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Ruthenium-catalysed alkoxy carbonylation of alkenes with carbon dioxide

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Alkene carbonylations represent a major technology for the production of value-added bulk and fine chemicals. Nowadays, all industrial carbonylation processes make use of highly toxic and flammable carbon monoxide. Here we show the application of abundantly available carbon dioxide as C1 building block for the alkoxy carbonylations of industrially important olefins in the presence of a convenient and inexpensive ruthenium catalyst system. In our system, carbon dioxide works much better than the traditional combination of carbon monoxide and alcohols. The unprecedented *in situ* formation of carbon monoxide from carbon dioxide and alcohols permits an efficient synthesis of carboxylic acid esters, which can be used as detergents and polymer-building blocks. Notably, this transformation allows the catalytic formation of C–C bonds with carbon dioxide as C1 source and avoids the use of sensitive and/or expensive reducing agents (for example, Grignard reagents, diethylzinc or triethylaluminum).

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The functionalization of lower aliphatic alkenes constitutes an important basis of today's chemical industry. Apart from polymerization and oxidation^{1,2}, carbonylation reactions using carbon monoxide represent a major technology for the production of value-added bulk and fine chemicals from olefins³. In addition to industrial hydroformylation processes that provide aldehydes^{4–7}, the alkoxycarbonylation of alkenes constitutes a straightforward approach to carboxylic acid esters⁸. On an industrial scale, the resulting aliphatic esters are mainly used for the production of detergents and polymer-building blocks. For example, the current state-of-the-art commercial process for methyl methacrylate polymers is based on the palladium-catalysed methoxycarbonylation reaction of ethylene (Fig. 1a)⁹. In this reaction, the catalytically active palladium(II)-hydride species is generated with the assistance of a Brønsted acid co-catalyst^{10,11}.

Generally, all these carbonylation processes make use of toxic and flammable carbon monoxide, which is also difficult to transport on a bulk scale. More than 110,000 people protested against a pipeline for CO transport by Bayer AG in Germany. The company had to stop the installation because of this public protest; see: <http://www.stopp-co-pipeline.de/>. Hence, performing carbonylations without carbon monoxide is highly desired and would further advance this area¹². So far, all used carbon monoxide surrogates have significant drawbacks with respect to atom efficiency and/or price. For example, aldehydes¹³ and higher alcohols like cinnamyl alcohol¹⁴ or polyols¹⁵ were used as carbon monoxide source especially in hydroformylation and Pauson–Khand-type reactions. For alkoxycarbonylation reactions, formates are known to be a CO substitute¹⁶. Apart from above-mentioned CO sources, stoichiometric amounts of metal carbonyls such as Mo(CO)₆ and W(CO)₆ are also applied to deliver carbon monoxide¹⁷. In contrast to all these protocols, the use of abundant CO₂ is desirable. However, because of its thermodynamic and kinetic stability^{18–21}, the catalytic C–C bond formation between carbon dioxide and olefins constitutes one of the most challenging tasks for organometallic chemistry. So far, the reported carboxylation of alkenes with carbon dioxide proceeds only in the presence of

(over)stoichiometric amounts of strong or expensive reductants like Et₂Zn and silanes^{22–24}. Obviously, such reactions are restricted because of the sensitivity and price of the reagents as well as the waste generated.

In contrast, herein we describe the use of carbon dioxide as C1 source in the alkoxycarbonylation reaction of industrially important alkenes (Fig. 1b) and avoid the use of sensitive and/or expensive reducing agents (for example, Grignard reagents, Et₂Zn or Et₃Al). Furthermore, compared with the present state-of-the-art palladium-catalysed alkoxycarbonylation, advantageously in our protocol less expensive triruthenium dodecacarbonyl is applied as a convenient and stable catalyst without the usage of sensitive or acidic reagents.

Results

Effect of reaction parameters. In addition to traditional carbonylation catalysts, recently ruthenium complexes demonstrated their potential in hydroformylation^{25,26} and hydroaminomethylation reactions using CO²⁷. On the basis of our expertise in this area, we became interested to use carbon dioxide as CO surrogate for such reactions. The initial experiments were carried out in high-pressure Parr reactors with 1-octene **1a** in the presence of 0.5 mol% Ru₃(CO)₁₂ under 40 bar carbon dioxide at 160 °C using methanol and *N*-methyl-2-pyrrolidone as solvent (Supplementary Table 1). To our surprise, methoxycarbonylation products **2a** and octane **3a** were obtained in 11 and 40% yield, respectively, without any hydrogen or additional reducing agents present. Besides, significant amounts of internal octenes **4a** were formed. This latter reaction is explained by the formation of ruthenium–hydride complexes, which constitute well-known alkene isomerization catalysts^{28,29}.

To favour the unusual carbonylation process, substoichiometric amounts of LiCl (0.25 equiv. to 1-octene) were added to the reaction, which are known to suppress alkene hydrogenation in the ruthenium-catalysed hydroformylation^{25,30,31}. Indeed, the yield of **2a** was improved to 31% (Supplementary Table 1, entry 2). Next, we investigated the role of additives, catalyst loading, temperature as well as solvent effects (Supplementary Tables 1–6). To our delight, the corresponding methyl esters were obtained in excellent yield (>90%) using methanol as the solvent in the presence of ionic liquid as additive at 160 °C (Fig. 2). Notably, good yields of the products were still achieved at lower reaction temperature (145 °C, 81% yield; Supplementary Table 1, entry 10).

Substrate scope. Encouraged by these results, we studied the reactivity of different alkenes and various alcohols with carbon dioxide (Table 1). Apart from methanol, 1-octene reacted well with ethanol and benzyl alcohol to produce the corresponding carboxylic acid esters in high yields (84–92%; entries 1–3). For lower terminal aliphatic alkenes, 95% of esters **5a** and **6a** were obtained (entries 4 and 5). In all these examples, a mixture of the branched and linear ester was formed. Looking at the kinetic profile of the benchmark reaction (Supplementary Fig. 1) revealed fast conversion of **1a** into 2-octene. Then, the esters **2a** were

Figure 1 | Catalytic carbonylation of alkenes. (a) Palladium-catalysed methoxycarbonylation of alkenes with carbon monoxide and methanol to produce esters in the presence of acid co-catalyst. (b) This work: ruthenium-catalysed methoxycarbonylation of alkenes with carbon dioxide and methanol.

Figure 2 | Methoxycarbonylation of 1-octene with carbon dioxide and methanol. 1-octene 10 mmol, [Bmim]Cl 20 mmol, Ru₃(CO)₁₂ 1.0 mol%, CO₂ 40 bar, methanol 20 ml, 160 °C, 20 h.

Table 1 | Alkoxy carbonylation of alkenes with carbon dioxide and alcohols*.

Entry	Alkenes	Alcohols	Products	Yield (%) [†]	Entry	Alkenes	Alcohols	Products	Yield (%) [†]
1		methanol	2a (R = Me)	92 [‡]	20	(4-methoxyphenyl) methanol		8i (R = CH ₂ C ₆ H ₄ -p-MeO)	71
2		ethanol	2b (R = Et)	84 [‡]	21	(3-methoxyphenyl) methanol		8j (R = CH ₂ C ₆ H ₄ -m-MeO)	55
3		benzyl alcohol	2c (R = Bn)	90 [‡]	22	(4-fluorophenyl) methanol		8k (R = CH ₂ C ₆ H ₄ -p-F)	88
4		methanol	5a	95 [‡]	23	tetrahydro-2-furanyl methanol		8l (R = tetrahydro-2-furanylmethylene)	60
5		methanol	6a	95 [‡]					
6		methanol	2a (R = Me)	90 [‡]	24		ethanol	9a (R = Et)	87
7		ethanol	2b (R = Et)	80 [‡]	25		benzyl alcohol	9b (R = Bn)	91
8		benzyl alcohol	2c (R = Bn)	89 [‡]	26		ethanol	10a	56
9		methanol	2a	83 [‡]				11a (R = Me)	60
10		methanol	7a (R = Me)	94	27		methanol	11b (R = Et)	53
11		ethanol	7b (R = Et)	82	28		ethanol	12a (R = Me)	82 [§]
12		methanol	8a (R = Me)	95	29	R ¹ = H	methanol	12b (R = Et)	64 [§]
13		ethanol	8b (R = Et)	85	30	R ¹ = H	ethanol	12c (R = Et)	56 [§]
14	1-butanol		8c (R = nBu)	72	31	R ¹ = 4-Me	ethanol	12d (R = Et)	65 [§]
15	1-nonanol		8d (R = nC ₉ H ₁₉)	41	32	R ¹ = 4-Cl	ethanol	12e (R = Et)	51 [§]
16	isopropanol		8e (R = iPr)	75	33	R ¹ = 2-naphthyl	ethanol	12f (R = Et)	56 [§]
17	benzyl alcohol		8f (R = Bn)	74	34	R ¹ = 4-isopropenyl	ethanol	13a	87 ^{§‡}
18	2-phenyl ethanol		8g (R = CH ₂ CH ₂ C ₆ H ₅)	68	35		methanol	14a	76
19	1-phenyl ethanol		8h (R = CH(CH ₃)C ₆ H ₅)	77	36		methanol		

*Alkenes 10.0 mmol, [Bmim]Cl two equivalents with respect to alkene, Ru₃(CO)₁₂ 1.0 mol%, CO₂ 40 bar, 160 °C, alcohols 20 ml, 20–36 h.[†]Yield was determined by GC analysis using isooctane (1.0 ml) as an internal standard.[‡]*in* *iso* ≈ 1:1 (detail: 2a: 1-COOMe 45%, 2-COOMe 38%, 3-COOMe 9%, 4-COOMe 8%; 2b: 1-COOEt 45%, 2-COOEt 38%, 3-COOEt 9%, 4-COOEt 8%; 2c: 1-COOBn 50%, 2-COOBn 37%, 3-COOBn 7%, 4-COOBn 6%; 5a: 1-COOMe 44%, 2-COOMe 45%, 3-COOMe 11%; 6a: 1-COOMe 50%, 2-COOMe 44%, 3-COOMe 6%; 13a: 1-COOMe 50%, 2-COOMe 41%, 3-COOMe 9%).[§]Isolated yields.||Ethylene 7.1 mmol, Ru₃(CO)₁₂ 2.1 mol%, [Bmim]Cl 20.0 mmol, reaction time 20 h.

produced at a lower rate along with the appearance of octane **3a** and other internal octenes **4a**. Thus, reactions of internal alkenes, like 2-octene, with different alcohols gave almost the same yields and selectivities compared with 1-octene (entries 6–8). In case of 1,7-octadiene, product **2a** was produced with one double bond being reduced (entry 9). 3,3-Dimethylbut-1-ene gave highly selectively the corresponding terminal ester in very good yield (entries 10 and 11). Applying cyclohexene as the starting material, the generality of the process with more functionalized alcohols was studied (entries 12–23). Not only primary alcohols but also secondary alcohols reacted smoothly in moderate to excellent yields, although a longer reaction time was needed for secondary alcohols. Functionalized alcohols with halide and ether groups were well tolerated too (entries 20–23). Other cyclic olefins, for example, cyclopentene (entries 24 and 25), *cis*-cyclooctene (entry 26) as well as norbornene (entries 27 and 28) led to esters in 53–91% yield. Furthermore, different aromatic olefins and allyl

benzene reacted with methanol or ethanol to afford a series of araliphatic esters in good yields as well (entries 29–35). Finally, methyl propionate, a bulk-scale intermediate in the manufacture of methyl methacrylate (Lucite α -process), was achieved in 76% yield using ethylene as substrate (entry 36).

Control experiments. To gain more insight into this ruthenium-catalysed C–C bond formation^{32,33} with carbon dioxide, a series of control experiments were performed. Initially, the reaction of carbon dioxide and methanol under catalytic conditions without any olefin present was studied (Fig. 3a). Interestingly, CO and H₂ were detected in the gas phase (Supplementary Figs 3 and 4). At the same time, methyl formate was observed in the liquid phase. Therefore, reactions of 1-octene with these intermediates (CO, methyl formate) were conducted (Fig. 3b,c). As expected, ruthenium-catalysed methoxycarbonylation occurred with CO.

Figure 3 | Control experiments. (a) Analysis of standard reaction without the presence of 1-octene **1a**. (b) Reaction of 1-octene **1a** with CO (different pressures) and CO₂. (c) Reaction of 1-octene **1a** with methyl formate.

Figure 4 | Isotope labelling experiments. (a,b) Reactions were run in 2 mmol scale under 12 bar ¹³CO₂, other conditions were the same as in Fig. 2. (c) Reaction was run in 2 mmol scale with 6 ml ¹³CH₃OH, other conditions were the same as in Fig. 2.

This reaction is best achieved at low concentration of carbon monoxide (Supplementary Table 7). When the carbon monoxide pressure was increased from 2 to 40 bar, the yield of the ester **2a** was reduced from 70 to 31% (Fig. 3b). Comparing CO with CO₂, the latter reagent is more efficient in this process (92% yield of **2a**; Fig. 3b). We explain this unusual behaviour by the *in situ* formation of carbon monoxide from carbon dioxide and methanol. In addition, the control experiment with methyl formate³⁴ also showed esterification of the alkene **1a** albeit in significantly lower yield (Fig. 3c).

Isotope-labelling experiments. To prove the origin of carbon monoxide, isotope-labelling experiments were performed. Applying ¹³C-labelled carbon dioxide (12 bar) in the reactions of methanol and ethanol 82 and 86% of the carbon in the carbonyl

group, respectively, were ¹³C labelled (Fig. 4a,b). In agreement with this observation, it was revealed that only a minor amount of the carbon of the carbonyl group was ¹³C labelled when ¹³C-labelled methanol was applied under the same conditions (Fig. 4c). This result clearly demonstrated carbon dioxide as the main carbonyl source of this transformation (Supplementary Figs 5–9).

Discussion

On the basis of all these results, we suggest the following reaction pathways for alkoxycarbonylations with carbon dioxide (Fig. 5): Initially, carbon dioxide is reduced by the alcohol through the so-called 'hydrogen-borrowing'^{35–37} to carbon monoxide (path I) or alkyl formates (path II). Both CO and formate are detected in our reaction system and react with the alkene affording esters as

Figure 5 | Possible reaction pathways for the carbonylation using carbon dioxide. Path I contribute mainly to the ester production. Only minor amount of esters come from path II and III.

discussed above. On the basis of the significantly lower yield (17%) with formate (Fig. 3c), we propose path I to be the major reaction pathway for this transformation. Meanwhile, the alcohol undergoes dehydrogenation to form carbonyl compounds (formaldehyde in the case of methanol; Fig. 5, path III)³⁸. Interestingly, a minor amount of the CO comes from further decarbonylation reactions as shown by the isotope-labelling experiments (Fig. 4). Accordingly using *p*-methoxyphenyl methanol as the alcohol, small amounts of the decarbonylated product methyl phenyl ether are detected in solution³⁹.

While alkoxycarbonylation reactions are generally performed with homogenous catalysts, alcohol dehydrogenations are catalysed by heterogeneous catalysts. Therefore, efforts were undertaken to understand the nature of the active catalyst in this process (Supplementary Methods). Key experiments using 1-octene, carbon dioxide and methanol included the following: (a) the standard Hg(0) poisoning test; (b) the hot filtration test; (c) ligand poisoning and (d) control reactions with self-made ruthenium nanoparticles stabilized by ionic liquids (Supplementary Fig. 2)^{40–42}. All these tests uncovered the homogenous nature of the catalyst in this reaction system (Supplementary Tables 8–11).

In conclusion, we demonstrate the feasibility to use carbon dioxide and alcohols for alkoxycarbonylation processes of olefins without any additional strong reductant. A number of aliphatic olefins as well as styrenes can be transformed in high yields to industrially relevant carboxylic acid esters, for example, methyl propionate. In this process, carbon dioxide is reduced by the parent alcohol using convenient triruthenium dodecacarbonyl. The present catalyst system does not need any sensitive ligands or expensive additives. Notably, in the current ruthenium-catalysed alkoxycarbonylation process, the use of carbon dioxide and alcohols works much better than the combination of carbon monoxide and alcohols. Conceptually, it is shown that toxic carbon monoxide can be replaced by CO₂. We estimate that this novel methodology is applicable to other carbonylation reactions too. Therefore, we anticipate that this work will contribute substantially to the development of next-generation CO₂ utilization.

Methods

General analytic methods. NMR spectra were recorded on Bruker Avance 300 (300 MHz) and Bruker Avance 400 (400 MHz) NMR spectrometers. Chemical shifts (p.p.m.) are given relative to solvent: references for CDCl₃ were 7.26 p.p.m. (¹H NMR) and 77.00 p.p.m. (¹³C NMR). ¹³C NMR spectra were acquired on a broad band-decoupled mode. Multiplets were assigned as singlet, doublet, triplet, doublet of doublet, multiplet and broad singlet. All measurements were carried out at room temperature unless otherwise stated (Supplementary Figs 10–32). Electron impact mass spectra were recorded on AMD 402 mass spectrometer (70 eV). High

resolution mass spectra were recorded on Agilent 6210. The data are given as mass units per charge (*m/z*). For gas chromatography (GC) analyses, HP 7890 chromatograph with a 30-m HP5 column was used. Gas-phase GC were performed on Agilent 6890N (G1530N). Isooctane is used as an internal standard for GC analysis. The products were isolated from the reaction mixture by solvent evaporation and following column chromatography on silica gel 60, 0.063–0.2 mm, 70–230 mesh (Merck) or bulb-to-bulb distillation using Büchi Glass oven B-585 wherever necessary. Linear to branched ratios were determined by GC analysis of the crude reaction mixture.

Materials. All commercial reagents were ordered from Acros Organics, Alfa Aesar, Aldrich or Strem. Alkenes were dried according to standard procedures. Methanol was distilled without being dried from industrial methanol. Ru₃(CO)₁₂ (triruthenium dodecacarbonyl 99%) and 1-methyl-2-pyrrolidinone anhydrous (99.5%) was ordered from Aldrich and used as received. [Bmim]Cl (1-butyl-3-methylimidazolium chloride) was produced by BASF, ≥95% purity. Carbon dioxide (4.8) was received from Linde Gas. All operations were carried out by using standard high vacuum and Schlenk techniques unless otherwise noted.

General procedure for the alkoxycarbonylation reaction. A 100-ml autoclave was charged with Ru₃(CO)₁₂ (63.9 mg, 100 μmol), [Bmim]Cl (1-butyl-3-methylimidazolium chloride, 3.48 g, 20 mmol), 20 ml alcohols and 10 mmol alkenes. Then, 40 bar of carbon dioxide was introduced before the autoclave was heated to 160 °C. After 20–36 h, the reaction was stopped by cooling down and releasing the pressure. The reaction solution was diluted with acetone and analysed by GC using isooctane as an internal standard. The products were isolated from the reaction mixture by solvent evaporation and following column chromatography on silica gel 60, 0.063–0.2 mm, 70–230 mesh (Merck) or bulb-to-bulb distillation using Büchi Glass oven B-585 wherever necessary.

Methoxycarbonylation of 1-octene with CO and methanol. A 100-ml autoclave was charged with Ru₃(CO)₁₂ (64 mg, 100 μmol), [Bmim]Cl (1-butyl-3-methylimidazolium chloride, 3.48 g, 20 mmol), 20 ml CH₃OH and 1.6 ml 1-octene (1.12 g, 10 mmol). Then, 2 or 40 bar of CO was introduced before the autoclave was heated to 160 °C. After 20 h, the reaction was stopped by cooling down and releasing the pressure. The reaction solution was diluted with acetone and analysed by GC using isooctane as the internal standard. The yields of corresponding products were determined as following: (1) 2 bar CO: **2a** 70%, **3a** 16%, **4a** 11%. (2) 40 bar CO: **2a** 31%, **3a** 21%, **4a** 44%.

Methoxycarbonylation of 1-octene with methyl formate. A 100-ml autoclave was charged with Ru₃(CO)₁₂ (64 mg, 100 μmol), [Bmim]Cl (1-butyl-3-methylimidazolium chloride, 3.48 g, 20 mmol), 20 ml CH₃OH and 1.6 ml 1-octene (1.12 g, 10 mmol). Methyl formate (1.2 ml) was added, and then the autoclave was heated to 160 °C. After 20 h, the reaction was stopped by cooling down and releasing the pressure (gas evolution during the reaction process). The reaction solution was diluted with acetone and analysed by GC using isooctane as the internal standard. The yields of corresponding products were determined as following: **2a** 17%, **3a** 41%, **4a** 39%.

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Author contributions

M.B., L.W. and Q.L. designed this project. L.W., Q.L., I.F., R.J. and M.B. developed this project. L.W. and Q.L. performed the catalytic experiments and data analysis. L.W., Q.L. and M.B. wrote the manuscript.

Additional information

Supplementary Information accompanies this paper at <http://www.nature.com/naturecommunications>

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