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FULL PAPER

Selective Production of Linear Aldehydes and Alcohols from Alkenes using Formic Acid as Syngas Surrogate

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Abstract: Performing carbonylation without the use of carbon monoxide for high-value-added products is an attractive yet challenging topic in sustainable chemistry. Herein, effective methods for producing linear aldehydes or alcohols selectively with formic acid as both carbon monoxide and hydrogen source have been described. Linear-selective hydroformylation of alkenes proceeds smoothly with up to 88% yield and > 30 regioselectivity in the presence of single Rh catalyst. Strikingly, introducing Ru into the system, the dual Rh/Ru catalysts accomplish efficient and regioselective hydroxymethylation in one pot. The present processes utilizing formic acid as syngas surrogate operate simply under mild condition, which opens a sustainable way for production of linear aldehydes and alcohols without the need for gas cylinders and autoclaves. As formic acid can be readily produced via CO_2 hydrogenation, the protocols represent indirect approaches for chemical valorization of CO_2.

Introduction

Carbonylation especially hydroformylation of alkenes are among the most important industrially homogeneous catalytic transformations. Nowadays, aliphatic alkenes are converted on a million-ton scale by hydroformylation into the primary products linear aldehydes, [1] and further on into linear alcohols, [2]which are used as major components of plasticizers, detergents, solvents etc. However, the processes suffer from the handling of toxic and flammable syngas under high pressure and forcing reaction conditions.

To overcome these problems, substantial attention has been paid to the development of carbonylation reactions with syngas surrogates, [3] such as formic acid, [4] formaldehyde, [4a, 5] diboron/silacarboxylic acid/H_2O, [6] CO_2/hydrosilane, [7] and even CO_2/H_2. [3b, 8] Among these, formic acid is probably the most convenient syngas surrogate as a nontoxic, renewable liquid which is readily produced by catalytic hydrogenation of CO_2[9] or oxidation of biomass. [10] Clearly, formic acid is able to decompose and generate CO by dehydration[11] and/or H_2 via catalyst, [12] rendering it a feasible replacement for syngas (or single CO gas). For example, formic acid could be used as an *in situ* source of CO in the hydrocarboxylation and alkoxycarbonylation of alkenes. [13] Recently, an effective hydroformylation of alkenes using formic acid in the presence of 5 mol% Pd catalyst to form linear aldehydes has been described. [14] By contrast, the more challenging regioselective hydroxymethylation of alkenes with formic acid to produce linear alcohols remains elusive. [15] Obviously, to achieve such a transformation, the linear-selective hydroformylation of alkenes with HCOOH as both C1 and hydrogen source has to be combined with the efficient (transfer) hydrogenation of aldehydes in one process.

Herein, we report an operationally safe and highly efficient strategy for selective hydroformylation and hydroxymethylation of alkenes utilizing formic acid as both C1 and hydrogen source. In the presence of single rhodium catalyst (as low as 0.1 mol%), various alkenes are effectively converted to linear aldehydes in up to 88% yield and n/i > 30 regioselectivity. Notably, the admixture of Rh/Ru dual system can accomplish efficient production of linear alcohols (up to 87% yield and n/i > 20) by a simple one-pot process.

Results and Discussion

Hydroformylation/hydroxymethylation of alkenes catalyzed by single Rh and dual Rh/Ru system

We initially carried out the selective hydroformylation of 1-decene with formic acid at 90 °C in NMP (1-methyl-2-pyrrolidinone) with 0.5 mol% $Rh(acac)(CO)_2$ as a catalyst precursor and acetic anhydride (Ac_2O) as a dehydrant. Screening of various phosphine

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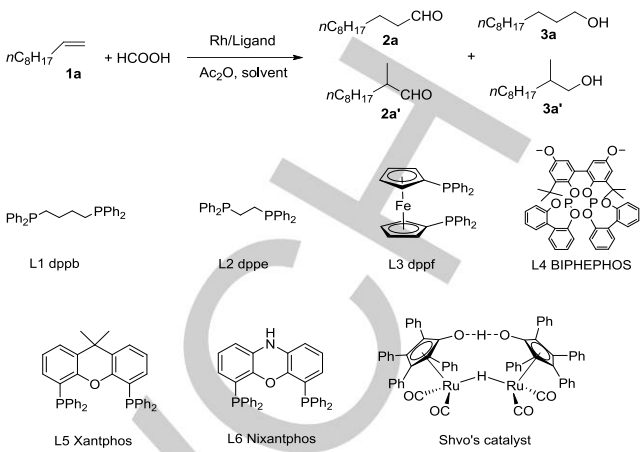
ligands showed that the nature of the ligand markedly affected the reaction performance especially regioselectivity (Table 1 and Table S1, detailed products distribution can be found in Table S6). With simple PPh_3, acceptable yield of C1-elongated aldehyde could be obtained albeit with poor linear selectivity (Table 1, entry 1). The regular bidentate ligands including dppb, dppe and dppf moderately improved the regioselectivity (entries 2-4). Another bidentate ligand Biphephos, well known for efficient regioselective hydroformylation of alkenes with syngas, afforded unsatisfactory aldehyde yield and regioselectivity (entry 5), which was ascribed to its susceptibility towards acid (formic acid in the present case). By contrast, Xantphos gave decent yield of linear aldehyde and regioselectivity (49% and n/i = 9.8, entry 6). Moderate yield and regioselectivity of linear aldehyde were achieved in the presence of Nixantphos ligand with identical xanthene structure (entry 7). The nice performance especially linearity for Xantphos-type ligands could be attributed to their rigid backbone, large bite angle and strong acid resistance. [16]

Encouraged by this result, additional reaction parameters were further investigated with Xantphos as the ligand. Screening of rhodium precursor (Table S2, Supporting Information) and its dosage (Figure S1) showed 0.5 mol% $Rh(acac)(CO)_2$ was best and as low as 0.1 mol% Rh could give modest yield coupled with intact linearity. Increasing the ratio of the ligand to Rh from 2 to 6 markedly improved the linearity (Table S3). No reaction occurred in the absence of an anhydride, which was necessary for the decomposition of formic acid to CO. Other than acetic anhydride, trifluoroacetic anhydride and benzoic anhydride could also be used (Table S4). Raising the amount of formic acid to 6 equiv. would somewhat boost the aldehyde yield (Figure S2). In addition, the effects of reaction temperature were evaluated, which indicated 90 ºC was optimal, as lower temperature suppressed catalytic activity while higher one led to undesired isomerization of alkenes (Figure S3). From a plot of conversion/yield versus reaction time, we observed that yield increased with reaction time, and reached a plateau after 16 h (Figure S4). Through above optimization, the yield of linear aldehyde and regioselectivity could be improved to 71% and >30, respectively (entry 8). It was worth noting that further hydrogenated products undecanol (**3a**+**3a'**) held an unignorable proportion in most cases. The solvent was found to be an important factor for the competition between hydroformylation and hydroxymethylation. When the reactions were carried out in acetonitrile (MeCN) or cyclohexane (CYH), the formation of alcohols was suppressed below 5%, coupled with improved chemo- and regioselectivity of linear aldehyde **2a** (over 80% yield and 40 n/i ratio, entries 9 and 10). As shown in Table S5, there seemed to be a roughly positive correlation between alcohol yield and electron donatability of solvents.

Having established the efficient aldehyde synthesis from alkene and formic acid, the more challenging regioselective hydroxymethylation with formic acid to produce linear alcohols in one pot was explored. We became interested in the admixture of two catalysts, as each catalyst operates one reaction with high efficiency without disturbing the other reaction. The additional catalyst should be relatively inert in the hydroformylation step compared to the rapid hydroformylation by Rh. Possible side reactions like hydrogenation of 1-decene to decane or isomerization to 2-decenes should be suppressed. Ruthenium-based catalysts were therefore selected for aldehyde-selective (transfer) hydrogenation. Among the Ru catalysts we examined,

Table 1. hydroformylation/hydroxymethylation of alkenes to linear aldehydes or alcohols selectively [a]



Entry	Ru cat.	L	Solvent	Yield[b] [%]			
				2a	**2a'**	**3a**	**3a'**
1	-	PPh_3	NMP	22	30	2	trace
2	-	L1	NMP	71	25	trace	trace
3	-	L2	NMP	42	16	trace	trace
4	-	L3	NMP	19	8	6	trace
5	-	L4	NMP	14	2	trace	trace
6	-	L5	NMP	49	5	7	trace
7	-	L6	NMP	26	3	trace	trace
8[c]	-	L5	NMP	71	2	20	trace
9[c]	-	L5	MeCN	83	2	4	trace
10[c]	-	L5	CYH	81	2	4	trace
11[d]	Shvo's cat.	L5	NMP	1	trace	87	5
12[d]	$Ru(acac)_3$	L5	NMP	1	trace	87	6
13[d]	$RuCl_3$	L5	NMP	34	2	52	3
14[d]	$RuCl_2(PPh_3)_3$	L5	NMP	1	trace	80	4

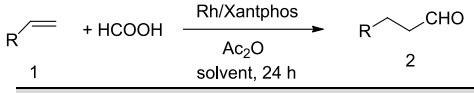
[a]. Reaction condition: 1-decene (1.0 mmol), $Rh(acac)(CO)_2$ (0.5 mol%), Rh:L=1:2, solvent (4.0 mL), HCOOH (4 equiv.), Ac_2O (2 equiv.), 90 ºC, 12 h; [b]. Yields were determined by GC analysis using isooctane as internal standard; [c]. Rh:L=1:6, 6 equiv. HCOOH, 3 equiv. Ac_2O, 24 h; [d]. Rh:L=1:6, 9 equiv. HCOOH, 3 equiv. Ac_2O, 1.25 mol% [Ru], 24 h.

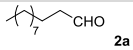
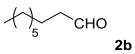
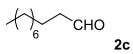
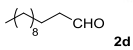
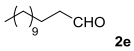
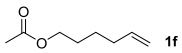
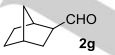
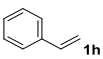
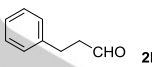
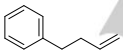
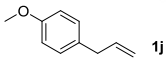
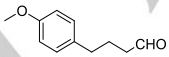
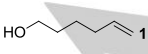
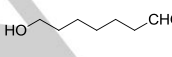
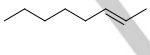
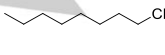
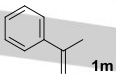
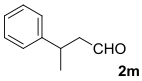
the use of Shvo's complex gave the best result (linear alcohol 87%, n/i = 17.4) with additional 3 equiv. HCOOH. Other Ru catalysts also work, delivering comparable or moderate yield and linearity (entries 11-14). The universality of Ru catalysts was different from that under syngas atmosphere, [17] which might be attributed to low local concentration of CO in the present system. In a word, a high-yielding synthesis of linear alcohol (87%) by the reaction of a terminal olefin with formic acid has been achieved using Rh/Ru dual catalysts in one pot.

Substrate scope

With the optimized reaction conditions in hand, we investigated the hydroformylation of other alkenes with formic acid (Table 2). Aliphatic terminal alkenes **1a-1e** demonstrated similar reactivity profiles irrespective of the length of the carbon chain, affording the corresponding linear aldehydes **2a-2e** in good to excellent yield (73%-88%) and regioselectivity (>30). Remarkably, ester group was well tolerated for **1f**. It's gratifying that cyclic alkene norbornene **1g** was quantitatively transformed into aldehyde **2g**. Moreover, aryl alkenes styrene **1h** was also converted into linear aldehyde in good yield (60%), albeit with reduced regioselectivity (71/29), which might be due to the stability of the benzylic Rh-species. [14a, 18] By contrast, the hydroformylation of phenylbutene **1i** and allylbenzene derivative **1j** furnished the corresponding aldehydes **2i** and **2j** in excellent yield and high regioselectivity. Notably, the ether group in **1j** was retained in the transformation. In addition, this protocol was compatiable with hydroxyl group (**1k**), showing good compatibility of functional groups. However, the present catalytic system was not very suitable for internal alkenes with only 15% linear aldehyde yield for 2-octene **1l**. Similarly, the hydroformylation of 1,1-disubstituted alkene **1m** gave very poor yield of aldehyde **2m**, which was due to its large steric hindrance.

Table 2. Rh-catalyzed hydroformylation of alkenes[a].

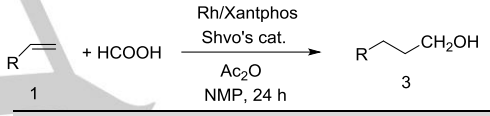


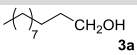
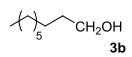
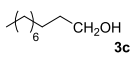
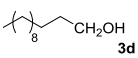
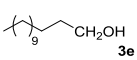
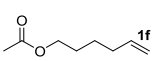
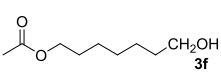
Entry	Substrate	Product	Yield[b] [%] (n:i)
1[c]	 1a	 2a	83 (97:3)
2	 1b	 2b	73 (97:3)
3	 1c	 2c	88 (97:3)
4	 1d	 2d	78 (97:3)
5	 1e	 2e	77 (96:4)
6[d]	 1f	 2f	69 (96:4)
7[d]	 1g	 2g	99 (-)
8[d]	 1h	 2h	60 (71:29)
9	 1i	 2i	84 (95:5)
10[d]	 1j	 2j	83 (95:5)
11	 1k	 2k	71 (84:16)
12[d]	 1l	 2l	15 (50:50)
13	 1m	 2m	5 (100:0)

[a]. Reaction condition: alkene (1.0 mmol), $Rh(acac)(CO)_2$ (0.5 mol%), Rh:L=1:6, NMP (4.0 mL), HCOOH (6 equiv.), Ac_2O (3 equiv.), 90 °C, 24 h; [b]. The yields of linear aldehydes were determined by GC analysis using isooctane as internal standard; [c]. With 4 mL acetonitrile; [d]. With 1.0 mol% $Rh(acac)(CO)_2$.

Furthermore, we explored the utility of the hydroxymethylation of alkenes with formic acid by using Rh/Ru dual system (Table 3). Aliphatic terminal alkenes **1a-1e** provided the linear alcohols **3a-3e** in good to excellent yields and high regioselectivity (59%-87%, n/i=11.5-24). The reaction also proceeded smoothly with alkene **1f** with ester group. Furthermore, cycloalkene norbornene **1g** was effective substrate for the hydroxymethylation process, giving alcohol **3g** in 98% yield. Compared with hydroformylation process, the hydroxymethylation of styrene **1h** halved the yield of alcohols, coupled with more undesired hydrogenation of alkene due to the strong hydrogenation ability of Ru towards aryl alkenes. Besides, the hydroxymethylation can be extended to phenylbutene **1i** and allylbenzene derivative **1j**, albeit with lower regioselectivity which might be attributed to mild interference of Ru towards the hydroformylation step. In a word, by introducing Shvo's catalyst, equal or moderately inferior yield and regioselectivity of linear alcohols compared to those of linear aldehydes could be obtained.

Table 3. Rh/Ru-catalyzed hydroxymethylation of alkenes[a].



Entry	Substrate	Product	Yield[b] (%)(n:i)
1	 1a	 3a	87 (96:4)
2	 1b	 3b	59 (97:3)
3	 1c	 3c	76 (96:4)
4	 1d	 3d	84 (96:4)
5	 1e	 3e	63 (92:8)
6[c]	 1f	 3f	64 (86:14)
7[c]	1g	3g	98 (-)
8[c]	1h	3h	30 (71:29)
9[c]	1i	3i	56 (90:10)
10[c]	1j	3j	56 (90:10)

[a]. Reaction condition: alkene (1.0 mmol), $Rh(acac)(CO)_2$ (0.5 mol%), Shvo's catalyst (2.5 mol%), Rh:L=1:6, NMP (4.0 mL), HCOOH (9 equiv.), Ac_2O(3 equiv.), 90 °C, 24 h; [b]. The yields of linear alcohols were determined by GC analysis using isooctane as internal standard; [c]. $Rh(acac)(CO)_2$ (1.0 mol%).

Control experiments

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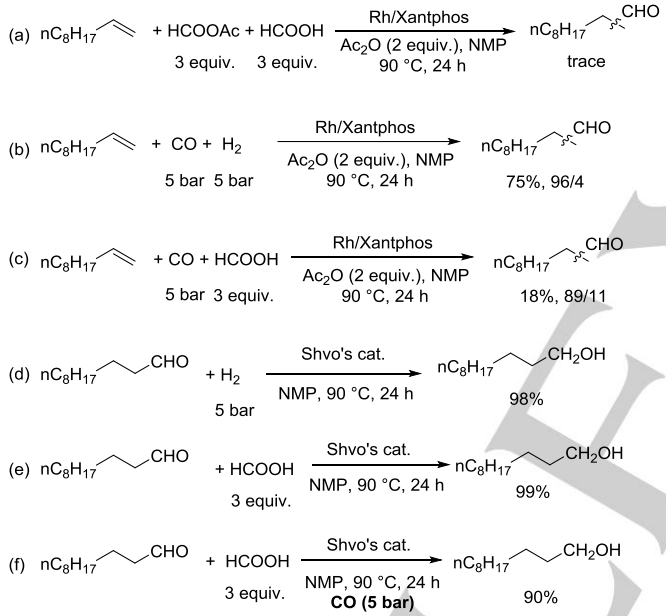
Several control experiments were performed to explore possible intermediates in the hydroformylation/hydrogenation tandem reaction (Scheme 1). When the reaction was carried out in the presence of HCOOAc (generated from HCOOH and Ac_2O), previously proposed by Shi *et al.* as C1 source, [14a] trace of aldehyde could be obtained (Scheme 1a), which excluded the possibility of HCOOAc as C1 intermediate. Delightedly, the reaction could proceed smoothly with 5/5 bar CO/H_2, affording excellent yield and selectivity comparable to those of bench reaction (Scheme 1b), which proved *in situ* syngas from formic acid acted as major C1 and hydrogen source. Using HCOOH instead of H_2, mediocre performance (18% aldehyde yield) was achieved (Scheme 1c), indicating that HCOOH could also serve as a hydrogen source in the hydroformylation step. Next, the hydrogenation step was investigated. Experimental results demonstrated that both formic acid and molecular hydrogen could fulfill the function of hydrogen source (Scheme 1d and 1e). It was worth noting that even in the CO atmosphere, 90% yield of alcohols could be observed with Shvo's catalyst (Scheme 1f), which was owed to the tolerance of Shvo's catalyst against CO poisoning. [19]



Scheme 1. Control experiments. The yields of linear aldehydes and alcohols were determined by GC analysis using isooctane as internal standard.

Time course of the hydroxymethylation

To gain further mechanistic information on this tandem reaction, the conversion/time profile for Rh/Ru-mediated hydroxymethylation of 1-decene with formic acid was depicted in Figure 1. More than 90% of 1-decene was gradually converted within 8 h. In contrast, the yield of undecanal reached a maximum after 3 h (41%) and then was reduced coupled with constant growth of undecanol yield, which proved again the tandem pathway via aldehyde intermediate was feasible. It should be noted that undecanol could be observed from the very beginning and kept up with the production of undecanal in the initial 4 h, which implied the hydroformylation was the rate-determining step of the present tandem reaction.

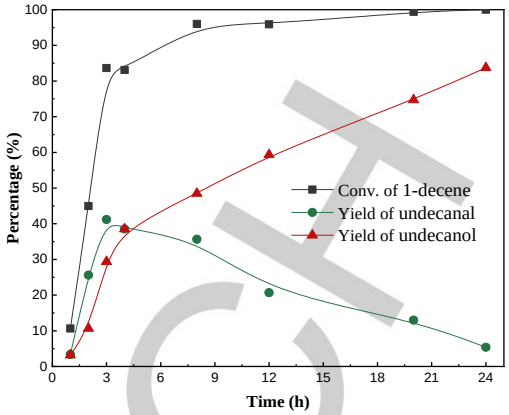


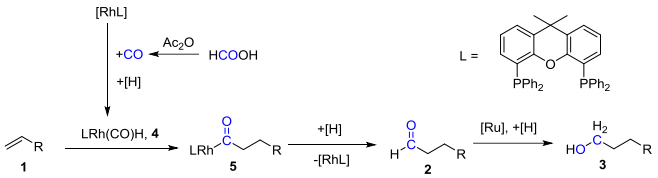
Figure 1. Conversion and yield of aldehyde and alcohol with respect to the reaction time. Reaction conditions: 1-decane (1.0 mmol), $Rh(acac)(CO)_2$ (0.5 mol%), Rh:L=1:6, Shvo's catalyst (0.625 mol%), HCOOH (9 equiv.), Ac_2O (3 equiv.), NMP (4.0 mL), 90 °C. Yields were determined by GC analysis using isooctane as internal standard.

On the basis of these studies and previous mechanistic investigations, [18] we proposed the following mechanism for hydroformylation/hydroxymethylation of alkenes as shown in Scheme 2. In the presence of Xantphos and *in situ* CO and H_2 generated from formic acid, Rh precursor is converted into hydridorhodium carbonyl complex **4**. Subsequently, alkene coordination and insertion towards **4** leads to acylrhodium complex **5** upon CO migratory insertion. Further hydrogenolysis of the M–acyl bond in **5** liberates the linear aldehyde **2** coupled with regeneration of Rh catalyst. Finally, the aldehyde will undergo (transfer) hydrogenation to afford the desired linear alcohol **3** mediated by Ru catalyst. Rh/Ru tandem catalysis plays an essential part in alcohol synthesis.

To identify efficient catalytic system for hydroformylation, several important factors should be taken into consideration. Firstly, as the control experiments has demonstrated, the hydroformylation was conducted under low carbon monoxide pressure (presumably lower than 10 bar), noble metals e.g. Rh, Ru, Ir, Pt and Pd were better choice than Co, Mn or Fe, which generally needed high operation pressure. Secondly, the present acidic environment induced by formic acid required the ligand with stringent acid-resistance character. For example, phosphites and phosphoramidites which were extremely sensitive to acids should be excluded, although they were well-known for efficient regioselective hydroformylation of alkenes with syngas. By contrast, phosphines characterized by three carbon atoms surrounding the central phosphorus atom would be focused. Lastly, as the ligand with rigid backbone and suitable bite angle favored linear hydroformylation, [1] bidentate ligands were preferable. In a word, noble metal precursor in combination with bidentate phosphine ligands proved to be the privileged catalytic system for the present hydroformylation. The results of the ligand screening also confirmed this in Table 1 and Table S1.

Next, the protocols for direct synthesis of linear alcohols from alkenes with formic acid were analyzed. [2a] In comparison with catalytic systems depending on one single metal catalyst to perform the two different reactions, the admixture of two catalysts, each of which operates one reaction with high efficiency without disturbing the other reaction would be more desired. In addition, the additional catalyst should be relatively inert in the

hydroformylation step compared to the rapid hydroformylation by Rh. Possible side reactions like alkenes hydrogenation or isomerization should be suppressed. Rh/Ru dual catalyst system which was efficient for tandem hydroformylation/hydrogenation with syngas[17,19] proved to be suitable for our present system with formic acid. Actually, the catalytic systems applied in regioselective hydroxymethylation with syngas could be competent alternative for that using formic acid, which thus shed light on designing efficient single-component catalyst.



Scheme 2. Proposed mechanism for regioselective hydroformylation and hydroxymethylation.

Conclusion

In summary, effective hydroformylation and hydroxymethylation protocols have been developed using HCOOH/Ac_2O under mild reaction conditions. With single Rh catalyst, a wide variety of linear aldehydes can be obtained in good yields with high regioselectivities. Introducing Ru into the system, the dual Rh/Ru catalysts enable efficient conversion of alkenes to linear alcohols. Both protocols operate simply and avoid using flammable and toxic syngas, which represents a sustainable approach for the preparation of value-added compounds. Considering the readily availability of HCOOH, the present methods provide alternatives for hydroformylation and hydroxymethylation in both industry and laboratory.

Acknowledgements

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Keywords: hydroformylation • hydroxymethylation • linear alcohol • formic acid • tandem reaction

[1] R. Franke, D. Selent, A. Borner, *Chem. Rev.* **2012**, *112*, 5675-5732.

[2] Selected examples for linear alcohol synthesis from tandem hydroformylation/hydrogenation reaction with syngas: a) G. M. Torres, R. Frauenlob, R. Franke, A. Börner, *Catal. Sci. Technol.* **2015**, *5*, 34-54. b) I. I. F. Boogaerts, D. F. S. White, D. J. Cole-Hamilton, *Chem. Commun.* **2010**, *46*, 2194-2196; c) O. Diebolt, C. Müller, D. Vogt, *Catal. Sci. Technol.* **2012**, *2*, 773-777; d) D. Fuchs, G. Rousseau, L. Diab, U. Gellrich, B. Breit, *Angew. Chem. Int. Ed.* **2012**, *51*, 2178-2182; *Angew. Chem.* **2012**, *124*, 2220-2224; e) K. Takahashi, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* **2012**, *134*, 18746-18757; f) L. Wu, I. Fleischer, R. Jackstell, I. Profir, R. Franke, M. Beller, *J. Am. Chem. Soc.* **2013**, *135*, 14306-14312; g) Y. Yuki, K. Takahashi, Y. Tanaka, K. Nozaki, *J. Am. Chem. Soc.* **2013**, *135*, 17393-17400.

[3] Selected reviews for carbonylation with syngas surrogates: a) T. Morimoto, K. Kakiuchi, *Angew. Chem. Int. Ed.* **2004**, *43*, 5580-5588; b) L. Wu, Q. Liu, R. Jackstell, M. Beller, *Angew. Chem. Int. Ed.* **2014**, *53*, 6310-6320; c) D. N. Gorbunov, M. V. Nenasheva, Y. S. Kardasheva, E. A. Karakhanov, *Russ. Chem. B.* **2020**, *69*, 625-634.

[4] Recent representative examples on carbonylation with formic acid: a) J. Cao, Z.-J. Zheng, Z. Xu, L.-W. Xu, *Coordin. Chem. Rev.* **2017**, *336*, 43-53; b) J. B. Peng, W. F. Wang, F. P. Wu, J. Ying, X. X. Qi, X. F. Wu, *J. Catal.* **2018**, *368*, 275-278; c) L. Wang, H. Neumann, M. Beller, *Angew. Chem. Int. Ed.* **2018**, *57*, 6910-6914; *Angew. Chem.* **2018**, *130*, 7026-7030; d) R. Yang, J. T. Yu, S. Sun, J. Cheng, *Org. Chem. Front.* **2018**, *5*, 962-966; e) X.-D. Lang, F. You, X. He, Y.-C. Yu, L.-N. He, *Green Chem.* **2019**, *21*, 509-514; f) W. L. Ren, J. X. Chu, F. Sun, Y. A. Shi, *Org. Lett.* **2019**, *21*, 5967-5970; g) L. Liu, H. Gao, S.-Q. Yang, X.-C. Chen, Y. Lu, Y. Liu, F. Xia, *J. Catal.* **2020**, *385*, 183-193; h) Z. K. Chen, L. C. Wang, X. F. Wu, *Chem. Commun.* **2020**, *56*, 6016-6030; i) R. Geitner, A. Gurinov, T. B. Huang, S. Kupfer, S. Grafe, B. M. Weckhuysen, *Angew. Chem. Int. Ed.* **2021**, *60*,3422-3427; *Angew. Chem.* **2021**, *133*,3464-3469.

[5] Recent representative examples on carbonylation with formaldehyde: a) G. Makado, T. Morimoto, Y. Sugimoto, K. Tsutsumi, N. Kagawa, K. Kakiuchi, *Adv. Synth. Catal.* **2010**, *352*, 299-304; b) Q. Liu, K. Yuan, P.-B. Arockiam, R. Franke, H. Doucet, R. Jackstell, M. Beller, *Angew. Chem. Int. Ed.* **2015**, *54*, 4493-4497; c) V. J. Garza, M. J. Krische, *J. Am. Chem. Soc.* **2016**, *138*, 3655-3658; d) T. Meyer, R. Konrath, P. C. J. Kamer, X. F. Wu, *Asian J. Org. Chem.* **2021**, *10*, 245-250.

[6] S. K. Pedersen, H. G. Gudmundsson, D. U. Nielsen, B. S. Donslund, H. C. D. Hammershøj, K. Daasbjerg, T. Skrydstrup, *Nat. Catal.* **2020**, *3*, 843-850.

[7] Selected examples for hydroformylation/hydroxymethylation with CO_2/hydrosilane: a) Y. Tani, K. Kuga, T. Fujihara, J. Terao, Y. Tsuji, *Chem. Commun.* **2015**, *51*, 13020-13023; b) X.-W. Chen, L. Zhu, Y.-Y. Gui, K. Jing, Y.-X. Jiang, Z.-Y. Bo, Y. Lan, J. Li, D.-G. Yu, *J. Am. Chem. Soc.* **2019**, *141*, 18825-18835; c) J. Qiu, S. Gao, C. Li, L. Zhang, Z. Wang, X. Wang, K. Ding, *Chem. –Eur. J.* **2019**, *25*, 13874-13878; d) M.-Y. Wang, X. Jin, X. Wang, S. Xia, Y. Wang, S. Huang, Y. Li, L.-N. He, X. Ma, *Angew. Chem. Int. Ed.* **2021**, *60*, 3984-3988; *Angew. Chem.* **2021**, *133*, 4030-4034.

[8] Recent representative examples on hydroformylation/hydroxymethylation with CO_2/H_2: a) K. Hua, X. Liu, B. Wei, S. Zhang, H. Wang, Y. Sun, *Acta Phy.-Chim. Sin.* **2021**, DOI: 10.3866/PKU.WHXB202009098; b) K.-i. Tominaga, Y. Sasaki, *Catal. Commun.* **2000**, *1*, 1-3; c) Q. Liu, L. Wu, I. Fleischer, D. Selent, R. Franke, R. Jackstell, M. Beller, *Chem.–Eur. J.* **2014**, *20*, 6888-6894; d) J. Klankermayer, S. Wesselbaum, K. Beydoun, W. Leitner, *Angew. Chem. Int. Ed.* **2016**, *55*, 7296-7343; e) K. Hua, X. Liu, B. Wei, Z. Shao, Y. Deng, L. Zhong, H. Wang, Y. Sun, *Green Chemistry* **2021**, DOI:10.1039/D0GC03913F.

[9] G. H. Gunasekar, K. Park, K.-D. Jung, S. Yoon, *Inorg. Chem. Front.* **2016**, *3*, 882-895.

[10] Y. C. Hou, M. G. Niu, W. Z. Wu, *Ind. Eng. Chem. Res.* **2020**, *59*, 16899-16910.

[11] J. B. Peng, X. X. Qi, X. F. Wu, *Synlett*, **2017**, *28*, 175-194.

[12] K. Sordakis, C. Tang, L. K. Vogt, H. Junge, P. J. Dyson, M. Beller, G. Laurenczy, *Chem. Rev.* **2018**, *118*, 372-433.

[13] a) R. Sang, P. Kucmierczyk, K. Dong, R. Franke, H. Neumann, R. Jackstell, M. Beller, *J. Am. Chem. Soc.* **2018**, *140*, 5217-5223; b) D.-S. Kim, W.-J. Park, C.-H. Lee, C.-H. Jun, *J. Org. Chem.* **2014**, *79*, 12191-12196; c) Y. Wang, W. Ren, J. Li, H. Wang, Y. Shi, *Org. Lett.* **2014**, *16*, 5960-5963; d) Y. Wang, W. Ren, Y. Shi, *Org. Biomol. Chem.* **2015**, *13*, 8416-8419.

[14] a) W. Ren, W. Chang, J. Dai, Y. Shi, J. Li, Y. Shi, *J. Am. Chem. Soc.* **2016**, *138*, 14864-14867; b) During the preparation of this manuscript, the Liu group reported similar Rh-catalyzed hydroformylation with formic acid, though with much lower regioselecitivity, which might be due to deficient coordination towards Rh. Furthermore, the more challenging hydroxymethylation has not been mentioned at all: L. Liu, X.-C. Chen, S.-Q. Yang, Y.-Q. Yao, Y. Lu, Y. Liu, *J. Catal.* **2020,** *394*, 406-415.

[15] Only a two-chamber system was developed to produce alcohols from alkenes and formic acid with mediocre regioselectivity (around 80:20) in the presence of linear terminal alkenes, see: M. G. Mura, L. D. Luca, G. Giacomelli, A. Porcheddu, *Adv. Synth. Catal.* **2012**, *354*, 3180-3186.

10.1002/chem.202100849

[16] P. W. N. M. van Leeuwen, P. C. J. Kamer, *Catal. Sci. Technol.* **2018**, *8*, 26-113.
[17] K. Takahashi, M. Yamashita, T. Ichihara, K. Nakano, K. Nozaki, *Angew. Chem. Int. Ed.* **2010**, *49*, 4488-4490; *Angew. Chem.* **2010**, *122*, 4590-4592.
[18] a) C. B. Dieleman, P. C. L. Kamer, J. N. H. Reek, P. van Leeuwen, *Helv. Chim. Acta.* **2001**, *84*, 3269-3280; b) P. Dydio, J. N. H. Reek, *Angew. Chem. Int. Ed.* **2013**, *52*, 3878-3882; *Angew. Chem.* **2013**, *125*, 4132-4132 c) S. Yu, Y.-m. Chie, Z.-h. Guan, Y. Zou, W. Li, X. Zhang, *Org. Lett.* **2009**, *11*, 241-244.
[19] K. Takahashi, K. Nozaki, *Org. Lett.* **2014**, *16*, 5846-5849.

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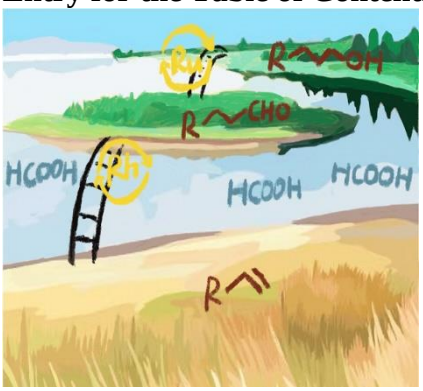

Effective methods for producing linear aldehydes or alcohols selectively with formic acid as both carbon monoxide and hydrogen source have been described. Linear-selective hydroformylation of alkenes proceeds smoothly in the presence of single Rh catalyst, strikingly, the dual Rh/Ru catalysts accomplish efficient and regioselective hydroxymethylation in one pot. Both protocols operate simply and avoid using flammable and toxic syngas, which represents a sustainable approach for the preparation of value-added compounds.