Carbonylation

Carbonylations of Alkenes with CO Surrogates

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Alkene carbonylation reactions are important for the production of value-added bulk and fine chemicals. Nowadays, all industrial carbonylation processes make use of highly toxic and flammable carbon monoxide. In fact, these properties impede the wider use of carbonylation reactions in industry and academia. Hence, performing carbonylations without the use of CO is highly desired and will contribute to the further advancement of sustainable chemistry. Although the use of carbon monoxide surrogates in alkene carbonylation reactions has been reported intermittently in the last 30 years, only recently has this area attracted significant interest. This Minireview summarizes carbonylation reactions of alkenes using different carbon monoxide surrogates.

1. Introduction

The functionalization of lower aliphatic alkenes constitutes an important basis of today's chemical industry. Apart from polymerization and oxidation, carbonylation reactions using CO represent a major technology for the production of value-added bulk and fine chemicals from olefins. As an example, methyl propionate, a key intermediate for polymethacrylates, is produced on the scale of > 300 000 tons per annum by the palladium-catalyzed methoxycarbonylation of ethylene.[1] Besides, over 10 million tons of oxo products are produced every year from alkenes via hydroformylation and related tandem reactions.[2] Notably, all these processes make use of toxic carbon monoxide, which is also difficult to transport in bulk. As a result of the physical properties of carbon monoxide, its use in the fine chemical industry and academia is limited. In this respect, carbonylations conducted without carbon monoxide would be reliable and accessible tools for synthetic organic chemists. Ten years ago, Morimoto and Kakiuchi summarized the use of carbon monoxide surrogates mainly in Pauson–Khand reactions, carbonylation reactions with aromatic halides, and few cases of reactions with alkenes.[3] Since then, many research projects have addressed new strategies and new carbonyl sources.[4] For example, carbon dioxide,[5] methanol,[6] and even biomass[7] have been reported to be renewable carbonyl sources in alkene carbonylation reactions. Moreover, milder reaction conditions and better regioselectivities were reported recently. The present Minireview focuses on alkene carbonylation reactions performed without the use of carbon monoxide.

2. Carbon Dioxide

Though chemical activation of CO_2 is problematic due to its high thermodynamic and kinetic stability, chemists have continued to explore useful carbon dioxide transformations.[8] Latest examples include the transformation of carbon dioxide to methanol in the presence of homogeneous catalysts.[9] Also the recent production of cyclic carbonates[10] and copolymers[11] is noteworthy. Moreover, advanced synthetic technologies like the hydrogenation of carbon dioxide to formic acid and its derivatives,[12] the chemisorption of carbon dioxide with amine absorbent,[13] and the carboxylation of arylmetallic species[14] and C−H bonds[15] as well as carbon–carbon multiple bonds[16] to give carboxylic acid derivatives directly have seen highly dynamic development. However, the related utilization of carbon dioxide as a carbonyl source in alkene carbonylation reactions has been less thoroughly studied.

The general strategy of the use of carbon dioxide as a carbonyl source is the reduction of carbon dioxide in situ to carbon monoxide which can be used in the subsequent carbonylation processes (Scheme 1, path a). The crucial step

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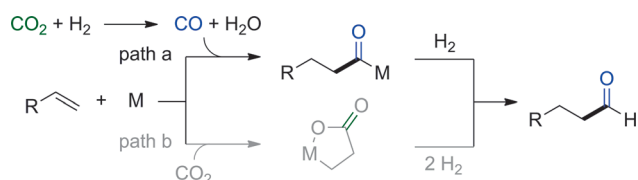
Scheme 1. Reaction of alkenes with carbon dioxide and hydrogen.

is known as reverse water–gas shift reaction (RWGS). Based on their previous studies on RWGS reactions,[17] Tominaga and Sasaki reported in 2000 the first ruthenium-catalyzed hydroformylation/reduction of alkenes with carbon dioxide.[18] They found that at 140°C cyclohexylmethanol was obtained in 88% yield directly from cyclohexene, carbon dioxide, and hydrogen in the presence of LiCl and [$H_4Ru_4(CO)_{12}$] (Scheme 2). This result was even better than
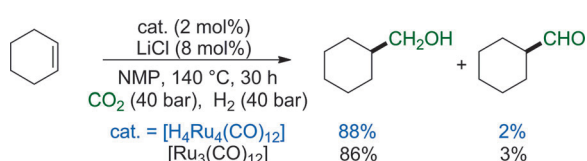
Scheme 2. Ruthenium-catalyzed hydroformylation/reduction of cyclo-hexene with carbon dioxide.

that from the reaction with carbon monoxide and hydrogen under otherwise identical conditions. Tominaga also pointed out that the hydrocarboxylation of alkenes with carbon dioxide (Scheme 1, path b) as the reaction pathway could be ruled out since the corresponding carboxylic acid did not

form. In agreement with their proposal, a significant amount of carbon monoxide in the gas phase was detected.

Four years later, the same group reported a detailed study on the above-mentioned reaction.[19] They found that the catalytic activity of the ruthenium complex was strongly affected by salt additives (Table 1). The reaction rate

Table 1: Effect of salts on the hydroformylation/reduction of alkenes with carbon dioxide.[a]

Salt	Yield [%]	Salt	Yield [%]
LiCl	88	[PPN]Cl	82
LiBr	76	–	0
LiI	29		

[a] Conditions: [$H_4Ru_4(CO)_{12}$] (0.1 mmol), salt (0.4 mmol), cyclohexene (5.0 mmol), NMP (8.0 mL), CO_2 (40 bar), H_2 (40 bar), 140°C, 30 h.

increased on the order of $I^- < Br^- < Cl^-$, which is also the order of their proton affinities. With regard to cations other than Li^+, some organic cations like $(PPh_3)_2N^+$ (PPN^+) gave similar results. Then, the authors studied the effect of other reaction parameters like temperature and solvents, and found that the temperature was important for the in situ formation of carbon monoxide since no carbon monoxide was detected below 100°C. The solvent had no effect on the overall reaction.

To elucidate the catalytically active species, ESI-MS analysis was conducted. Four ruthenium species could be identified in the catalytic system: [$H_3Ru_4(CO)_{12}$]$^-$ (**1**), [$HRu_3(CO)_{11}$]$^-$ (**2**), [$RuCl_3(CO)_3$]$^-$ (**3**), and [$RuCl_2(CO)_3$-(C_6H_{10})]$^-$ (**4**). After several control experiments, Tominaga

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Qiang Liu received his BSc in Chemistry at Wuhan University in 2007. He earned his PhD there under the supervision of Aiwen Lei in 2012. Then, he joined Matthias Beller's group at LIKAT as a Humboldt postdoctoral fellow. His current research interest is applied homogenous catalysis for carbon dioxide activation and alkene carbonylation reactions.

Matthias Beller earned his PhD in 1989 under the supervision of Lutz F. Tietze at the University of Göttingen. After postdoctoral research at MIT with Barry Sharpless, he gained industrial experience at Hoechst AG in Frankfurt from 1991 until 1995. Subsequently, he started his independent career at TU Munich as professor for inorganic chemistry. In 1998 he moved to Rostock. Since 2006 he has been the director of LIKAT. His research concerns applied homogeneous catalysis for the synthesis of fine and large-scale chemicals, as well as for energy technology.
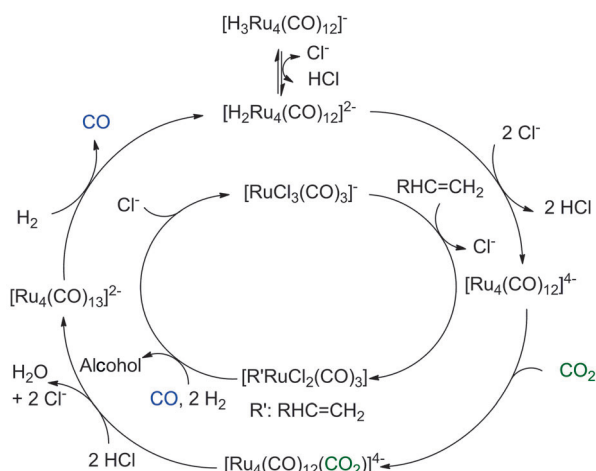
Scheme 3. Two catalytic cycles for the ruthenium-catalyzed hydroformylation/reduction of alkenes with carbon dioxide.

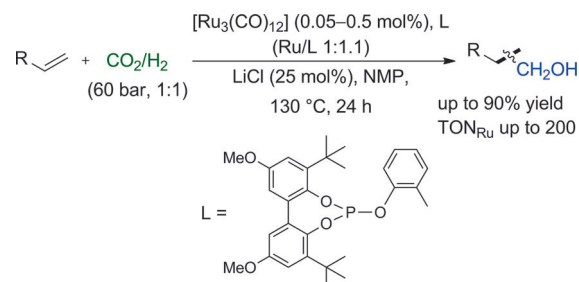**Scheme 4.** Hydroxymethylation of olefins using a phosphite-ligand-modified ruthenium catalyst system.

and Sasaki figured out that the combination of complex **1** and **3** or **2** and **3** was critical for successful conversion.

Based on all these observations, the reaction mechanism shown in Scheme 3 was proposed. A key step was the deprotonation of the hydride complex with Cl^- to give the hydrogen-free low-valent complex $[Ru_4(CO)_{12}]^{4-}$, which can coordinate CO_2 and catalyzed CO formation.

Initially, the reactions of terminal aliphatic alkenes gave much worse yields and lower selectivities due to alkene hydrogenation as a side reaction. This problem was solved by using a ruthenium complex immobilized by ionic liquids.[5b] The mixed ionic liquids [Bmim][Cl+NTf₂] (Bmim: 1-butyl-3-methyllimidazolium) were used not only as the promoter but also as the solvent, so that no volatile solvents have to be used. In this case, for 1-hexene the yield of alcohol reached 82% and at 160°C with only 8% of the hexane as side product. Furthermore, the reaction medium containing the ruthenium catalyst could be recycled to provide a 76% yield of alcohol even after five runs.

Haukka and co-workers also reported studies on this hydroformylation/reduction reaction of 1-hexene with carbon dioxide and hydrogen in 2003[20] and 2009.[21] Their contributions to this transformation can be summarized as follows: 1) They found that apart from ruthenium clusters such as $[H_4Ru_4(CO)_{12}]$ and $[Ru_3(CO)_{12}]$, $[\{Ru(CO)_3Cl_2\}_2]$ could also be applied as a catalyst precursor. 2) They elucidated the correlations between halides/counterions and reaction activities. As a result they declared that the halide was indispensable for active catalysts. In general, the chloride ions could either originate from the additive salts or the catalyst precursor. For example, the best results were obtained by using $[\{Ru(CO)_3Cl_2\}_2]/Li_2CO_3$. 3) In their reaction system even HCl (37%) could be used as a promoter. 4) They also discovered that polymeric 1D metal atom chain $[Ru(CO)_4]_n$ could replace other ruthenium clusters to give the same results. This time DMF was the solvent of choice.

In 2014 our group reported a novel ruthenium system[22] for the production of alcohols from alkenes, carbon dioxide, and hydrogen (Scheme 4). This was the first example of
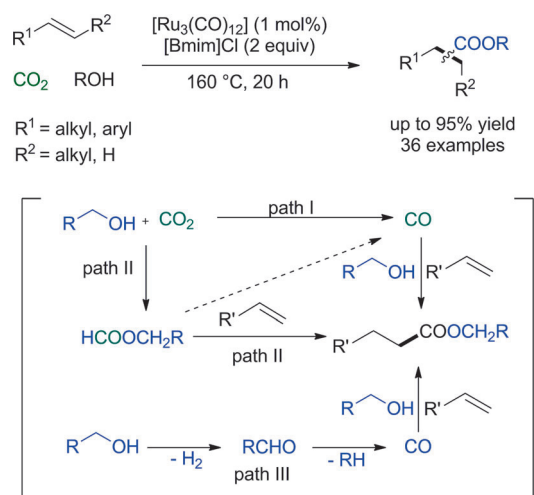
phosphite ligands applied in hydroformylation and RWGS processes using carbon dioxide. Compared to previous ligand-free systems, the ligand modified reaction gave higher yields of alcohols with reduced alkane side products. Moreover, the best catalyst turnover numbers (TONs) to date were achieved with this system. Detailed studies focusing on the nature of the ruthenium catalyst found that the active catalyst is a homogenous species. We also found that the ligand does not accelerate the RWGS reaction, while it has a positive effect on the hydroformylation step.

Another application of carbonylations with carbon dioxide is the so-called hydroaminomethylation reaction. Here, amines are employed in the current system. In 2009 Eilbracht and co-workers[23] reported the ruthenium-catalyzed reaction of alkenes with carbon dioxide, hydrogen, and amines. In their process the in situ formed aldehydes are trapped by the amines (primary or secondary) to form enamines or imines, which are subsequently reduced to the corresponding amines (secondary or tertiary). The presence of amines can cause problems like the aldol condensation of aldehydes under the basic conditions. Hence, higher catalyst loading and an extended reaction time (5 days) were required (Scheme 5).
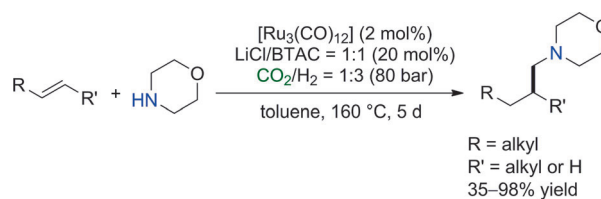
Scheme 5. Hydroaminomethylation of alkenes with carbon dioxide, hydrogen, and amines. BTAC = benzyltrimethylammonium chloride.

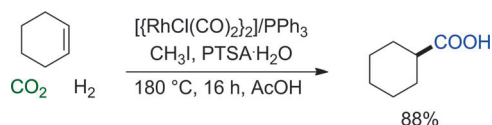We recently reported a new process in the use of carbon dioxide as the carbonyl source.[24] Based on our experience in hydrogen-borrowing reactions of alcohols, carbon dioxide reduction, and alkene carbonylation reactions, the in situ formation of carbon monoxide was achieved for the first time using alcohols as the reducing agent. Notably, the reaction of alcohols and alkenes in the presence of the in situ formed carbon monoxide gave carboxylic acid esters as the final products via alkoxycarbonylation reactions (Scheme 6). Isotope-labeling experiments showed unequivocally that carbon

Scheme 6. Alkoxycarbonylation of alkenes with carbon dioxide and alcohols.

Scheme 8. Reaction pathway for the activation of formaldehyde in the presence of alkenes.

Scheme 9. Rhodium-catalyzed hydroformylation of 1-hexene using formaldehyde.

dioxide was the main carbonyl source (path I), and only a small fraction of the carbonyl froup originates from alcohols (path III).

In the above-mentioned carbonylation reactions via RWSG strategies, water is always produced as a side product and is not involved in the subsequent alkene carbonylation reactions. However, Leitner and colleagues reported a rhodium-catalyzed hydrocarboxylation of alkenes with carbon dioxide and hydrogen to produce carboxylic acids (Scheme 7).[25]
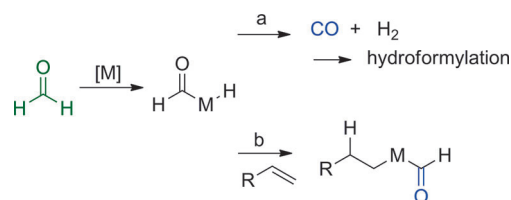
When 1-hexene was used as the substrate, the corresponding aldehyde was obtained in moderate yield (67%). A small amount of the alcohol was also produced through hydrogenation of the aldehyde (Scheme 9).

Almost 20 years later, Seok's group[29] used [RhHCO-(PPh₃)₃] in the presence of excess amount PPh₃ (5 equiv) to catalyze the reaction of alkenes with paraformaldehyde. The authors found that allyl alcohol and methyl acrylate, which both have oxygen at the β-position to the double bond, showed higher reactivity and regioselectivity to give the linear aldehyde than olefins without oxygen atoms such as propylene and hexene. The formation of a thermodynamically stable five-membered metallacycle is the explanation for these observations (Scheme 10). In situ IR experiments and variable-temperature NMR studies suggested the formation of a formyl metal complex and subsequent addition of the olefin to the Rh−H bond (Scheme 8, path b).

Scheme 7. Hydrocarboxylation of cyclohexene with carbon dioxide and hydrogen.

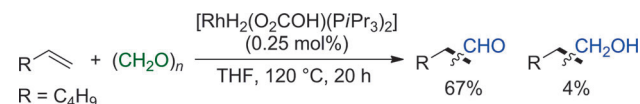
Scheme 10. Oxygen-directed metallacycle formation.

3. Formaldehyde

The transition-metal-catalyzed decarbonylation of higher aldehydes[26] and the hydroacylation[27] of olefins with aldehydes constitute well-established and valuable synthetic methods. Notably, the simplest aldehyde, formaldehyde, was less well studied in the carbonylation reactions of alkenes. There are two possible pathways for the reaction of formaldeyhde with alkenes: one is decarbonylation to syngas (CO and H₂), and the other is the formation of a formyl-ligated metal complex followed by olefin insertion (Scheme 8). Advantageously, formaldehyde can be used in solution-phase (formalin) as well as solid (paraformaldehyde) forms in the carbonylation reaction of alkenes without special high-pressure equipment.

The first example of using formaldehyde in the hydroformylation of alkenes was reported already in 1982 by Okano and co-workers.[28] More specifically, [RhH₂(O₂COH)-(P*i*Pr₃)₂] was applied as the catalyst without additional ligand.
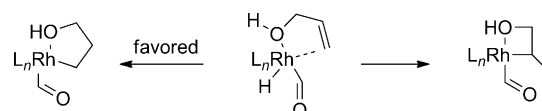
In 2005 Rosales et al. reported a study using 2 equiv of 1,2-bis(diphenylphosphino)ethane (dppe) with [Rh(acac)(CO)₂] as the catalytic system in the reaction of alkenes with paraformaldehyde in dioxane solution.[30] Alkenes like allyl alcohols were found to selectively produce branched aldehydes. A catalyst turnover number of 129 was achieved after 4 h. *n/iso* Ratios around 2 were obtained with hexene.

The same group also compared the hydroformylation of 1-hexene with syngas and with paraformaldehyde.[31] Diphosphine ligands such as Ph₂P(CH₂)ₙPPh₂ [n = 2 (dppe), 3 (dppp), and 4 (dppb)] were chosen for the study with [Rh-(acac)(CO)₂]. In the hydroformylation using syngas, the authors found that one equivalent of diphosphine relative to rhodium generated a more active catalyst with activity increasing on the order of the bite angle (dppb > dppp >

dppe). In contrast, in the reaction with paraformaldehyde, two equivalents of diphosphine ligand were needed and the best results were achieved using dppe. This observation is explained by a more sterically hindered metal center, which decreased the reactivity for the oxidative addition of CH_2O.

The first highly linear selective hydroformylation of terminal alkenes was achieved in 2010 by Morimoto and co-workers,[32] who used BINAP and Xantphos as mixed ligands (Scheme 11). [{RhCl(cod)}₂] was applied with these two
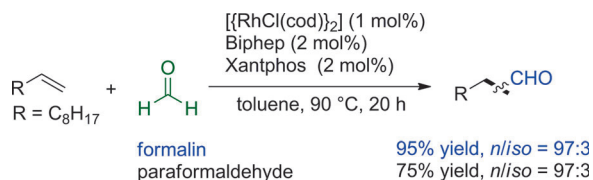
Scheme 11. Highly n-selective hydroformylation of alkenes with formaldehyde.

phosphane ligands to generate rhodium complexes: [{Rh(Cl)binap}₂] and [RhCl(cod)(xantphos)], respectively. The former was responsible for formaldehyde decarbonylation and the latter was effective for highly selective hydroformylation. Indeed, 95% yield and linear selectivity up to 98% were achieved with 1-decene. Notably, functionalized alkenes with ether, ester, and siloxy as well as phthaloyl groups were well tolerated.

Based on Morimoto's system, Taddei et al. reported a microwave-assisted domino hydroformylation of β,γ-unsaturated amides with formaldehyde.[33] Firstly, they proved that similar results were achieved under microwave dielectric heating in 30 min (nonanal was obtained in 90% yield and 98% linear selectivity from 1-octene). Then they optimized the conditions for the reaction of a specific chiral substrate (Scheme 12). Using Biphep and Nixantphos as ligands with formalin in toluene at 90°C gave the best results.
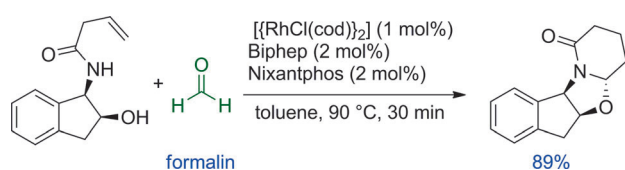
Scheme 12. Microwave-assisted domino hydroformylation of β,γ-unsaturated amides with formaldehyde.

Interestingly, in 2013 Börner and co-workers reported a Rh-dppp-catalyzed hydroformylation of olefins using formaldehyde and hydrogen.[34] In all cases, when 10 bar of hydrogen was added to the system, the conversion, yields, and regioselectivities improved significantly. Also the catalyst turnover numbers (TONs) and turnover frequencies (TOFs) were two to three times higher than the system without hydrogen.

While the hydroformylation of alkenes is highly effective, the corresponding reactions of conjugate dienes generally

provide mixtures of regioisomers. Notably, in 2013 Krische, Breit, and co-workers reported the reductive coupling of dienes with paraformaldehyde.[35] Nickel catalysts were found to promote this coupling selectively in the C1 position while for 1,3-dienes with 2-silyl and 2-stannyl substituents the coupling occurred selectively at the C4 position (Scheme 13).
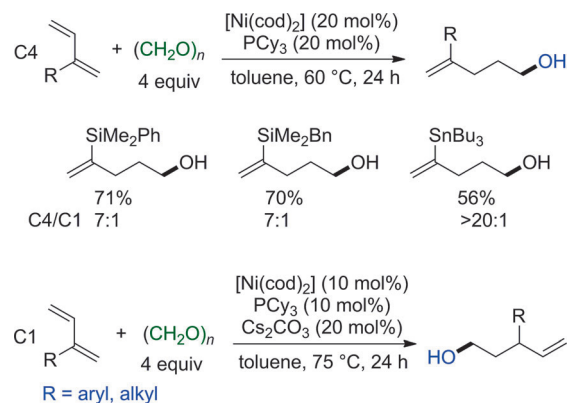
Scheme 13. Selective coupling of 1,3-dienes to paraformaldehyde at the C1 or C4 position.

Interestingly, when cationic ruthenium and neutral ruthenium precatalysts were used, regiodivergent reductive coupling took place at positions C2 and C3 of the 1,3-diene, respectively.
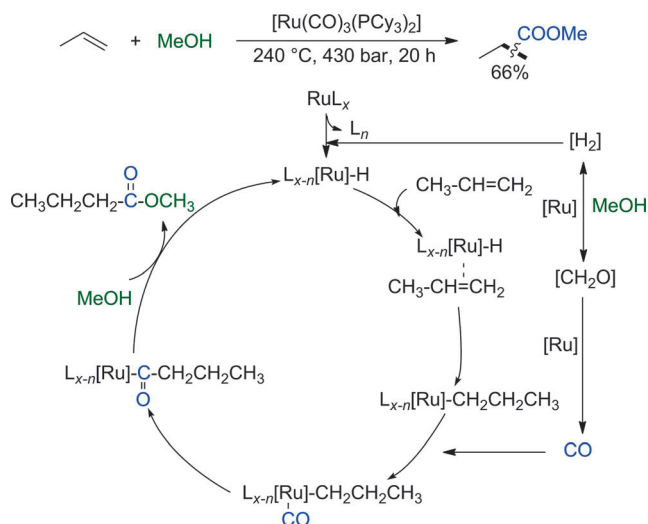
4. Methanol

Methanol is an abundant and potentially renewable chemical that is produced on the order of 35 million metric tons every year. Though the decarbonylation of higher alcohols like benzyl alcohol was known,[4h] the use of methanol as a carbonyl source is quite underdeveloped (Scheme 14). This can be explained by the relatively high
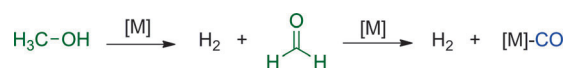
Scheme 14. Methanol decarbonylation.

energetic demand of methanol dehydrogenation ($\Delta H = +84\ kJ\,mol^{-1}$). Compared with formaldehyde as a CO surrogate one more molecule of dihydrogen has to be removed from methanol by dehydrogenation. In general, the olefin substrates as well as the carbonylated products might undergo subsequent hydrogenations. Consequently, diverse products can be obtained from methanol and alkenes.
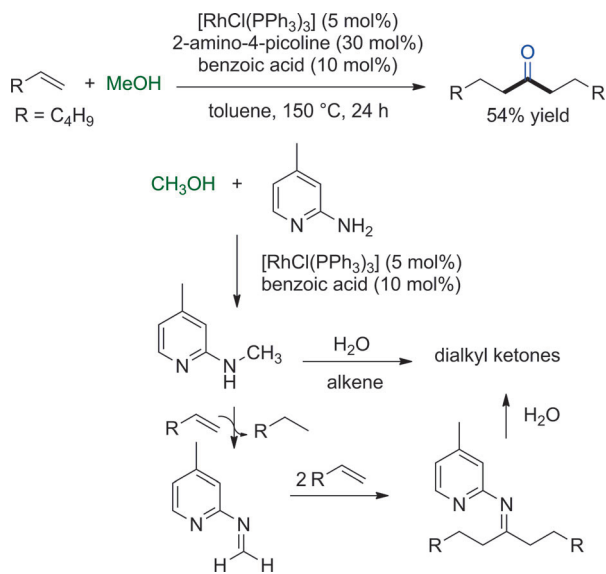
In 1986 Keim and co-workers reported the use of methanol as a CO and H_2 source in ruthenium-catalyzed hydroesterfication reactions.[36] Due to the high energetic demand of the dehydrogenation of methanol, the reaction was temperature dependent. Thus, at temperatures of 230–250°C methyl butanoate was obtained from propylene and
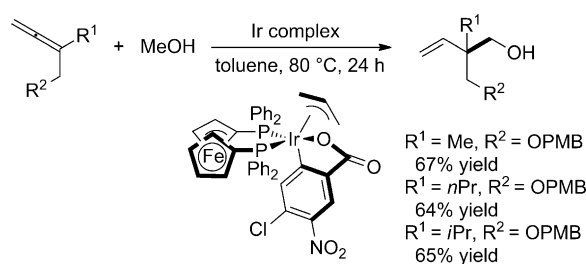
Scheme 15. First example using methanol as the CO and H$_2$ source in alkene hydroesterfication reactions.

Scheme 17. Iridium-catalyzed reactions of allenes with methanol.

methanol in 65% yield. In addition, high pressure (150–530 bar propylene with nitrogen or carbon dioxide to ensure high pressure) was required. The presence of CO coordinated to the ruthenium center was confirmed by in situ IR measurements. Based on their studies, a mechanism was proposed (in Scheme 15).

In 2008 Jun and co-workers reported the synthesis of dialkyl ketones from methanol and alkenes.[6] Though the yields were not very high, the temperature (150°C) was much lower than that reported in Keim's work (230–250°C). Their catalytic system consisted of Rh^I, 2-amino-4-picoline, and benzoic acid. The reaction was speculated to occur by the initial N-methylation of 2-amino-4-picoline with methanol, subsequent dehydrogenation and chelation-assisted hydro-imination of the alkene, and finally hydrolysis to give the ketone (Scheme 16).

In the course of their development of hydrogen mediated C–C coupling of alcohols with unsaturated reactants, Krische's group established an iridium-catalyzed reaction of allenes with methanol to furnish higher alcohols with quaternary centers under milder reaction conditions in 2011 (Scheme 17).[37]

5. Formic Acid

Formic acid has been traditionally produced from methanol and carbon monoxide. However, in the future new processes based on the hydrogenation of carbon dioxide might be realized. In this respect, formic acid represents an interesting and potential bio-renewable compound that can be transported and stored as an activated carbon dioxide for the production of value-added chemicals.

In 2001 Simonato et al. reported the first iridium-catalyzed hydroxycarbonylation of alkenes with formic acid.[38] Here, formic acid is first dehydrated to give carbon monoxide and water at elevated temperature under acidic conditions (acetic acid, >160°C). Then, iridium-catalyzed hydroxycarbonylation takes place. Interestingly, not only alkenes but also alcohols that are dehydrated under these conditions were suitable starting materials and gave carboxylic acids in good yields (Scheme 18).

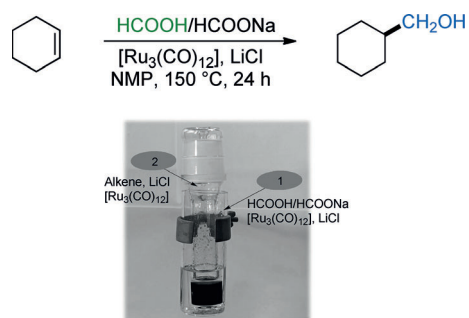**Scheme 16.** Rhodium-catalyzed synthesis of dialkyl ketones from methanol and alkenes.
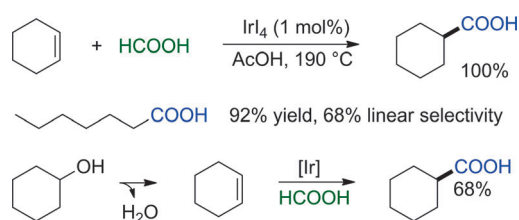
Scheme 18. Iridium-catalyzed hydroxycarbonylation of alkenes with formic acid.

In 2012 Porcheddu and co-workers developed an elegant two-chamber system to produce alcohols from alkenes and formic acid.[39] The main idea of this process is based on the ruthenium-catalyzed conversion of formic acid to carbon dioxide and hydrogen in one chamber and the ruthenium-catalyzed domino RWGS–hydroformylation in the other chamber (Scheme 19). The authors found that addition of a small quantity of HCOONa accelerates the decomposition
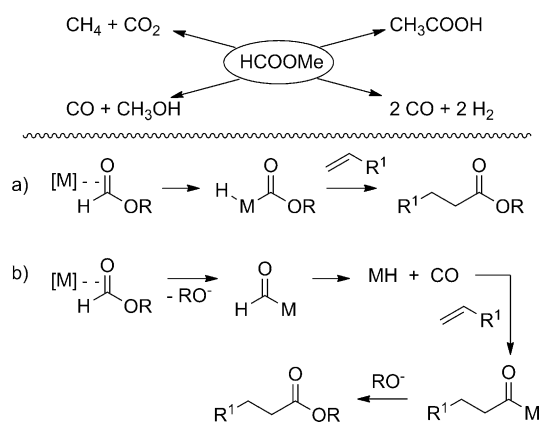
Scheme 19. Ruthenium-catalyzed synthesis of alcohols from alkenes and formic acid.

In 1983 Sneeden and Cognion reported a ruthenium-catalyzed reaction of formates with ethylene.[41] The authors found that methyl formate was a much better reactant than other alkyl formates. The optimal reaction yield was achieved in neat medium without any solvent. Hence, the use of alkyl formates represents an alternative to the alkoxycarbonylation of alkenes with carbon monoxide and alcohols (Scheme 21).

Scheme 21. Ruthenium-catalyzed reaction of ethylene with methyl formate.

of HCOOH to CO_2 and H_2 in the presence of $[Ru_3(CO)_{12}]$ and LiCl. Though the catalyst for formic acid decomposition and alkene hydroformylation is the same, the two-chamber system was necessary for obtaining acceptable yields (51% in two chambers vs. 10% in one chamber). For cyclohexene 86% yield of the corresponding product was achieved. With linear terminal alkenes the alcohols are obtained in around 70% yield with almost 80:20 regioselectivity.
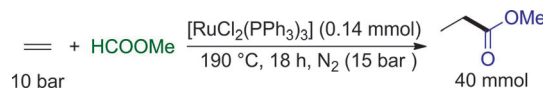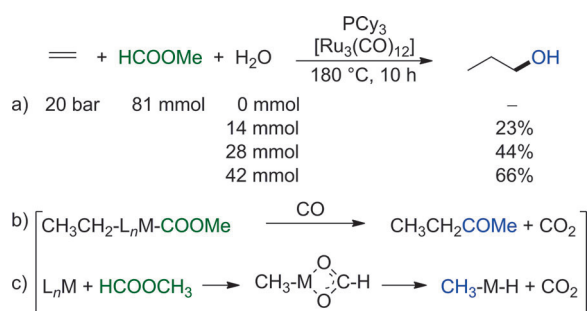
6. Formates

The simplest formate, methyl formate, is produced industrially from methanol and carbon monoxide in the presence of a strong base or by methanol dehydrogenation over a Cu-based oxide catalyst. Due to its physical properties, methyl formate represents an interesting C_1 building block, especially on the laboratory scale. Keim and Becker described the reaction of methyl formate with olefins (Scheme 20).[40] In analogy to formaldehyde (Scheme 8), there are two general mechanisms for the reaction of formates with alkenes: a) oxidative C−H addition of the formyl group to the metal center then alkene insertion, and b) decomposition of formates to carbon monoxide and alcohols, and subsequent transition-metal-catalyzed alkoxycarbonylation (Scheme 20).

Scheme 20. Transformation of methyl formate and reaction with alkenes.

The same group also studied the decarbonylation reaction of methyl formate to give carbon monoxide and found that in polar solvents like DMF, carbon monoxide was more easily produced than in nonpolar solvents like toluene (225 vs. 5 mmol).

In 1988 Ueda reported the olefin esterification with methyl formate under much milder reaction conditions.[42] In their process $[RuH_2(PPh_3)_3]$ was used as a precatalyst in THF at 90°C; however, only a TON of 5.4 was obtained. One year later, Keim and co-workers found that when $[Ru_3(CO)_{12}]$ was used as the catalyst at higher temperature (230°C), methyl propionate could be obtained in 92% yield from ethylene and methyl formate.[40] Besides, they also found that with $PdCl_2$ as the catalyst pentenoic ester was produced in 10% yield from butadiene and methyl formate in the presence of extra CO. Jenner et al. also reported a ruthenium–phosphine system for the reaction between alkenes and formates.[43] They found that longer alkyl formates reacted much more readily than methyl formate. Though with cyclic alkenes the yields were good, only 28% yield was achieved with linear alkenes.

Based on their initial studies on the use of aqueous methyl formate as a syngas source,[44] Jenner and Taleb[45] showed that propanol can be produced from the reaction of ethylene and aqueous methyl formate catalyzed by $[Ru_3(CO)_{12}]$ and PCy_3. The amount of water is crucial for this transformation (Scheme 22a). A water–gas shift reaction of water with in situ generated carbon monoxide was assumed to be the main reaction pathway. Interestingly, in the absence of water, butanone was also formed as product. This unusual formation was explained by either reduction of the intermediate M-COOMe species to M-COMe by carbon monoxide (Scheme 22b) or formation of the formyl metal complex (Scheme 22c).

In 1992 Lavigne described the synthesis of ruthenium carbonyl halide complexes. They explored the potential of these complexes in ethylene hydrosterification reactions using methyl formate.[46] With $[Ru_3(CO)_{12}]$ and [PPN]Cl a catalyst TON of 339 was achieved. Kalck and co-workers later extended this work by identifying several ruthenium species containing chloride anion as the ligand.[47] In addition, two years later the group led by Mortreux developed a novel catalyst system based on $RuCl_3$.[48] More specifically, they used covalent iodides RI or ammonium salts NR_4I in an amide solvent for the direct hydroesterification of ethylene

Scheme 22. Ruthenium-catalyzed synthesis of propanol and butanone from methyl formate and ethylene.

with methyl formate. Here, a catalyst TOF of 2300 h^{-1} was achieved.

In 2002 Chang discovered a chelation-assisted hydroesterification of alkenes using ruthenium catalysis.[49] 2-Pyridylmethyl formate, which can act via a six-membered ring intermediate, was used as the substrate (Scheme 23). This
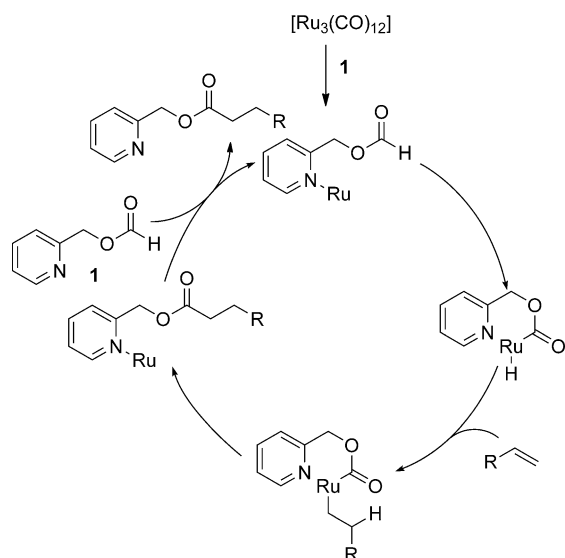

Scheme 23. Chelation-assisted ruthenium-catalyzed hydroesterification of alkenes.

reaction can also be classified as an intermolecular hydroacylation reaction which has been well documented by the groups of Krische[27a] and Willis.[27b]

Though significant work addressed the hydroesterification of alkenes with formates, in general these methods are restricted to special substrates such as ethylene and methyl formate.[41] Besides, the reaction conditions were harsh in terms of high temperature and high pressure (extra nitrogen gas) to ensure crucial substrate concentration in solution.[40] A breakthrough in this area was reported in 2012 by Manabe, who demonstrated a general ruthenium-catalyzed hydroesterification of alkenes with a broad substrate scope.[50] The key to success was the use of imidazole derivatives to suppress

the undesired decomposition of formates. Notably, the direct synthesis of lactones through intramolecular hydroesterification was also investigated (Scheme 24).
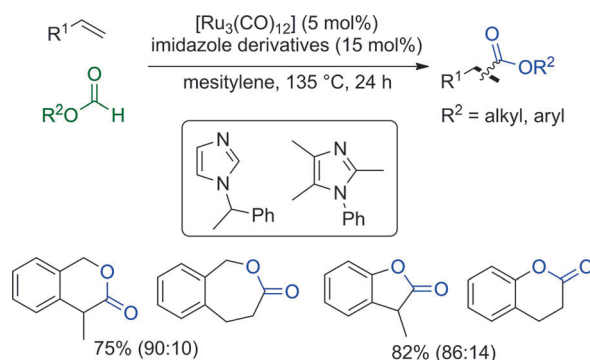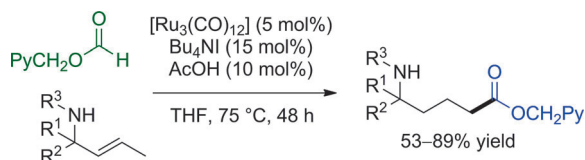

Scheme 24. Hydroesterification of alkenes with formates improved by the addition of imidazole derivatives.

Alper and co-workers reported in 1989 the regioselective palladium-catalyzed carbonylation of alkenes with formate;[51] however, excess carbon monoxide was needed in this reaction. The first palladium-catalyzed carbonylation reaction of alkenes with methyl formate without extra carbon monoxide was reported by Kalck and Grévin.[52] NaBH$_4$ and [PdCl$_2$(PBu$_3$)$_2$] were used in a 1:1 ratio and methyl propanoate was produced from ethylene at 130°C in 90% yield with a TOF of 30 h^{-1}; the active catalyst was the in situ generated [PdH(Cl)(PBu$_3$)$_2$]. In 2011 Tsuji reported an efficient palladium-catalyzed hydroesterfication of alkynes and examples of norbornene and terminal alkenes were also shown. The mechanistic study showed that conversion of aryl formates to carbon monoxide and phenol derivatives occurred under the hydroesterification conditions.[4f] Notably, very recently our group reported a general and efficient alkoxycarbonylation of olefins with formates, too.[53] The combination of palladium(II) acetyl acetonate and 1,2-bis(di-*tert*-butylphosphinomethyl)benzene as the catalyst system promoted ester formation at milder conditions with a loading of only 0.038 mol% Pd. The addition of an acidic co-catalyst with a weakly coordinating anion to form a cationic P-ligated Pd−H species was crucial. These reaction conditions worked for both alkyl and phenyl formate as well as with functionalized alkenes. More importantly, the conversion of internal alkenes to linear esters was accomplished with very good regioselectivities (Scheme 25).

Very recently, Carreira and co-workers[54] reported an interesting example of so-called autotandem catalysis. [Ru$_3$(CO)$_{12}$] firstly catalyzed the isomerization of allylic amides. Subsequently, hydroesterification of terminal alkenes proceeded with pyridine-2-ylmethyl formate. The addition of acetic acid and Bu$_4$NI were crucial for the formation of the active ruthenium hydride species which allowed the reaction to take place under milder conditions (Scheme 26).
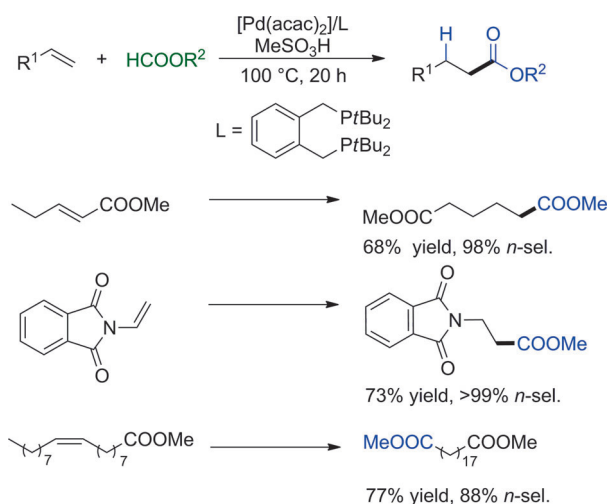
Scheme 25. Palladium-catalyzed regioselective and efficient alkoxycarbonylation of alkenes with formates.

**Scheme 26.** Remote hydroesterification of allylic amides.

6. Formamide

Kondo and Watanabe were the first to report the one-to-one addition of *N*-substituted formamides to olefins with extra carbon monoxide.[55] Here, CO is needed for maintaining the activity of the catalyst in this reaction. Ten years later Kondo discovered the first CO-free system which allowed the direct addition of formamides to olefins.[56] Under optimal reaction conditions the addition product was obtained from formanilide and 2-norbornene in 97% yield (Scheme 27).
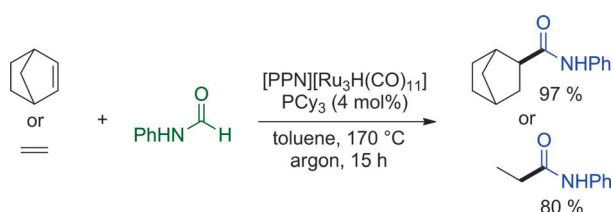
Scheme 27. Ruthenium-catalyzed direct addition of amides to olefins.

A chelate-assisted activation of formamide and addition to alkenes was reported also by Chang et al.[57] Moderate to good yields and selectivities were achieved using [Ru$_3$(CO)$_{12}$] as the catalyst at 135 °C (Scheme 28).

R = nBu, 67% (n/iso = 80:20)
R = Cy, 75% (n/iso = 93:7)
R = C$_6$H$_5$, 72% (n/iso = 76:24)
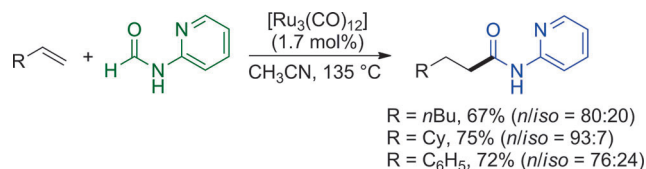
Scheme 28. Ruthenium-catalyzed hydroamidation of alkenes with chelation assistance.

7. Biomass

The conversion of biomass to value-added renewable products is a highly topical and promising research area. In this respect, polyols constitute interesting platform chemicals, which are readily available. Well-developed methods for transforming biomass to syngas include gasification at higher temperatures (> 700 °C) and aqueous-phase reforming processes.[58] Still, the use of polyols as a syngas source in carbonylation reactions was not known until Andersson's group reported ex situ produced carbon monoxide and hydrogen in hydroformylation using a dual-reactor setup in 2013.[7] More specifically, iridium-catalyzed dehydrogenation–decarbonylation of polyols took place in reactor A and the rhodium-catalyzed hydroformylation of styrene occurred in reactor B. Relatively inexpensive C$_3$–C$_6$ polyols were used as the syngas sources. Yields from 46 to 83% were achieved with glycerol as the best syngas source (Scheme 29).
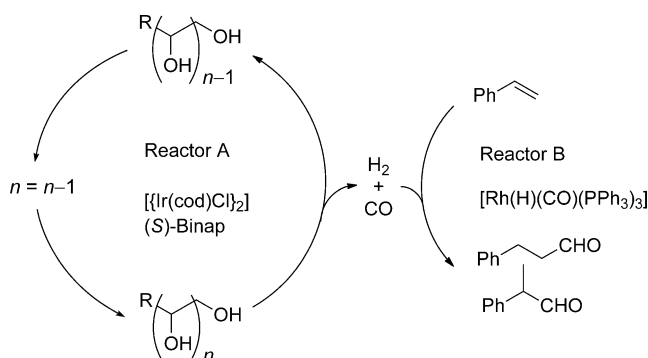
Scheme 29. Transfer of H$_2$ and CO from polyols to alkenes.

8. Summary and Outlook

Carbonylation reactions belong to the most important methods for organic synthesis in academic as well as industrial settings. The use of inexpensive, easily available, and less toxic CO surrogates is an current topic in this area. Clearly, in the last decade several new reactions have been developed, including alkene carbonylations. Despite this elegant work, several problems still exist, which need to be solved. In general, harsh reaction conditions and additional additives are needed to activate the alternative C$_1$ sources which implies extra cost and waste. Besides, the regioselectivities in most cases were low probably because of the problematic coexistence of ligand and additives. Here, more selective

systems are needed. So far, most catalyst developments have been based on ruthenium complexes in the carbonylation reactions of alkenes with CO surrogates. Inspired by the recently developed highly regioselective ruthenium-catalyzed hydroformylation reactions,[59] we are optimistic that in the near future the regioselectivity problem will be solved. In addition, as in other areas, the discovery of base-metal-catalyzed reactions, for example, with iron, is important.

Finally, it is worth noting that the most promising alternative CO source is certainly carbon dioxide, which should be further investigated. In addition, biomass, which is also a readily available and renewable resource, offers opportunities for future carbonylation reactions.

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