Carbonylation

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Regioselective Pd-Catalyzed Methoxycarbonylation of Alkenes Using both Paraformaldehyde and Methanol as CO Surrogates[**]

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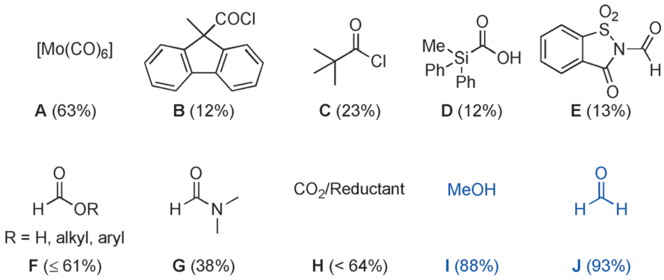
Abstract: *In recent years, considerable effort has focused on the development of novel carbonylative transformations using CO surrogates. Consequently, toxic CO gas can be replaced by more convenient inorganic or organic carbonyl compounds. Herein, the first regioselective methoxycarbonylation of alkenes with paraformaldehyde and methanol as CO substitutes is reported. This new procedure is applicable to a series of alkenes in the presence of a palladium catalyst under relatively mild conditions and is highly atom efficient.*

Transition-metal-catalyzed carbonylation reactions have become a powerful tool in both organic synthesis and industrial production for constructing various carbonyl compounds such as esters, amides, ketones, and aldehydes.[1] However, synthetic chemists are still hesitant to apply carbon monoxide in a more general manner because of its toxicity and gaseous nature. To solve these problems, the development of "CO-free" carbonylation methods based on easy to handle inorganic or organic carbonyl compounds has attracted substantial interest in the past three decades.[2] The typical known CO surrogate compounds are listed in Scheme 1. Unfortunately, most of these alternative carbonyl resources suffer from significant drawbacks in terms of atom efficiency, reactivity, toxicity, and price. For example, metal carbonyls such as [Mo(CO)$_6$] (**A**) are applied to deliver CO in various carbonylation reactions.[3] The main disadvantages of this approach are the presence of stoichiometric amounts of additional transition metals in the reaction mixture and harsh reaction conditions for CO release from these toxic metal carbonyls. Notably, Skrydstrup and co-workers developed a new technique for the ex situ generation of carbon monoxide and its application in palladium-catalyzed carbonylation reactions by using a sealed two-chamber system.[4] Here, near-stoichiometric quantities of CO precursors, including "CO gen" (**B**),[4a] pivaloyl chloride (**C**),[4a] as well as silacarboxylic acids (**D**),[4b] are sufficient to promote carbonylative transformations. *N*-Formylsaccharin (**E**) is also known as a CO source for the palladium-catalyzed reductive carbonylation of aryl halides to access aryl aldehydes.[5] However, concerns about the atom efficiency and waste generation for CO alternatives **B**–**E** still remain. Hence, cheaper and more readily available carbonyl reagents are highly desired.



Scheme 1. Typical CO surrogates (the percentage by molecular weight of the CO unit is shown in parenthesis).

It is well known that CO can be released from formic acid (**F**; R = H) by dehydration in sulfuric acid (Morgan reaction).[6] Additionally, olefin carbonylation reactions in the presence of formic acid as a carbonyl source are also achieved through sequential dehydrogenation and reverse water gas shift processes at elevated temperature (> 150 °C).[7] Moreover, formates (**F**; R = alkyl, aryl)[8] and formamides (**G**)[9] have also been used for the carbonylation of olefins and aryl halides. In general, harsh conditions, poor selectivity in the presence of additional nucleophiles, and/or the necessity for external CO pressure restrict the further application of formic acid derivatives as a CO source. CO$_2$ (**H**) is an ideal C1 building block in organic synthesis due to its abundance, nontoxicity, and recyclability. Remarkably, the catalytic in situ generation of CO from CO$_2$ reduction and its incorporation in the following carbonylation reactions has been realized.[10] This is a promising process that uses CO$_2$ instead of CO as a C$_1$ resource for carbonylations, but the substrate scope is so far limited by the required reductants and the regioselectivity cannot so far be controlled.

Although methanol is an abundant and potentially renewable chemical and can be a potential carbonyl source, this area

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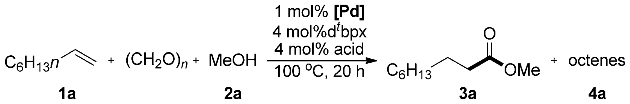
is underdeveloped because of the high energetic demand for methanol dehydrogenation.[11] Undoubtedly, the simplest aldehyde, formaldehyde (**J**), is the most atom economic CO surrogate for carbonylation reactions with suitable reactivity. The percentage by molecular weight of the CO unit in this molecule is 93 %. While the transition-metal-catalyzed decarbonylation of higher aldehydes[12] and hydroacylation of alkenes with aldehydes[13] has been well-established, formaldehyde is less applied as a carbonyl source.[14] In fact, to the best of our knowledge, only two alkoxycarbonylation reactions have been reported by us which uses formaldehyde as the carbonyl source.[15] More specifically, we developed the catalytic alkoxycarbonylation of aryl bromides[15a] and also very recently the first ruthenium-catalyzed alkoxycarbonylation of alkenes using formaldehyde.[15b] The olefin alkoxycarbonylation reaction represents an important approach for the production of value-added bulk and fine chemicals. For example, methyl propionate, a key intermediate for polymethacrylates, is produced on a scale of > 300 000 tons per year by the methoxycarbonylation of ethylene.[16] However, in our previous study, the Ru catalyst does not promote the regioselective carbonylations of industrially interesting aliphatic alkenes. To solve this challenging problem, herein we report for the first time highly linear selective methoxycarbonylation reactions of alkenes by using paraformaldehyde and methanol as inexpensive and atom-efficient CO surrogates simultaneously. This approach offers a convenient synthesis of various methyl esters through a "CO-free" Pd-catalyzed carbonylative process.

Initially, we examined the feasibility of the Pd-catalyzed methoxycarbonylation of 1-octene (**1a**) with paraformaldehyde and methanol (**2a**) to give methyl nonanoate (**3a**). First, the activities of different in situ generated palladium phosphine complexes were studied. A series of bidentate and monodentate ligands were tested using palladium(II) acetylacetonate as the catalyst precursor and PTSA as the acid co-catalyst (see Scheme S1 in the Supporting Information). Interestingly, almost all of the ligands we examined gave quite low catalytic activity with less than 5 % yield of the desired product **3a**, except for d^{t}bpx [α,α′-bis(di-*tert*-butylphosphino)-*o*-xylene], from which a 74 % yield of **3a** along with 95 % *n*-selectivity was obtained. It should be noted that isomerized octenes **4a** were generated as by-products in all the cases. Next, we investigated the impact of key reaction parameters for the desired transformation (Table 1). After exploring a wide array of conditions, we found that using $Pd(OAc)_2$ (1 mol %), d^{t}bpx (4 mol %), PTSA (4 mol %), and paraformaldehyde (6.7 equiv of -CH_2O) in MeOH at 100 °C furnished a good yield (78 %) of the desired product with 95 % *n*-selectivity (Table 1, entry 7). Adding an acidic co-catalyst with a weakly coordinating anion such as PTSA and MSA, is crucial to the success of this methoxycarbonylation process (Table 1, entries 1 and 2). Other tested acids did not afford any carbonylation product **3a** (Table 1, entries 3–6). The effect of different palladium catalyst precursors was also explored. $Pd(OAc)_2$ and $[Pd(acac)_2]$ (acac = acetylacetonate) showed similarly good reactivity compared to other tested Pd^0 and Pd^{II} complexes (Table 1, entries 7–13).

Table 1: Optimization studies for the Pd-catalyzed methoxycarbonylation of 1-octene (**1a**).[a]



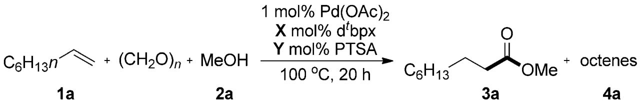
Entry	[Pd]	Acid	Yield **3a** [%] (l/b)	Yield **4a** [%]
1	$[Pd(acac)_2]$	PTSA	74 (95:5)	25
2	$[Pd(acac)_2]$	MSA	74 (95:5)	24
3	$[Pd(acac)_2]$	H_2SO_4	0 (N.D)	57
4	$[Pd(acac)_2]$	TFA	0 (N.D)	77
5	$[Pd(acac)_2]$	AcOH	0 (N.D)	89
6	$[Pd(acac)_2]$	HCO_2H	0 (N.D)	79
7	**$Pd(OAc)_2$**	**PTSA**	**78 (95:5)**	**22**
8	$PdCl_2$	PTSA	1 (99:1)	99
9	$[Pd(cod)Cl_2]$	PTSA	10 (91:9)	90
10	$[Pd(MeCN)_2Cl_2]$	PTSA	10 (97:3)	90
11	$Pd(TFA)_2$	PTSA	0 (N.D)	99
12	$[Pd_2(dba)_3]$	PTSA	16 (96:4)	82
13	Pd/C	PTSA	0 (N.D)	99

[a] Reaction conditions: **1a** (1 mmol), "CH_2O" monomer (6.7 mmol), [Pd] (1 mol %), d^{t}bpx (4 mol %), acid (4 mol %) in 2 mL of methanol (**2a**) at 100 °C for 20 h. Yields determined by GC analysis. l/b = linear/branched. N.D. = not determined. cod = 1,5-cyclooctadiene, PTSA = *p*-toluenesulfonic acid, MSA = methanesulfonic acid, TFA = trifluoroacetate acid, dba = dibenzylideneacetone.

Then, the effects of the amounts of ligand and acid co-catalyst were investigated using $Pd(OAc)_2$ as the catalyst precursor. Remarkably, both the the concentration of the acidic co-catalyst PTSA and the ligand have a profound influence on the yield of **3a**. To our delight, the desired product is obtained in 96 % yield under optimized conditions (Table 2, entry 3). Notably, higher loadings of the co-catalyst suppressed the reaction efficiency (Table 2, entries 4 and 5). Similarly, an excess of d^{t}bpx with respect to PTSA completely inhibited this transformation (Table 2, entries 2 and 6).

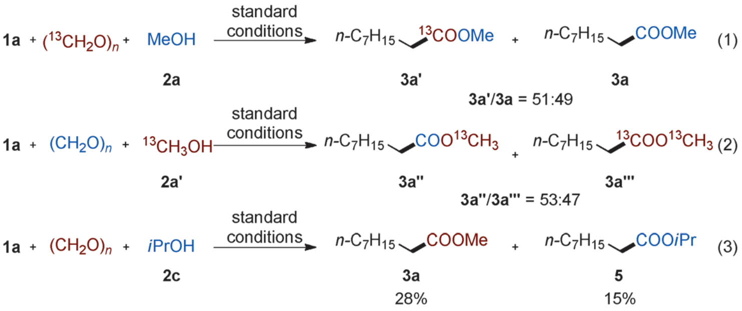
To gain further insights into this reaction, ^{13}C isotope labeling experiments were implemented (Scheme 2). When

Table 2: Effect of ligand and acid co-catalyst on the methoxycarbonylation of **1a**.[a]



Entry	X	Y	Yield **3a** [%] (l/b)	Yield **4a** [%]
1	4	4	78 (95:5)	22
2	4	3	0 (N.D)	97
3	**4**	**5**	**96 (95:5)**	**4**
4	4	6	68 (95:5)	38
5	4	8	64 (95:5)	36
6	5	4	0 (N.D)	100
7	2	2	0 (N.D)	92
8	2	4	17 (96:4)	74

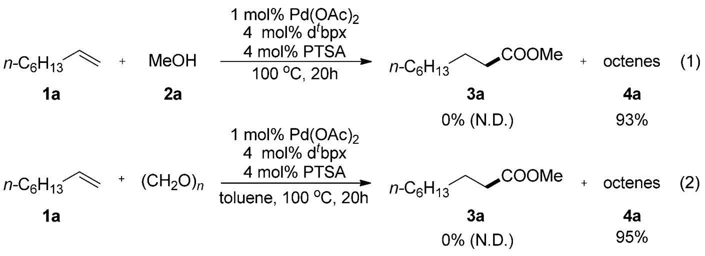
[a] Reaction conditions: **1a** (1 mmol), $(CH_2O)_n$ (200 mg, 6.7 mmol of -CH_2O), $Pd(OAc)_2$ (1 mol %), d^{t}bpx (X mol %), PTSA (Y mol %) in 2 mL of methanol (**2a**) at 100 °C for 20 h. Yields determined by GC analysis.



Scheme 2. ^{13}C Isotope labeling experiments and control experiments using other alcohols.

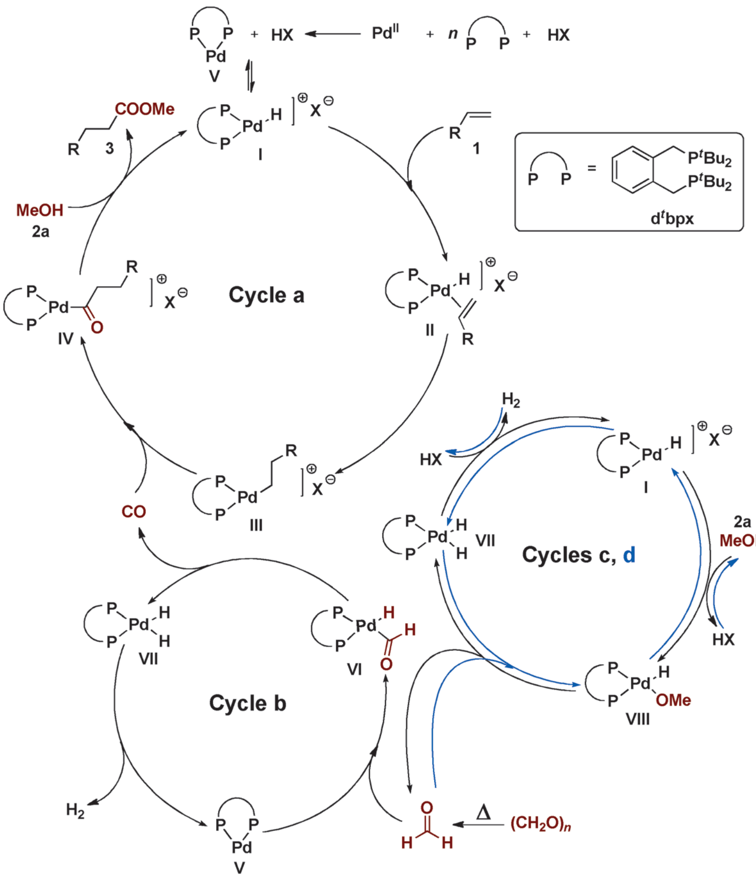
^{13}C-labeled paraformaldehyde was applied in this transformation, surprisingly only 51 % of the ester product was ^{13}C-labeled methyl nonanoate **3a'** along with 49 % nonlabeled product **3a** [Scheme 2, Eq. (1)]. In addition, a similar distribution of the ^{13}C-labeled methoxycarbonylation product was observed for the reaction using $^{13}CH_3OH$ as the solvent [Scheme 2, Eq. (2)]. These results indicate that both formaldehyde and methanol act as the carbonyl source in this process simultaneously. Apparently, CO release from methanol proceeds by sequential dehydrogenation and decarbonylation processes.[17] Actually, palladium-catalyzed alcohol dehydrogenation under such acidic conditions is rather unusual but it also takes place with other alcohols under these standard conditions. Interestingly, methyl nonanoate (**3a**) and isopropyl nonanoate (**5**) were both produced in the reaction of isopropanol [Scheme 2, Eq. (3)]. This demonstrates that under our catalytic conditions methanol is also generated from formaldehyde through transfer hydrogenation with isopropanol.

Encouraged by the hydrogenation/dehydrogenation reactivity of this catalytic system, we wondered if methanol or paraformaldehyde alone could act as both the CO surrogate and nucleophile for the methoxcarbonylation reaction. Unfortunately, no desired product was attained (Scheme 3). This finding illustrates that methanol dehydrogenation occurs only in the presence of formaldehyde as the hydrogen acceptor.



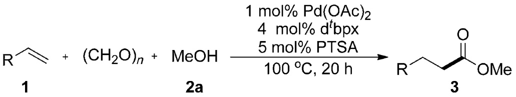
Scheme 3. Methoxycarbonylation of **1a** using only $(CH_2O)_n$ or MeOH (**2a**).

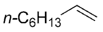
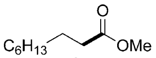
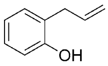
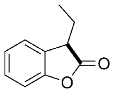
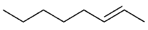
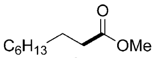
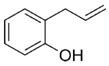
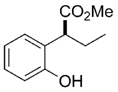
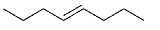
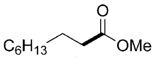
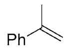
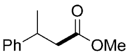
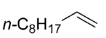
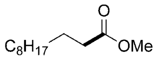
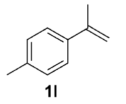
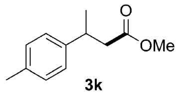
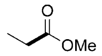
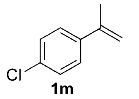
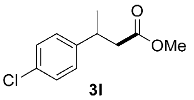
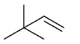
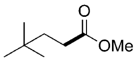
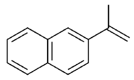
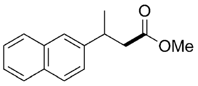
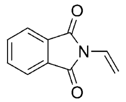
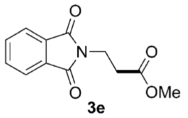
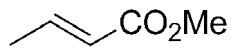
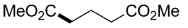
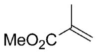
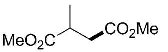
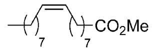
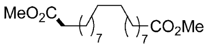
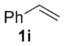
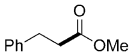
Based on the experimental findings, a reaction mechanism incorporating synchronous quadruple catalytic cycles is proposed (Scheme 4). It is known that a Pd^{II} catalyst precursor can be reduced in situ to Pd^0 species **V** in the presence of excess phosphine ligands.[18] Under acidic conditions, Pd^0 complex **V** is in an equilibrium with Pd^{II} hydride complex **I**,[19] which is the key catalytically active species to initiate the methoxycarbonylation cycle **a**. Subsequent insertions of alkene **1** and CO followed by alcoholysis of the acyl Pd^{II} complex **IV** form ester **3** and regenerate the Pd hydride species **I**. The CO consumed in cycle **a** was produced from catalytic cycle **b**. More specifically, at elevated temperature paraformaldehyde can depolymerize to produce formaldehyde, which will undergo an oxidative addition with Pd^0 species **V** to generate the (hydrido)(acyl)palladium(II) complex **VI**. Upon decarbonylation, this latter complex provides Pd^{II} dihydride complex **VII** and releases CO gas for the methoxycarbonylation process. The reductive elimination of **VII** regenerates Pd^0 catalyst **V** and produces hydrogen. Meanwhile, the dehydrogenation of methanol (**2a**) is also catalyzed by Pd^{II} hydride **I** to afford formaldehyde through catalytic cycle **c**. In this cycle, the coordination of methanol to complex **I**



Scheme 4. Proposed reaction mechanism: Quadruple catalytic cycles.

Table 3: Pd-catalyzed methoxycarbonylation of alkenes **1** with paraformaldehyde and methanol (**2a**).[a]



Entry	Substrate **1**	Product **3**[b]	Yield **3** [%] (l/b)[c]	Entry	Substrate **1**	Product **3**[b]	Yield **3** [%] (l/b)[c]
1	 **1a**	 **3a**	93 (95:5)	10	 **1j**	 **3h**	58, 8 h[e]
2	 **1b**	 **3a**	93 (94:6)	11	 **1j**	 **3i**	75, 36 h[e]
3	 **1c**	 **3a**	75 (89:11)	12	 **1k**	 **3j**	76 (>99:1)
4	 **1d**	 **3b**	92 (95:5)	13	 **1l**	 **3k**	69 (>99:1)
5[d]	 **1e**	 **3c**	99	14	 **1m**	 **3l**	43 (>99:1)
6	 **1f**	 **3d**	85 (>99:1)	15	 **1n**	 **3m**	73 (>99:1)
7	 **1g**	 **3e**	55 (>99:1)	16	 **1o**	 **3n**	92 (>99:1)
8	 **1h**	 **3f**	89 (>99:1)	17	 **1p**	 **3o**	86 (94:6)
9	 **1i**	 **3g**	90 (78:22)				

[a] Reaction conditions: 1 (1 mmol). $(CH_2O)_n$ (200 mg, 6.7 mmol of $-CH_2O$), $Pd(OAc)_2$ (1 mol%), d^tbpx (4 mol%), PTSA (5 mol%) in 2 mL of methanol (**2a**) at 100°C for 20 h. [b] The main isomer of a mixture of methyl ester products is shown. [c] Yield of isolated product for a mixture of methyl ester isomers. [d] See the Supportorting Information for detail conditions. [e] Reaction time.

provides (hydrido)(methoxy)palladium(II) species **VIII**, which gives Pd^{II} dihydride complex **VII** by β-hydride elimination. Finally, intermediate **VII** undergoes reductive elimination and oxidative addition with HX to close this catalytic cycle and also liberate hydrogen. Simultaneously, formaldehyde can enter catalytic cycle **d**, which is the reverse process of cycle **c**. Accordingly, an equilibrium between methanol and formaldehyde is established through these two palladium-catalyzed processes.

With the optimized reaction conditions in hand, we continued to probe the scope of alkenes **1** for the Pd-catalyzed methoxycarbonylation reaction with paraformaldehyde and methanol (**2a**; Table 3). The reactions of terminal aliphatic alkenes such as 1-octene (**1a**) and 1-decene (**1d**) were very efficient with >90% yields and up to 95% *n*-selectivity (Table 3, entries 1 and 4). More significantly, mixtures of internal and terminal olefins are usually preferred as less expensive start materials in industrial manufacture. Therefore, double-bond isomerization followed by carbonylation process is of great industrial interest. Delightfully, this catalytic system was able to convert aliphatic internal olefins including 2-octene and 4-octene into the corresponding linear methyl nonanoate with high yield and *n*-selectivity (Table 3, entries 2 and 3). Moreover, a more-stable internal conjugated ester underwent the same isomerization/methoxycarbonylation transformation as well to provide industrially essential dimethyl glutarate (**3n**) in 92% yield and up to over 99% *n*-selectivity (Table 3, entry 16).

Terminal functionalization of fatty acids is another synthetic challenge. The isomerizing methoxycarbonylation of renewable methyl oleate (**1p**) again proceeded smoothly under optimized conditions and led to the selective formation of the respective linear diester product (Table 3, entry 17). Methyl propionate (**3c**) was obtained in 99% yield using ethylene (**1e**) as the substrate with a TON of 536 for the palladium catalyst (Table 3, entry 5).

Aromatic olefins such as styrene (**1i**) are usually carbonylated at the *iso*-position due to the benzylic stabilization of the metal center. Conversely, the present system enabled a good *n*-selective carbonylation (Table 3, entry 9). The reactions of α-methylstyrene derivatives afforded a series of terminal araliphatic esters selectively in good yields (Table 3, entries 12–15). Furthermore, methoxycarbonylation of 2-allylphenol (**1j**) proceeded the double-bond isomerization and consecutive carbonylation at the benzyl position to produce lactone **3h** after 8 h. Under the same reaction conditions, the corresponding methoxycarbonylation product **3i** was generated after a longer reaction time (36 h) in 75 % yield by alcoholysis of the cyclic ester intermediate **3h** with methanol (**2a**).

In conclusion, we developed a general and benign methoxycarbonylation of alkenes with paraformaldehyde and methanol as the CO surrogates to produce a variety of industrially important and functionalized methyl esters. Interestingly, this reaction proceeds through synergetic multiple catalytic cycles. In view of the easy availability of the substrates, the stable and atom-economic paraformaldehyde and methanol as CO substitutes, the excellent regioselectivity, as well as the easy to handle "CO-free" reaction process, this procedure is expected to complement the present methods for carbonylations in both organic synthesis and industrial production.

Keywords: carbonylation · CO surrogates · formaldehyde · methanol · palladium

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