del> OAc 1c	TMS	75
3	TMS OAc 1d	™S-= COOH 2d	79
4	TMS TMS (CH <sub>2</sub> ) <sub>4</sub> COOMe OAc 1e (CH) CI	ТМS-=-(CH <sub>2</sub> ) <sub>4</sub> COOMe СООН <b>2e</b>	65
5	$TMS \xrightarrow{(CH_2)_4CI}_{OAc}$	TMS	85
6	(CH <sub>2</sub> ) <sub>3</sub> CH=CH <sub>2</sub> TMS────〈 OAc <b>1g</b>	(CH <sub>2</sub> ) <sub>3</sub> CH=CH <sub>2</sub> TMS──── COOH <b>2g</b>	73
7	TMS Me OAc 1h mixture of diastereomers in 4:5	TMS	87
8 <sup>c</sup>	TMS 1i Me OAc	тмs-—- соон 2i	71
9 <sup>c</sup>	TMS — OAc	тмз	80
10 <sup>c</sup>	TMS- Hex OAc	тмs-= соон <b>2k</b>	80
11 <sup>c</sup>			46
12	TMS-=OAc 1m	тмs-=соон 2m	40
13	TBS	TBS-= COOH	88
14	Me OTBS OAc 10	Me → → → → → → → Me OTBS COOH 20	55
15	t-Bu	<i>t-</i> Вu− <u></u> — СООН <b>2р</b>	57
16	Cy———— <sup>Me</sup> OAc 1q	Cy──── COOH 2q	26

<sup>*a*</sup> Reaction conditions; propargyl acetate (1, 0.50 mmol),  $CoI_2$ (phen) (0.025 mmol, 5.0 mol%), Mn powder (1.5 mmol, 3.0 equiv.),  $CO_2$  (1 atm), in DMA (0.50 mL), at room temperature for 20 h. <sup>*b*</sup> Isolated yield. <sup>*c*</sup> CoI<sub>2</sub>(bpy) (0.025 mmol, 5.0 mol%) was used as a catalyst.



Scheme 1 Derivatization of carboxylated products.

introduced into the terminal alkyne moiety of **2u** and **2v** by the Sonogashira coupling reaction<sup>14a</sup> (**2w** and **2x**, Scheme 1d and e). Moreover, Au-catalyzed intra-molecular cyclization<sup>14b</sup> of **2v** provided unsaturated  $\gamma$ -lactone **2y** smoothly (Scheme 1f). Thus these TMS moieties are very useful for the further derivatization.

When optically pure (S)-1a was employed as the substrate in the present carboxylation, racemic 2a was obtained in 72% yield (eqn (1)).



A plausible reaction mechanism is shown in Scheme 2. Initially, the reduction of a Co(n) complex with manganese



Scheme 2 Plausible catalyst cycle.

affords a Co(1) catalyst species (**A**). Then, oxidative addition of a propargyl acetate (**1**) takes place *via* C–O bond cleavage, giving a Co(m) intermediate (**B**) (step a). Subsequent reduction of propargyl Co(m) with manganese gives the propargyl cobalt(n) species (**C**) (step b).<sup>*a,b*,15</sup> Then, the more nucleophilic<sup>*3b*</sup> Co(m) species (**C**) reacts with CO<sub>2</sub> to give the carboxylatocobalt intermediate (**D**) (step c). Finally, the reduction of **D** with manganese affords the corresponding manganese carboxylate and the Co(1) catalytic species (**A**) regenerates (step d). Further studies on the reaction mechanism are in progress.

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#### Communication

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