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## Article

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# Chemo- and Regioselective Hydroformylation of Alkenes with CO<sub>2</sub>/H<sub>2</sub> over a Bifunctional Catalyst

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**Abstract:** Combining CO<sub>2</sub> and H<sub>2</sub> to prepare building blocks for high-value-added products is an attractive yet challenging approach. A general and selective rhodium-catalyzed hydroformylation of alkenes using CO<sub>2</sub>/H<sub>2</sub> as a syngas surrogate is described here. With this protocol, the desired aldehydes can be obtained in up to 97% yield and 93/7 regioselectivity under mild reaction conditions (25 bar, 80 °C). Key-to-success is the use of bifunctional Rh/PTA catalyst (PTA: 1,3,5-triaza-7-phosphaadamantane), which facilitates both CO<sub>2</sub> hydrogenation and hydroformylation. Notably, monodentate PTA exhibited better activity and regioselectivity than common bidentate ligands, which might be ascribed to its built-in basic site and tris-chelated mode. Mechanistic studies indicate that the transformation proceeds through cascade steps, involving free HCOOH production through CO<sub>2</sub> hydrogenation, fast release of CO, and rhodium-catalyzed conventional hydroformylation. Moreover, the unconventional hydroformylation pathway, in which HCOOAc acts as a direct C1 source, has also been proved feasible with superior regioselectivity than that of CO pathway.

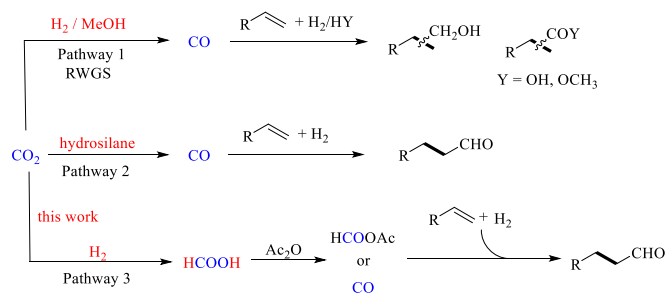
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With the concerns surrounding global warming caused by the ever-increasing carbon dioxide emissions, the catalytic reduction of CO<sub>2</sub> has been extensively explored as a strategy to generate high-value-added chemicals and energy-related products<sup>1-8</sup> such as CO<sup>9,10</sup>, formic acid<sup>11-13</sup>, methanol<sup>14-17</sup>, and gasoline<sup>18,19</sup>. CO<sub>2</sub> reduction to CO is of particular interest, as it can bridge the gap between CO<sub>2</sub> utilization and carbonylation of alkenes, the latter of which represents a major industrial technology for the production of valuable chemicals<sup>20,21</sup> such as aldehydes, alcohols, carboxylic acids, esters, though suffering from high toxicity and unsustainable fossil fuels source of CO. Therefore, reductive transformations using CO<sub>2</sub> for carbonylative alkene functionalization<sup>22-24</sup> with reductants<sup>25</sup> such as hydrosilane<sup>26,27</sup>, hydroborane, or CH<sub>3</sub>OH<sup>28,29</sup> have emerged as elegant alternative strategies. From a sustainable point of view, H<sub>2</sub> is a better choice of reductant<sup>30</sup>, as it can be generated by the photolysis of water<sup>31-33</sup>. Hence, the combination of CO<sub>2</sub> and H<sub>2</sub> for carbonylative alkene functionalization<sup>12,34</sup> has attracted much attention, and it has been demonstrated to afford high-value-added alcohols<sup>35-42</sup> and carboxylic acids<sup>43</sup>. However, owing to the intrinsic thermodynamic stability of CO<sub>2</sub> and the resulting deoxygenative cleavage of O=CO bond, reverse water gas shift (RWGS) (Scheme 1, Pathway 1)<sup>35,44</sup> generally requires high temperatures, which lead to overreduction of the carbonyl group, precluding the isolation of aldehydes and/or restricting the function of the ligands. As a result, poor regioselectivity is observed in this reaction.

Recently, Ding and Xia reported a one-pot hydroformylation of alkenes with CO<sub>2</sub> and H<sub>2</sub> to obtain aldehydes in good yields and regioselectivities (up to 70% and 90/10 l/b, respectively) through a sophisticated strategy (Scheme 1, Pathway 2)<sup>26</sup>. Unfortunately, an additional reductant, a hydrosilane, was required to mediate the reduction of CO<sub>2</sub> to CO. In addition, over 10 mol% of the alkene was inevitably hydrosilylated, causing the loss of starting materials and difficulty in product separation. Therefore, new strategies using CO<sub>2</sub>/H<sub>2</sub> as a syngas surrogate (especially with H<sub>2</sub> as the exclusive reductant) for chemo- and regioselective hydroformylation of alkenes are required<sup>45</sup>.

As is well known, HCOOH can be easily obtained by the catalytic hydrogenation of CO<sub>2</sub><sup>11-13,46,47</sup>. On the other hand, effective regioselective hydroformylation of alkenes with HCOOH has been realized<sup>48-50</sup> in which HCOOAc (generated from HCOOH and Ac<sub>2</sub>O) instead of conventional CO acts as intermediate<sup>49</sup>. Therefore, we envisaged the possibility of utilizing CO<sub>2</sub>/H<sub>2</sub> for the hydroformylation of alkenes via HCOOH. To achieve such a transformation,



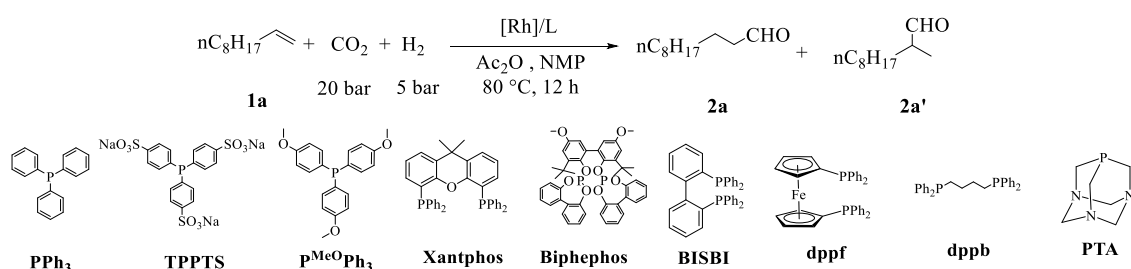
**Scheme 1. Strategies for the carbonylation of alkenes with CO<sub>2</sub>/H<sub>2</sub>.**

rapid production of HCOOH through CO<sub>2</sub> hydrogenation, HCOOAc formation/CO release should be coupled with regioselective hydroformylation in a single process (Scheme 1, Pathway 3). Herein, a bifunctional catalytic system composed of rhodium and PTA (1,3,5-triaza-7-phosphaadamantane), where Rh/PTA facilitates both CO<sub>2</sub> hydrogenation and hydroformylation, is developed for the efficient and selective hydroformylation of alkenes using CO<sub>2</sub>/H<sub>2</sub> as a syngas surrogate.

## Results

**Effects of ligands and reaction parameters.** Initially, Rh-catalyzed hydroformylation of 1-decene **1a** under 25 bar CO<sub>2</sub>/H<sub>2</sub> (4/1) in the presence of Ac<sub>2</sub>O was investigated using different ligands (Table 1). With the simple ligand PPh<sub>3</sub>, the aldehydes were obtained in 15% yield with a linear to branched ratio (l/b) of 74/26, which proved that tandem transformation was feasible (Table 1, entry 1). Derivatives of PPh<sub>3</sub> substituted with an electron-withdrawing or electron-donating group, such as TPPTS and P<sup>Me</sup>OPh<sub>3</sub>, showed slightly improved activity or regioselectivity (entries 2-3). The commonly used ligands Xantphos and Biphephos, which are well known to mediate highly regioselective hydroformylation, afforded negligible amounts of the aldehydes or no aldehydes, and hydrogenated byproducts dominated in both cases. In contrast, BISBI and metallocene-modified dppe displayed poor activity with excellent regioselectivity (entries 4-7). These results imply that hydroformylation with CO<sub>2</sub>/H<sub>2</sub> was blocked by the deficient CO/HCOOAc (the latter is generated from HCOOH and Ac<sub>2</sub>O, and acts as CO precursor) and that the critical step might be CO<sub>2</sub> hydrogenation into HCOOH, which promotes the subsequent hydroformylation, suppressing possible hydrogenation of alkene. Therefore, dppe<sup>51</sup> and PTA<sup>11</sup>, which show an outstanding ability for the hydrogenation of CO<sub>2</sub> to free HCOOH (as acetic acid from Ac<sub>2</sub>O created a weakly acidic medium), were explored for use in hydroformylation with CO<sub>2</sub>/H<sub>2</sub>. Indeed, when the reaction was performed with dppe, the aldehyde was obtained in 87% yield with an l/b

**Table 1. Ligand screening and optimization of reaction conditions for the hydroformylation of 1-decene **1a** with CO<sub>2</sub> and H<sub>2</sub> [a].**



Entry	L	Conv <sup>[b]</sup> /%	2a+2a' <sup>[b]</sup> /%	l/b <sup>[b]</sup>	Iso <sup>[b]</sup> /%	H <sup>[b]</sup> /%
1	PPh <sub>3</sub>	94	15	74/26	37	41
2	TPPTS	82	14	90/10	33	33
3	P <sup>Me</sup> OPh <sub>3</sub>	95	26	76/24	24	44
4	Xantphos	95	5	50/50	2	86
5	Biphephos	94	0	-	2	91
6	BISBI	90	20	92/8	13	55
7	dppf	73	6	93/7	6	60
8	dppb	99	87	78/22	4	8
9	PTA	99	90	89/11	5	3
10 <sup>[c]</sup>	PTA	98	80	90/10	8	9
11 <sup>[d]</sup>	PTA	99	74	94/6	11	13
12 <sup>[e]</sup>	PTA	99	92	90/10	3	3

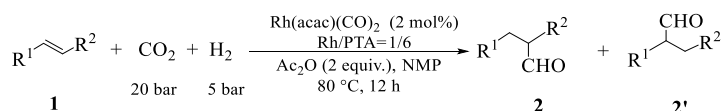
[a] Reaction conditions: 1-decene **1a** (1 mmol), Rh(acac)(CO)<sub>2</sub> (0.02 mmol), ligand (0.12 mmol), Ac<sub>2</sub>O (2.0 mmol), CO<sub>2</sub>/H<sub>2</sub> = 20/5 bar, 80 °C, 12 h, NMP (4 mL). [b] Determined by GC analysis with benzyl alcohol or isooctane as the internal standard. Iso = isomerized alkenes, H = decane. [c] 0.02 mmol Rh(OAc)<sub>3</sub>; instead of Rh(acac)(CO)<sub>2</sub>. [d] CO<sub>2</sub>/H<sub>2</sub> = 7/3 bar. [e] 2.2 mol % Rh(acac)(CO)<sub>2</sub>.

ratio of 78/22 (entry 8). Even better regioselectivity (89/11) but with a similar aldehyde yield was observed when using PTA (entry 9). Ten additional mono- and bidentate phosphine ligands such as CgPPh with a cage structure similar to that of PTA and dppp were also screened, and inferior results were obtained (Tables S1 and S2, SI). Hence, PTA was considered as the optimal ligand for this reaction.

Further investigations of the reaction conditions using the optimal ligand PTA revealed substantial effects of the rhodium precursor, PTA/Rh ratio, solvent type, temperature, and P<sub>CO<sub>2</sub></sub>/P<sub>H<sub>2</sub></sub> ratio on the aldehyde yield and regioselectivity. It is worth mentioning that the catalytic performance of (PPh<sub>3</sub>)<sub>3</sub>(CO)Rh-H is similar to that of PPh<sub>3</sub>, which implied that L<sub>3</sub>(CO)Rh-H could be the active intermediate (Table S3, SI). Specifically, a similar yield (80%) and regioselectivity (90/10) of the aldehyde were achieved when using Rh(OAc)<sub>3</sub> (Table 1, entry 10). Other rhodium salts could also promote this transformation but almost isomerization/hydrogenation products were observed (Table S3, SI). Decreasing or increasing the amount of PTA also weakened the aldehyde yield (Table S4, SI). A quick screening of solvents showed

that a solvent with high polarity, such as 1,3-dimethyl-2-imidazolidinone (DMI), N-methylpyrrolidone (NMP), or dimethyl sulfoxide (DMSO), was beneficial for the transformation; Among these, NMP was the optimal solvent. In contrast, the reactions carried out in toluene and THF afforded the aldehyde in a mediocre yield but with excellent regioselectivity (Table S5, SI). The aldehyde yield and l/b ratio could be maintained well when the reaction temperature was between 70 and 90 °C (Table S6, SI). The aldehyde yield and l/b ratio fluctuated marginally when the pressure of CO<sub>2</sub>/H<sub>2</sub> is doubled or halved (Table S7, SI). Notably, reducing the CO<sub>2</sub> pressure to 7 bar increased the regioselectivity (up to 94/6 l/b), but slightly decreased the aldehyde yield (Table 1, entry 11). Finally, the aldehyde yield could be improved to 92% with 90/10 l/b by optimizing the catalyst loading (Table 1, entry 12).

**Substrate scope.** With the optimized reaction conditions in hand, the generality of the reaction was investigated. As shown in Table 2, terminal alkenes (C<sub>5</sub>-C<sub>10</sub>) demonstrated similar reactivity irrespective of the carbon chain length, affording the corresponding aldehydes in over 90% yields

**Table 2. Substrate scope.**<sup>[a]</sup>

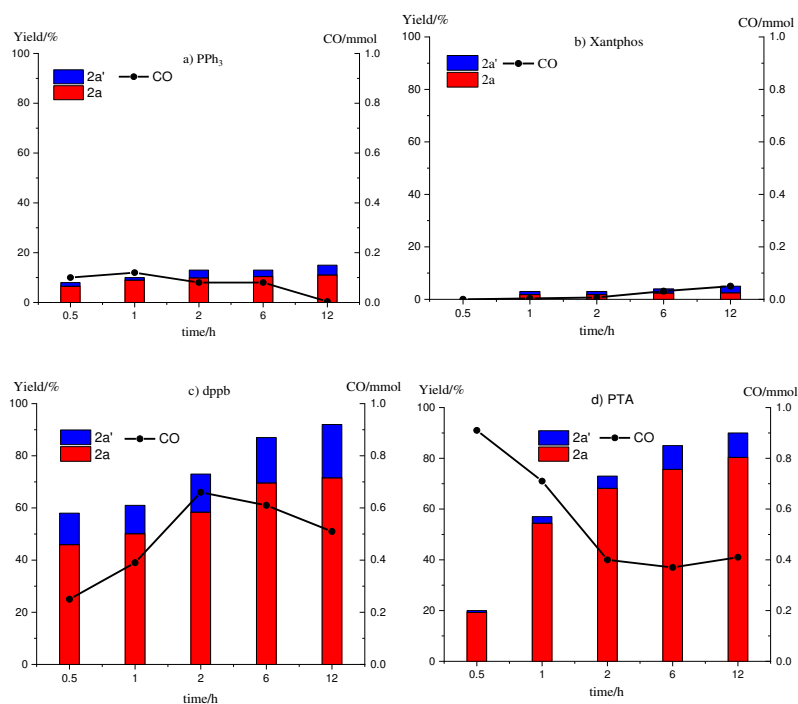
Entry	Alkene	Conv <sup>[b]</sup> / %	Yield [b]/%	l/b <sup>[b]</sup>	Iso <sup>[b]</sup> /%	H <sup>[b]</sup> /%
1		99	92	90/10	3	3
2		99	96	90/10	1	1
3		99	96	88/12	2	1
4		99	95	86/14	2	1
5		100	97	85/15	2	<1
6		99	95	86/14	2	2
7 <sup>[c]</sup>		-	77	93/7	-	-
8 <sup>[c]</sup>		-	73	85/15	-	-
9 <sup>[c]</sup>		-	72	-	-	-
10		98	87	87/13	2	8
11		99	92	73/27	1	6
12		98	90	85/15	3	4
13 <sup>[d]</sup>		76	75	-	0	1
14 <sup>[e]</sup>		90	64	-	25	1
15		99	90	10/90	0	1
16		98	47	17/83	0	4
17		94	91	16/84	0	<1

[a] Reaction conditions: Alkene (1 mmol), Rh(acac)(CO)<sub>2</sub> (0.022 mmol), PTA (0.132 mmol), Ac<sub>2</sub>O (2.0 mmol), NMP (4 mL), CO<sub>2</sub>/H<sub>2</sub> = 20/5 bar, 80 °C, 12 h. [b] Determined by GC analysis with benzyl alcohol or isooctane as the internal standard. [c] Alkene (3 mmol), Ac<sub>2</sub>O (4.5 mmol). [d] T = 90 °C. [e] T = 100 °C, 24 h. 1-CHO: 2-CHO: 3-CHO = 16:60:24

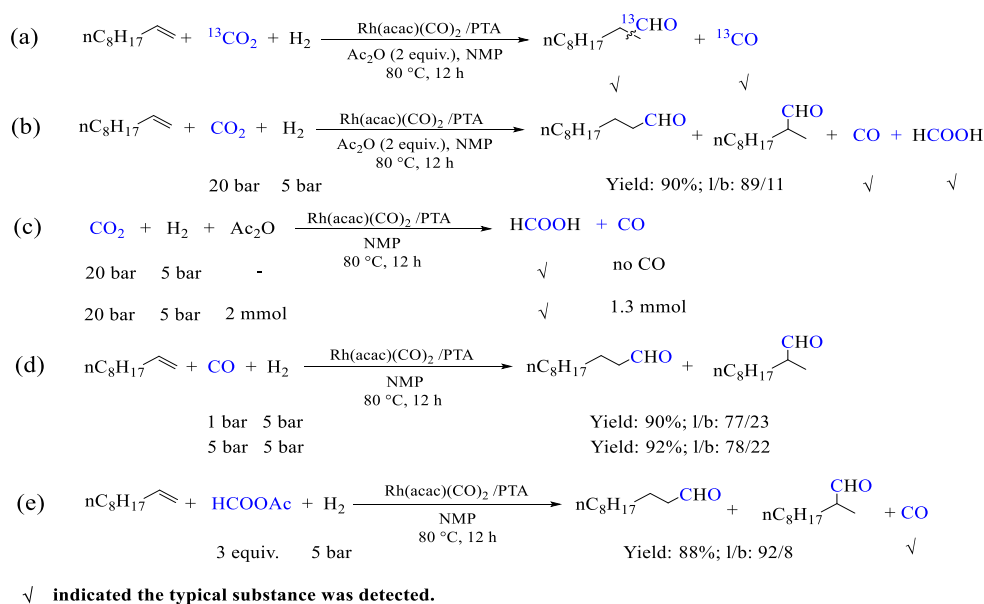
with good linear regioselectivities (l/b = 85/15–93/7) (entries 1-6). Bulk aldehydes were also achieved in 72% – 77% yield with good linear regioselectivity for the hydroformylation of ethene, propene, and butene (entries 7-9). Remarkably, good functional-group tolerance was observed for chloro, hydroxyl and ester groups (entries 10-12). The more challenging internal alkenes, norbornene and 2-octene, were transformed into corresponding aldehydes in good yield (entries 13-14). Finally, the reaction proceeded smoothly with styrene derivatives, furnishing aldehydes in moderate to excellent yields, though with opposite regioselectivities (entries 15-17).

**Role of the ligand.** As shown in Table 1, the ligand plays a critical role in the hydroformylation of alkene with CO<sub>2</sub>/H<sub>2</sub>.

Therefore, we selected typical ligands including PPh<sub>3</sub>, Xantphos, dppb, and PTA to compare the aldehyde yield, regioselectivities, and CO production under identical conditions (Figure 1). Analysis of gas products formed during the hydroformylation of **1a** promoted by Rh/PPh<sub>3</sub> revealed that the amount of CO remained approximately 0.1 mmol. The low CO content (decomposed from HCOOAc) led to the mediocre yield and regioselectivity. Although Xantphos exhibited excellent regioselective hydroformylation with CO/H<sub>2</sub><sup>20</sup>, it afforded a major hydrogenated by-product instead of the desired aldehyde, which can be attributed to its inferior ability to produce HCOOH through CO<sub>2</sub> hydrogenation and the resulting HCOOAc/CO. In the presence of dppb, the amount of produced CO increased and remained constant



**Figure 1. Control experiments with different ligands.** (a) PPh<sub>3</sub>, (b) Xantphos, (c) dppb, and (d) PTA in 0.5, 1, 2, 6, and 12 h. Reaction conditions: **1a** (1.0 mmol), Rh(acac)(CO)<sub>2</sub> (2 mol%), L (12 mol%), Ac<sub>2</sub>O (2.0 mmol), CO<sub>2</sub>/H<sub>2</sub> = 20/5 bar, 80 °C, NMP (4 mL) in a 50 mL autoclave.



## Scheme 2. Isotope-labeling experiments and control experiments.

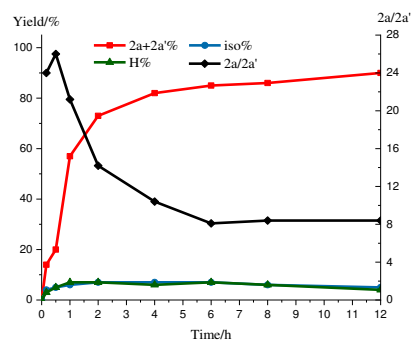
at a high level (over 0.5 mmol), which effectively promoted the subsequent hydroformylation to furnish aldehydes in 92% yield and with modest linear regioselectivity (80/20 l/b ratio). Gratifyingly, Rh/PTA displayed a better ability to generate CO, as 0.9 mmol CO in the initial 30 min could be detected and over 0.4 mmol CO could be maintained throughout. Notably, as CO was derived from HCOOH/HCOOAc decomposition, appreciable amounts of CO in the gas phase implied accumulation of HCOOH/HCOOAc in the liquid phase (actually, HCOOH production increased gradually over time, see Figure S2, SI). Therefore, the possibility of

HCOOH/HCOOAc acting as a direct C1 source could not be ruled out. These observations revealed that the key to distinguish PTA from other ligands is the efficient and rapid production of HCOOH/HCOOAc or CO, which originates from its outstanding ability to produce HCOOH through CO<sub>2</sub> hydrogenation in acidic media<sup>11</sup>. After excluding the influence of acids (Tables S10, SI) and sterically rigid structure of PTA (ligand CgPPh with similar cage structure showed poor activity and regioselectivity, see Tables S1, L6, SI), we presume it's the characteristic nitrogen atom in PTA acting as a built-in basic site<sup>52-55</sup> that thermodynamically shift

the equilibrium towards formation of free HCOOH. Another possible reason for superior regioselectivity of PTA over dppb is the tris-chelated mode of PTA towards Rh, similar to that of monodentate PPh<sub>3</sub> (Table S3, SI)<sup>56</sup>, and the resultant steric-hindered (PTA)<sub>3</sub>(CO)Rh-H (confirmed by ESI-MS, see Figure S3, SI) induces formation of linear aldehydes.

**Isotope-labelling and Control experiments.** To gain insight into the details of alkene hydroformylation with CO<sub>2</sub>/H<sub>2</sub>, a series of control experiments were designed (Scheme 2). Isotope-labeling experiments were performed using <sup>13</sup>CO<sub>2</sub> to verify the source of the carbon in the formyl group. Incorporation of <sup>13</sup>CO<sub>2</sub> into the formyl group was confirmed by <sup>13</sup>C NMR (Figure S4, SI) analysis. <sup>13</sup>CO was also detected by MS in the gas phase (Figure S6, SI). These results confirmed that CO<sub>2</sub> was involved in the formation of the formyl group (Scheme 2a).<sup>45</sup> Formation of HCOOH and CO was detected from the liquid and gas phases, respectively, under standard conditions (Scheme 2b). To explore the HCOOH source, hydrogenation of CO<sub>2</sub> was conducted in the presence of Rh/PTA. Signals attributed to HCOOH could be clearly observed in the <sup>1</sup>H NMR spectrum (Figure S7, SI). The addition of 2.0 mmol acetic anhydride to the above reactor generated 1.3 mmol CO (Scheme 2c). HCOOAc could not be detected in the system as it's highly reactive. Based on the above results, we speculated that CO<sub>2</sub> was readily hydrogenated to HCOOH, which produced HCOOAc in the presence of Ac<sub>2</sub>O. HCOOAc would be rapidly decomposed to CO. All these results together proved the feasibility of the CO<sub>2</sub>-HCOOH-HCOOAc-CO-formyl pathway in obtaining aldehydes. Similar aldehyde yields could be obtained, albeit with lower regioselectivity, when CO is used instead of CO<sub>2</sub> (Scheme 2d). A comparable performance was achieved with HCOOH as the C1 source (Scheme 11, SI). Notably, with HCOOAc as the direct carbon source, the reaction proceeded with superior regioselectivity and similar aldehyde yield (Scheme 2e). This unconventional pathway contributed to the exceptional regioselectivity, possibly owing to the coordination of HCOOAc with Rh/PTA<sup>49</sup>. In a word, two compatible pathways (HCOOAc one with 92/8 regioselectivity and CO one with 78/22) generates overall 90/10 regioselectivity.

**Time course of the reaction.** Results of the kinetic study (Figure 2) also confirmed the coexistence of both conventional and unconventional reaction pathways. In the first 10 min, 14% yield of aldehydes (**2a+2a'**) along with excellent 96/4 regioselectivity was observed. Subsequently, the yield exceeded 50% with the l/b ratio of 95/5 in 1 h. When **1a** was fully converted after 6 h, the aldehyde yield was approximately 90% with an l/b ratio of 90:10<sup>57,58</sup>. Hence, the



**Figure 2. Reaction profiles for the hydroformylation of **1a** with CO<sub>2</sub>/H<sub>2</sub>.** Reaction conditions: **1a** (1.0 mmol), Rh(acac)(CO)<sub>2</sub> (2 mol%), PTA (12 mol%), Ac<sub>2</sub>O (2.0 mmol), CO<sub>2</sub>/H<sub>2</sub> = 20/5 bar, 80 °C, NMP (4 mL) in a 50 mL autoclave.

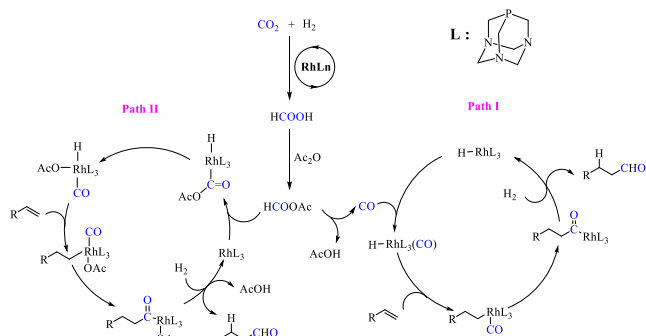
exceptionally high regioselectivity at the initial stage is attributed to the accumulation of HCOOAc, which follows the unconventional hydroformylation pathway. With time, HCOOAc rapidly decomposes to CO. High concentration of CO will divert the reaction to the conventional pathway, reducing the regioselectivity.

## Discussion

On the basis of all these results and previous reports<sup>20,45,49</sup>, we suggest the following reaction pathways for the hydroformylation of alkenes with CO<sub>2</sub>/H<sub>2</sub> (Scheme 3). Initially, CO<sub>2</sub> is hydrogenated by Rh/PTA to produce HCOOH, which readily decomposes to CO with the assistance of Ac<sub>2</sub>O. In the presence of H<sub>2</sub> and *in situ* generated CO, Rh/PTA-catalyzed conventional hydroformylation proceeds smoothly (pathway I). Compared with the conventional hydroformylation using CO/H<sub>2</sub>, unconventional pathway II in which HCOOAc acts as a direct carbon source proves plausible<sup>49</sup>. Pathway II dominates the early stage of the reaction and generates more linear aldehydes. Hence, two compatible pathways contribute to the excellent yield and regioselectivity in the hydroformylation of alkenes with CO<sub>2</sub>/H<sub>2</sub>, wherein the bifunctional Rh/PTA system plays a crucial role.

In summary, Rh/PTA, a bifunctional catalytic system that couples CO<sub>2</sub> hydrogenation and hydroformylation of alkenes, has been developed for the efficient production of linear aldehydes using CO<sub>2</sub>/H<sub>2</sub> as a syngas surrogate, which paves an innovative way for chemo- and regioselective synthesis of aldehyde. A number of aliphatic alkenes including internal alkenes and styrenes can be transformed in good to excellent yields and regioselectivities under mild conditions. Mechanistic studies revealed that the reaction proceeded through two pathways: via CO or via HCOOAc, where the HCOOAc pathway generated more linear aldehydes. We demonstrate the possibility of using CO<sub>2</sub> and





**Scheme 3. Proposed mechanism.**

H<sub>2</sub> for the selective hydroformylation of alkenes without any additional reductants. Further studies to enhance the catalytic activity and extend this approach to other types of carbonylations are in progress in our laboratory.

## Method

**General analytic methods.** All measurements were carried out at room temperature unless otherwise stated. GC analysis was performed on Shimadzu-2014 with a FID detector and a Stabilwax®-DA column (60 m, 0.53 mm, 0.5 μm). The gaseous mixture was collected and analyzed by gas chromatography equipped with thermal conductivity detector (Shimadzu GC-2014C) with Argon as the carrier gas. ESI-MS analysis was performed on WATERS 2695+ZQ2000. Detected masses are given in m/z and correlated to calculated masses of the respective species. High resolution MS (omni star gas analysis system) analyses were performed to detect <sup>13</sup>CO after <sup>13</sup>CO<sub>2</sub> Isotope experiment. Detected masses are given in m/z and correlated to calculated masses of the respective species. <sup>1</sup>H- and <sup>13</sup>C- NMR spectra were recorded on Bruker Avance III 400 MHz spectrometers. Chemical shifts (δ values) were reported in ppm relative to internal TMS.

**Materials.** Unless otherwise noted, all commercially available reagents were used without further purification. Among these, extra-dry solvents with water ≤ 50 ppm (by K.F.) were bought from Energy Chemical. All metallic reagents and ligands were ordered from Aldrich or Energy Chemical, and used as received.

**General procedure for the hydroformylation reaction.** All reactions and operations involving air- or moisture-sensitive compounds were performed in Ar-filled glove box. All reactions were carried out in a Teflon-lined stainless steel reactor of 50 mL capacity equipped with a magnetic stirrer. Typically, in a glovebox, 1-decene (1.0 mmol), Rh(acac)(CO)<sub>2</sub> (0.02 mmol), ligand (0.12 mmol), Ac<sub>2</sub>O (2.0 mmol) and NMP (4 mL) were loaded into the reactor. The autoclave was sealed and purged three times with CO<sub>2</sub> gas, subsequently charged with CO<sub>2</sub> (20 bar), then H<sub>2</sub> (5 bar) to total pressure of 5 bar. The autoclave was then heated at 80 °C for 12 h. After the reaction, the autoclave was cooled in ice water and then the gas was carefully vented into the airbag. The resulting clear solution was diluted with N-methyl-2-pyrrolidone (10 mL) and added benzyl alcohol (0.5 mmol) or isooctane (0.3 mmol) as internal standard. The sample was filtered through a short cotton plug, and the filtrate was firstly analyzed by GC-MS to determine the structures of the aldehyde products, then immediately analyzed by GC to determine the conversion of alkenes, yields of the aldehydes, and the regioselectivity (n/iso ratio) as well as percentage of isomerization and hydrogenation products. Yields were found to be reproducible within Y = ±5% in three independent runs for selected experiments.

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## Author contributions

K. Hua, Dr. X. Liu, Prof. H. Wang and Prof. Y. Sun designed and developed this project. K. Hua and Dr. X. Liu performed the catalytic experiments and data analysis. K. Hua, Dr. X. Liu and Prof. H. Wang wrote the manuscript. B. Wei, Z. Shao, Y. Deng, J. Zhang, L. Xia and Prof. L. Zhong performed some experiments and discussed the work.

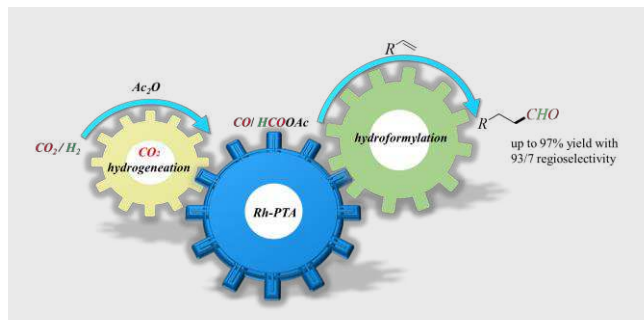
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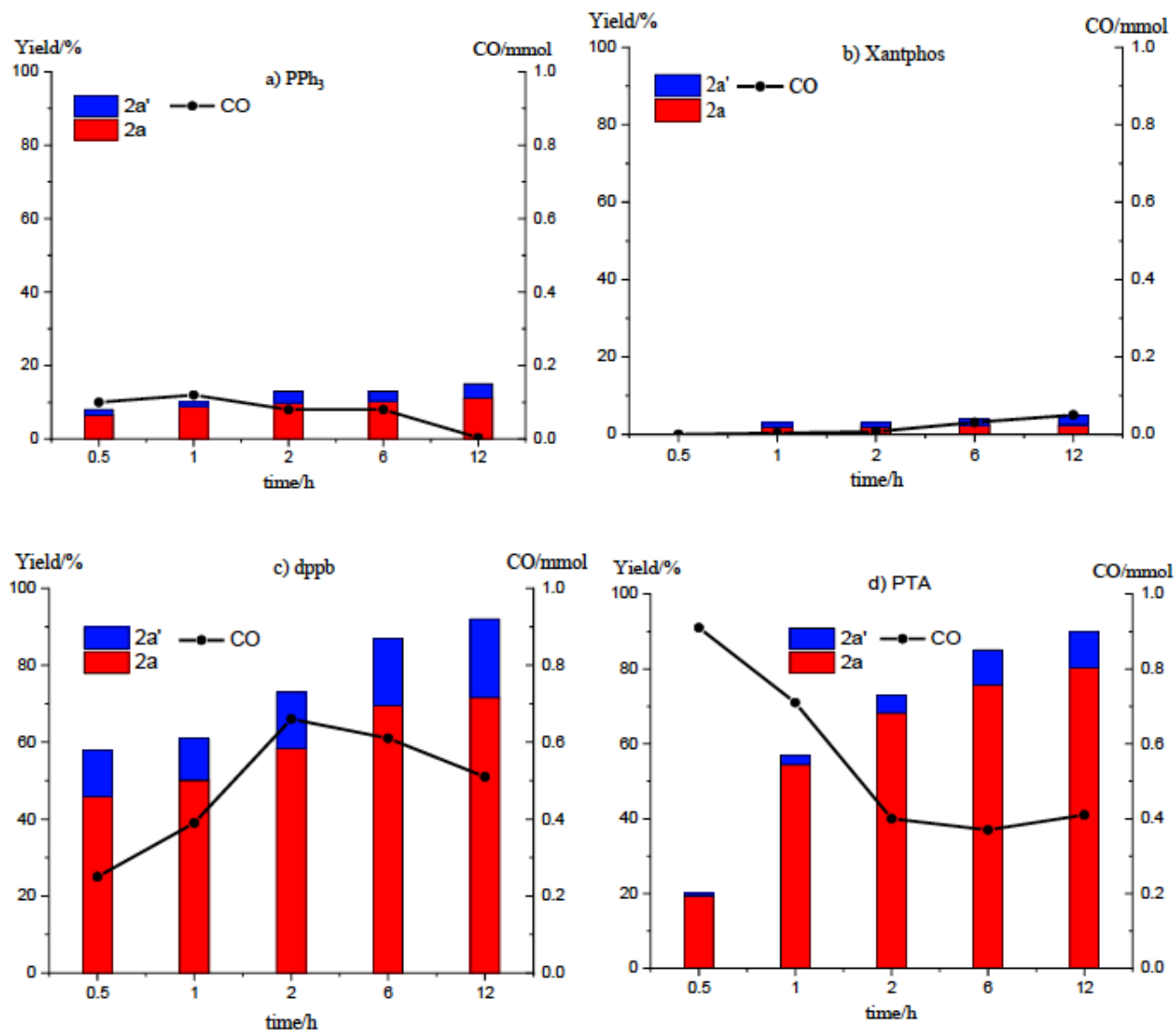
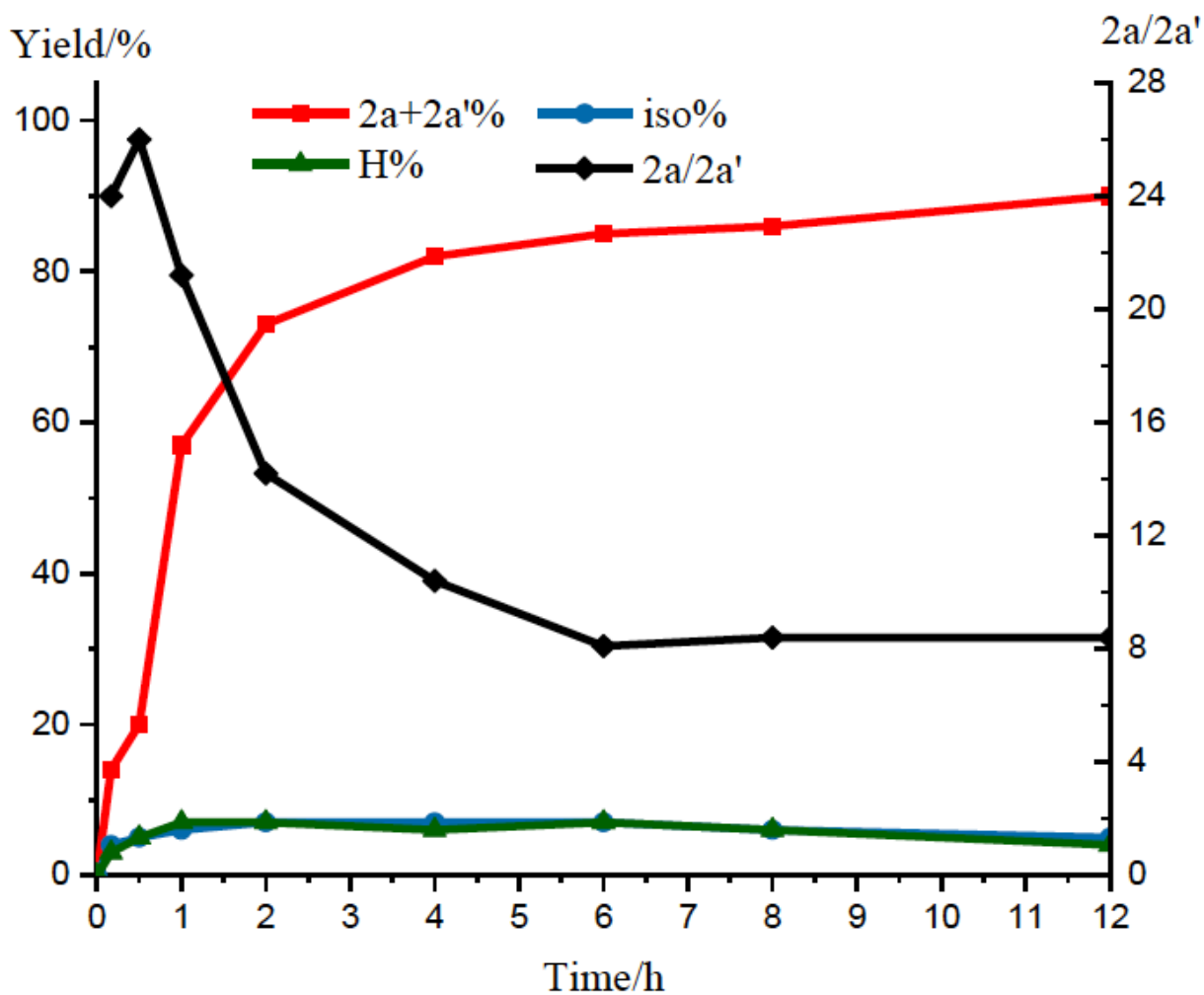


Figure 1

Control experiments with different ligands. (a) PPh<sub>3</sub>, (b) Xantphos, (c) dppb, and (d) PTA in 0.5, 1, 2, 6, and 12 h. Reaction conditions: 1a (1.0 mmol), Rh(acac)(CO)<sub>2</sub> (2 mol%), L (12 mol%), Ac<sub>2</sub>O (2.0 mmol), CO<sub>2</sub>/H<sub>2</sub> = 20/5 bar, 80 °C, NMP (4 mL) in a 50 mL autoclave.



**Figure 2**

Reaction profiles for the hydroformylation of 1a with CO<sub>2</sub>/H<sub>2</sub>. Reaction conditions: 1a (1.0 mmol), Rh(acac)(CO)<sub>2</sub> (2 mol%), PTA (12 mol%), Ac<sub>2</sub>O (2.0 mmol), CO<sub>2</sub>/H<sub>2</sub> = 20/5 bar, 80 °C, NMP (4 mL) in a 50 mL autoclave.

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