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Acetic anhydride as a versatile carbon source in carbonylation reactions

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Acetic anhydride (Ac_2O) is a cheap and easily available chemical feedstock that is widely used as an acetylating or dehydrating agent in organic synthesis. Here, we report Ac_2O as a novel and versatile carbon source in carbonylation reactions. Notably, besides CO, the acetic acid (AcOH), decomposed from the Ac_2O molecule, could participate in the reaction and simultaneously act as a necessary cosolvent. Acetate esters, aldehydes, and carboxylic acids could be produced separately by simply regulating the Pd-catalyzed reaction of olefins, Ac_2O and H_2. Remarkably, the reaction is applicable to various olefins, and high yields (up to 95%) as well as good regioselectivities of the acetate esters and aldehydes could be achieved. The outstanding results of acetate ester synthesis represent a successful and innovative cascade reaction, which demonstrates good atom economy. The mechanism of the reactions, especially the Ac_2O decomposition, has been studied by control experiments and DFT calculations. This work opens a new avenue for carbonylation reactions.

Introduction

Carbonylation reactions are of great significance in chemistry and the chemical industry.[1–3] In the past few decades, their versatility and increasing elaboration as synthetic tools have led to broader applications.[4] Carbonyl-containing chemicals (such as aldehydes, carboxylic acids and esters) are widely used as raw materials and solvents for producing medicines, pesticides, cosmetics, perfumes, shampoos, lubricants, food additives, *etc.* As a traditional feedstock, CO is widely used in carbonylation reactions,[1,5,6] but it is a flammable and toxic gas that encounters various inconveniences in many cases.

To address these problems, developing benign and safe CO surrogates has gained much attention in synthetic chemistry and catalysis.[7–9] The known CO surrogates include carbon dioxide (CO_2),[10–14] formic acid,[15,16] formates,[17,18] aldehydes,[19,20] formamides,[21,22] alcohols,[23,24] metal carbonyls,[25,26] chloroform,[27]

silacarboxylic acid,[28,29] glyoxylic acid and its acetal derivatives,[30,31] acid chlorides[32,33] and so on. In addition, a two-chamber reactor was developed, where CO was generated by controlled activation of a solid CO surrogate in one chamber and delivered to another chamber for carbonylation reactions.[28,33,34] In a pioneering study, in the presence of a sterically congested hydrosilane, aroyl chloride was used as a carbon electrophile and CO source for stereoselective carboformylation of alkynes, which was further extended to four chemodivergent carbonylation reactions.[32]

Ac_2O is a cheap and readily available chemical feedstock, and its annual world production is about 3 million tons. To our knowledge, direct valorization of Ac_2O as a CO surrogate in carbonylation reactions has not been reported yet. In this work, we disclosed Ac_2O as an unprecedented CO surrogate as well as
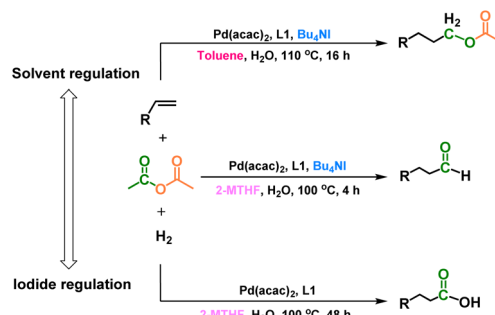
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Fig. 1 Pd-catalyzed olefin carbonylation reactions with Ac_2O as a carbon source.

a versatile carbon source, which was applied in Pd-catalyzed olefin carbonylation reactions (Fig. 1). Interestingly, by only subtle modification of the catalytic system, three categories of important carbonylation products (acetate esters, aldehydes and carboxylic acids) could be produced separately with moderate to excellent yields. It is worth noting that Ac_2O could not only act as a versatile feedstock but also engender necessary solvent conditions during the reaction.
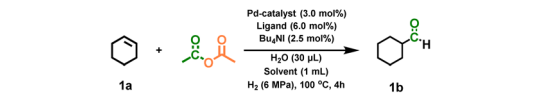
Results and discussion

Catalytic systems

Different parts of the Ac_2O molecule can be *in situ* transferred to a new carbonyl-containing molecule in the presence of an appropriate catalytic system. In this work, we started with the carbonylation of cyclohexene with Ac_2O and H_2. The results of catalyst screening are presented in Table 1. High yield (81%) of **1b** was achieved when the reaction was promoted by a $Pd(acac)_2$ catalyst, **L1** ligand and Bu_4NI additive in 2-methyl-tetrahydrofuran (2-MTHF) solvent. CO and methane (CH_4) were observed after the reaction, which may be from decomposition of Ac_2O (Fig. S1). Obviously, CO participated in the hydroformylation of cyclohexene. No **1b** was observed in the absence of H_2 because H_2 is necessary for the decomposition of Ac_2O as well as the hydroformylation of the olefin. Other Pd complexes were also tested, but the yields were lower ($Pd(OAc)_2$, $Pd(TFA)_2$ and $Pd_2(dba)_3$) or the reaction could hardly proceed ($PdCl_2$ and PdI_2) (Table S1). When other transition metal compounds (Co, Mn, Ru, Rh, Ni, Pt, and Ir) were used as catalysts, the target reaction did not occur. **1b** was not detected without the bidentate ligand **L1**. We tried monodentate ligands (**L2** and **L3**) as well, but they were ineffective. Other bidentate phosphine ligands such as **L4**, **L5**, **L6**, **L7**, and **L8** were also screened in the reaction. The results suggested that the distance between the phosphorus coordination sites and the rigidity of ligands significantly affected the reaction yields.

The iodide additive was necessary in the reaction, while the performances of its bromide and chloride counterparts were poor. Other iodides (NIS, NaI, and KI) were not as effective as Bu_4NI, while molecular iodine did not work at all (Table S2). Thus, the iodide anion was indispensable, and the cation of the additive may be responsible for the increased solubility of the reaction components. A notable solvent effect was observed, and 2-MTHF gave the best result in the reaction. Interestingly, the methyl group (–CH_3) on the THF ring had a remarkable promotive influence on the catalytic result, and the reaction yield decreased from 81% to 22% when THF was used as the solvent. However, the introduction of two methyl groups on the THF ring (2,5-DMTHF) also depressed the reaction rate. Some other ethers were also effective solvents, albeit with lower reaction yields than 2-MTHF (Table S3), while the commonly used solvents such as 1,2-dichloroethane, AcOH and NMP (N-methyl-2-pyrrolidone) were hardly usable. Although trace water (H_2O) was needed in the reaction, H_2O itself was not an effective solvent for the reaction. In short, the catalytic system consisting of $Pd(acac)_2$, **L1**, Bu_4NI and 2-MTHF was suitable to accelerate the reaction.

Table 1 Catalytic systems for synthesis of aldehydes, acetate esters, and carboxylic acids from olefin, Ac_2O and H_2[a]

Entry	Catalyst	Ligand[b]	Solvent	Yield[c] [%]
1	$Pd(acac)_2$	**L1**	2-MTHF	81
2	$Pd(OAc)_2$	**L1**	2-MTHF	68
3	PdI_2	**L1**	2-MTHF	0
4	$Pd(acac)_2$	—	2-MTHF	0
5	$Pd(acac)_2$	**L2**	2-MTHF	<1
6	$Pd(acac)_2$	**L3**	2-MTHF	<1
7	$Pd(acac)_2$	**L4**	2-MTHF	<1
8	$Pd(acac)_2$	**L5**	2-MTHF	35
9	$Pd(acac)_2$	**L6**	2-MTHF	<1
10	$Pd(acac)_2$	**L7**	2-MTHF	28
11	$Pd(acac)_2$	**L8**	2-MTHF	0
12	$Pd(acac)_2$	**L1**	THF	22
13	$Pd(acac)_2$	**L1**	2,5-DMTHF	73
14	$Pd(acac)_2$	**L1**	1,2-Dichloroethane	<1
15	$Pd(acac)_2$	**L1**	AcOH	<1
16	$Pd(acac)_2$	**L1**	NMP	<1
17	$Pd(acac)_2$	**L1**	H_2O	0
18	$Pd(acac)_2$	**L1**	Toluene	54[d]
19	$Pd(acac)_2$	**L1**	2-MTHF	1[e]

[a] Reaction conditions: 30 μmol Pd catalyst, 60 μmol ligand, 25 μmol Bu_4NI, 30 μL H_2O, 1 mL solvent, 1 mmol cyclohexene, 4 mmol Ac_2O, 6 MPa H_2, 100 °C, 4 h. [b] **L1**, 1,3-bis(diphenylphosphino)propane (DPPP); **L2**, triphenylphosphine (PPh_3); **L3**, tri-n-butylphosphine (P^nBu_3), **L4**, 1,2-bis(diphenylphosphino)ethane (DPPE); **L5**, 1,4-bis(diphenylphosphino)butane (DPPB); **L6**, 1,1'-bis(diphenylphosphino)ferrocene (DPPF); **L7**, (oxybis(2,1-phenylene))bis(diphenylphosphane) (DPEPhos); **L8**, (9,9-dimethyl-9H-xanthene-4,5-diyl)bis(diphenylphosphine) (Xantphos). [c] The yields of **1b** were GC yields, which were calculated on the basis of the cyclohexene substrate. [d] Remarkable cyclohexylmethyl acetate (**1d**, yield of 14%) was observed after the reaction, as shown in Table 2, and optimization of the conditions for this product is given in Table 3. [e] If no additive was added before the reaction, cyclohexanecarboxylic acid (**1e**, yield of 3%) was observed, and the yield could reach 69% when the reaction time was extended to 48 h. Abbreviations: dba (dibenzylideneacetone), TFA (trifluoroacetic acid), Bu_4NI (tetrabutylammonium iodide), Bu_4NBr (tetrabutylammonium bromide), Bu_4NCl (tetrabutylammonium chloride), 2,5-DMTHF (2,5-dimethyltetrahydrofuran).

Based on the optimized catalytic system for the synthesis of aldehydes, we conducted the reaction at different temperatures and found that 100 °C was appropriate (Fig. S2). The impact of dosages of the catalytic components on the hydroformylation was also systematically studied (Tables S4 and S5). The amount of the Pd catalyst and **L1** ligand had a marked impact on the reaction yields. In addition, the ratio of their dosages, which

may change the coordination state of the metal center, was also a key factor for the catalytic performance. The optimal dosage of Bu$_4$NI was slightly less than that of the Pd catalyst, which suggested that the halide-promoting effect only existed at one or several step(s) in the catalytic cycle.[35] Interestingly, the addition of a small amount of H$_2$O was needed for the reaction, and 30 μL (1.7 mmol) H$_2$O engendered the optimal result. Further studies indicated that the suitable amounts of Ac$_2$O and H$_2$ were 4 mmol and 6 MPa, respectively (Table S6). Within only 4 h, the reaction proceeded quickly and highly selectively to give **1b**, where only trace byproducts were observed (Fig. S3). Therefore, the conditions in entry 1 of Table 1 were the optimal conditions for the synthesis of aldehyde by carbonylation of olefin using Ac$_2$O as the carbonyl source.

Very interestingly, when the solvent was altered from 2-MTHF to toluene, the production of **1b** was restrained and a remarkable amount of acetate ester was observed (Table 1, entry 18). It was found that toluene as a solvent may promote the formation of cyclohexylmethanol more effectively, which may react *in situ* with acetic acid from Ac$_2$O to generate **1d** (Table 2). Synthesis of higher acetate esters from olefins is an interesting topic, and the previous reports generally utilized Rh or Ru catalysts, which encountered multi-step operations, low yields/regioselectivities and/or involvement of strong acidic conditions.[36–38] We further screened the different catalytic systems for this reaction (Table 3). The choice of catalyst precursors and ligands remarkably influences the generation of acetate esters. Through systematic screening, we identified Pd(acac)$_2$ as the optimal catalyst and **L1** as the most effective ligand. Building on this finding, we observed that variations in the solvent have a considerable impact on the formation of acetate esters. To facilitate a more comprehensive comparison of solvent effects, we conducted our studies with an extended reaction time of 16 h. Notably, aromatic solvents with structures analogous to toluene also demonstrated favorable outcomes, although they were not as good as toluene. The catalytic results with different dosages of reactants, temperature and reaction time are shown in Table S7. Under the optimal conditions, the

Table 2 Impact of 2-MTHF and toluene as solvents on the tandem reactions for the synthesis of cyclohexylmethyl acetate from cyclohexene, Ac$_2$O and H$_2$[a]

Entry	Solvent	Yield[b] [%]		
		1b	**1c**	**1d**
1	Toluene	54%	15%	14%
2	2-MTHF	81%	8%	2%

[a] Reaction conditions: 30 μmol Pd(acac)$_2$, 60 μmol **L1**, 25 μmol Bu$_4$NI, 30 μL H$_2$O, 1 mL solvent, 1 mmol cyclohexene, 4 mmol Ac$_2$O, 6 MPa H$_2$, 100 °C, 4 h. [b] The yields of **1b**, **1c** and **1e** were GC yields, which were calculated on the basis of the cyclohexene substrate.

Table 3 Catalytic systems for the synthesis of acetate esters from olefin, Ac$_2$O and H$_2$[a]

Entry	Catalyst	Ligand	Reaction time [h]	Solvent	Yield[b] [%]
1	Pd(acac)$_2$	**L1**	4	2-MTHF	2
2	PdI$_2$	**L1**	4	2-MTHF	0
3	Pd(dba)$_2$	**L1**	4	2-MTHF	<1
4	Pd(acac)$_2$	**L4**	4	2-MTHF	0
5	Pd(acac)$_2$	**L5**	4	2-MTHF	<1
6	Pd(acac)$_2$	**L6**	4	2-MTHF	0
7	Pd(acac)$_2$	**L7**	4	2-MTHF	0
8	Pd(acac)$_2$	**L8**	4	2-MTHF	0
9	Pd(acac)$_2$	**L1**	4	Toluene	14
10	Pd(acac)$_2$	**L1**	16	Toluene	69
11	Pd(acac)$_2$	**L1**	16	*p*-Xylene	54
12	Pd(acac)$_2$	**L1**	16	*m*-Xylene	43
13	Pd(acac)$_2$	**L1**	16	Mesitylene	46
14	Pd(acac)$_2$	**L1**	16	2-MTHF	21
15	Pd(acac)$_2$	**L1**	16	Toluene	90[c]

[a] Reaction conditions: 30 μmol Pd catalyst, 60 μmol ligand, 25 μmol Bu$_4$NI, 30 μL H$_2$O, 1 mL solvent, 1 mmol cyclohexene, 4 mmol Ac$_2$O, 6 MPa H$_2$, 100 °C. [b] The yields of **1d** were GC yields, which were calculated based on the cyclohexene substrate. [c] Reaction conditions: 30 μmol Pd(acac)$_2$, 60 μmol **L1**, 25 μmol Bu$_4$NI, 40 μL H$_2$O, 1 mL toluene, 1 mmol cyclohexene, 8 mmol Ac$_2$O, 6 MPa H$_2$, 110 °C.

yield of **1d** was 90%. It was found that the yield of **1e** showed an upward trend when the Bu$_4$NI additive was removed from the typical conditions of Table 1. When we extended the reaction time to 48 h, the yield of the acid product increased to 69%. In this way, acetate esters, aldehydes and carboxylic acids could be separately and efficiently produced from olefin, Ac$_2$O and H$_2$ by simply adjusting the catalytic system and the reaction conditions.

Synthesis of aldehydes

As can be seen in Fig. 2, the typical catalytic system for the hydroformylation can be directly applied to various olefin substrates, including linear olefins and cyclic olefins (**1a–13a**), where corresponding aldehydes were produced with yields up to 86%. Furthermore, excellent regioselectivities (up to l : b = 91 : 9) could be obtained with linear olefins as substrates. It is noteworthy that internal olefins from petroleum refineries, in particular the mixtures of their isomers, are cheap and readily available feedstocks for carbonylation reactions. However, internal alkenes are more stable and often less reactive than terminal ones.[39] To our delight, high yields of aldehydes and excellent regioselectivities for linear aldehydes can be obtained whether terminal olefins (**5a, 7a, 10a** and **12a**) or internal olefins (**6a, 8a, 9a, 11a** and **13a**) were used as substrates. This suggested that our catalytic system possesses both high olefin isomerization activity and efficient synergy among different catalytic steps.[40]
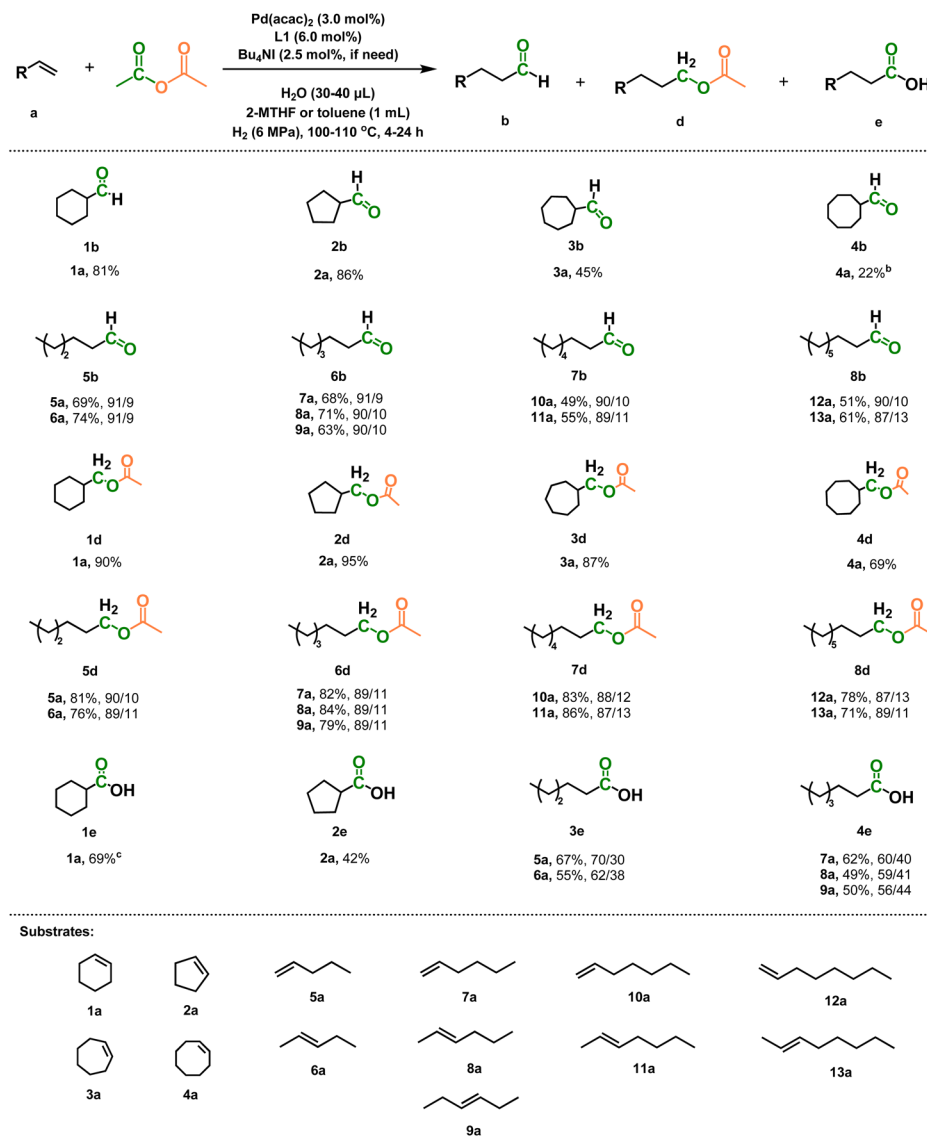
Fig. 2 Adaptability of the catalytic system with Ac_2O as the carbonyl and carbon sources. [a]Reaction conditions: for aldehydes, 30 μmol Pd(acac)$_2$, 60 μmol **L1**, 25 μmol Bu$_4$NI, 30 μL H_2O, 1 mL 2-MTHF, 1 mmol substrate, 4 mmol Ac_2O, 6 MPa H_2, 100 °C, 4 h. For acetate esters, 30 μmol Pd(acac)$_2$, 60 μmol **L1**, 25 μmol Bu$_4$NI, 40 μL H_2O, 1 mL toluene, 1 mmol substrate, 8 mmol Ac_2O, 6 MPa H_2, 110 °C, 16 h. For carboxylic acid, 30 μmol Pd(acac)$_2$, 60 μmol **L1**, 30 μL H_2O, 1 mL 2-MTHF, 1 mmol substrate, 4 mmol Ac_2O, 6 MPa H_2, 100 °C, 48 h. (a) The product yields were GC yields, which were calculated based on substrates, and the yield was the sum of linear and branch products when linear olefins were used as substrates. [b]The reaction time was 13 h when **4b** was synthesized. [c]The isolated yield of **1e** is 61%.

Synthesis of acetate esters

We are also pleased to find that high to excellent yields of acetate esters could be produced by simply switching the reaction solvent from 2-MTHF to toluene and increasing the temperature from 100 °C to 110 °C. As a whole, the yields of the acetate esters were obviously higher than those of the corresponding aldehydes discussed above. The regioselectivities of the linear acetate esters were also high in the case of linear olefins, whether they were terminal or internal ones, further demonstrating the efficient olefin isomerization capability of the catalytic system. This strategy exhibits good atom economy because most atoms of the Ac_2O molecule could be incorporated into the products (Fig. 3).

Synthesis of carboxylic acids

Previous studies showed that solvent was an important factor for the competition between hydroformylation and hydrocarboxylation,[16] while we discovered that the iodide additive can act as a switch for the reaction between hydroformylation and hydrocarboxylation in 2-MTHF solvent. As discussed above,
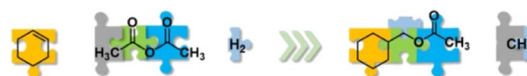

Fig. 3 The atomic economy for the synthesis of acetate ester with Ac_2O as a versatile reactant.

aldehydes of moderate to high yields could be generated with the Bu$_4$NI additive (**1b–8b**). Interestingly, without Bu$_4$NI, the production of aldehydes was almost completely suppressed and the corresponding carboxylic acids were formed with moderate yields (**1e–4e**), albeit with a longer reaction time and decreased regioselectivity (**3e, 4e**). The mass and NMR spectra of the target products in Fig. 2 are shown in Fig. S26–S44.

In short, by subtle adjustments of the reaction parameters, three categories of important products could be successfully synthesized *via* the carbonylation of olefins using Ac$_2$O as the versatile carbon feedstock and H$_2$ as the reductant. This discovery represents a significant advance in synthetic chemistry.

Mechanistic study of the carbonylation reactions

We started the mechanistic study with the synthesis of aldehyde from cyclohexene, Ac$_2$O and H$_2$. As mentioned above, the reaction could hardly occur without adding H$_2$O as a cosolvent (1.7 mmol). Additionally, the control experiments using an equivalent molar amount of DMSO (1.7 mmol) or 4 mmol AcOH instead of H$_2$O displayed a similar catalytic performance (Table S8), which may be ascribed to their comparable polarities. To further understand the role of the cosolvent, we carried out the hydroformylation of cyclohexene with CO and H$_2$, which revealed that H$_2$O was not needed in the presence of a certain carboxylic acid (Table S9). These results suggest that the role of the cosolvent may be to promote Ac$_2$O decomposition to generate CO and AcOH. The necessity of an acid cocatalyst in the Pd catalyzed hydroformylation has been explained elsewhere.[41]

To elucidate the molecular transformation pathway, a series of isotope labeling tests were carried out using (CH$_3$^{13}CO)$_2$O, (^{13}CH$_3$CO)$_2$O, (CD$_3$CO)$_2$O, H$_2$^{18}O, D$_2$, D$_2$O and THF-d$_8$, respectively (Fig. S4–S11), and the results are summarized in Fig. 4. It suggests that CO, decomposed from Ac$_2$O, participated in the formation of **1b** *via* hydroformylation. CH$_4$ was generated synchronously by decomposition of the acetyl group (CH$_3$CO–) in the Ac$_2$O molecule [(CH$_3$CO)$_2$O + H$_2$ → CO + CH$_4$ + CH$_3$-COOH]. In addition, remarkable H–D exchange was observed when the deuterated reagents ((CD$_3$CO)$_2$O, D$_2$ and D$_2$O) were utilized. We further conducted the *in situ* ^{1}H NMR and ^{31}P{^{1}H} NMR studies of the reaction process. The results suggest that at the start of the reaction, considerable AcOH produced, indicating it was a quick step (Fig. S12). With the accumulation of CO as well as the activation of the catalyst, **1b** was observed,
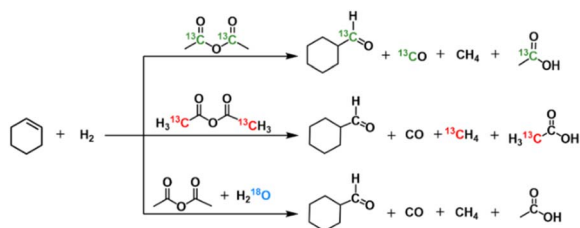
and its amount increased gradually. As the reaction progressed, the peak of H$_2$ became weaker because of its consumption during the reaction. In the NMR tube, the cyclohexene is in excess compared to H$_2$. Evident Pd–H signals were found (Fig. S13), which is a typical feature of a hydroformylation catalyst. Observation of a quintet hydride signal suggested the presence of binuclear Pd hydrides.[42] The *in situ* ^{31}P{^{1}H} NMR spectra demonstrated that DPPP coordinated with Pd in the reaction (Fig. S14).[16,35,43]

Based on the above results, we can deduce the reaction pathway for the synthesis of acetate esters, aldehydes and carboxylic acids using olefins, Ac$_2$O and H$_2$, as depicted in Fig. 5. The transformation of olefins follows the sequence: the isomerization of internal olefins to terminal ones, the hydrocarboxylation of terminal olefins to carboxylic acids or the hydroformylation of terminal olefins to aldehydes, the hydrogenation of aldehydes to alcohols, and the esterification of alcohols to acetate esters. These cascade steps could be verified by monitoring the reactive intermediates during the reaction (Fig. S15). Compared to 2-MTHF, toluene as a solvent may simultaneously and more effectively accelerate these steps (Tables 2 and 3).

The role of the iodide additive in switching between hydroformylation and hydrocarboxylation reactions is shown in Fig. 1. The halide anion could assist the heterolytic splitting of dihydrogen in the Pd-acyl species and promote the Pd-acyl hydrogenolysis step of the hydroformylation catalytic cycle, which is the rate-determining step.[40] Without the iodide additive, the hydroformylation reaction was inhibited, and the hydrocarboxylation reaction became predominant over a longer reaction time (48 h).

Besides Ac$_2$O, we also tried various other anhydrides, including n-anhydrides, iso-anhydrides and cyclic anhydrides, as the potential carbonyl source for the synthesis of **1b** (Table S10). It was found that most other anhydrides were ineffective for the reaction. Interestingly, acetic propionic anhydride could also engender good results, but the result using propanoic anhydride was poor. Furthermore, the acetyl group in acetaldehyde, acetate and acetyl iodide was not an effective CO source either (Table S11). Thus, the CH$_3$CO– group in the anhydride is key for the generation of CO. We also tried several other common carbonyl-containing chemicals (formic acid, paraformaldehyde, acetone, acetylacetone, oxalic acid, pyruvic acid, *etc.*), but they did not work. These results demonstrated that Ac$_2$O was a unique CO source.
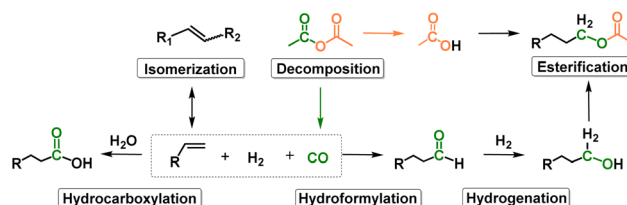

Fig. 4 Brief results of isotope labeling experiments.

Fig. 5 Pd-catalyzed synthesis of acetate esters, aldehydes and carboxylic acids with Ac$_2$O as a versatile reactant.

Ac_2O is a low-toxicity, easy-to-store, and transportable liquid. As a CO surrogate, it may significantly enhance operational safety by eliminating the need for high-pressure equipment and handling of the toxic CO gas. More importantly, Ac_2O played a multifunctional role in our system. It served as both the CO source and the carboxylate reagent for *in situ* ester formation, while the acetic acid byproduct provided the necessary acidic environment to promote the carbonylation reactions. This integrated design allows for an efficient process under mild conditions, improving the accessibility of this transformation for synthetic applications.

To our knowledge, this is the first report of Ac_2O as a versatile CO and carbon source. Therefore, a detailed study of the Ac_2O decomposition process in the reaction is highly desirable.

Mechanistic study of Ac_2O decomposition

Based on the systematic study of CO production from the reaction of Ac_2O and H_2, we found that the simplest catalytic components to decompose Ac_2O were $Pd(acac)_2$ and **L1** (Table S12). The decomposition rate increased quickly with increasing temperature, and the impact of temperature became less significant at above 110 °C (Fig. 6). The *in situ* ^1H NMR characterization was conducted to further monitor the Ac_2O decomposition process (Fig. S16). At the beginning of the reaction, AcOH and CH_4 were observed, which should form synchronously with CO. The analysis of the time course indicated that Ac_2O decomposition was a quick process (Fig. S17). CH_4 and CO of similar amounts were detected, formed by C–C bond breaking of the $CH_3CO–$ group in the presence of H_2. Besides CO and methane, equal moles of AcOH to Ac_2O could be produced *via* Ac_2O decomposition without H_2O. As discussed above, a cosolvent such as H_2O or DMSO was required in the hydroformylation of olefin with Ac_2O and H_2. This is mainly because the iodide additive of the catalytic system could significantly inhibit Ac_2O decomposition, which may be overcome by the use of a cosolvent with high polarity (Table S12, entries 7–10).

The *in situ* $^{31}P\{^1H\}$ NMR study of the Ac_2O decomposition showed that the active center of the reaction was mainly the Pd(0) complex formed by $Pd(acac)_2$ and a **L1** ligand (Fig. S18). Formation of minor hemioxide and oxide of **L1** was found,

which may be ascribed to the redox reaction between the Pd(II) precursor and the ligand.[44] The tendency to form a Pd(0) active center was further confirmed by a control experiment with another Pd(II) precursor, $Pd(OAc)_2(DPPP)$ (Fig. S19).[45] To learn more about the catalyst, we analyzed the solution quenching at 0.5 h of reaction by matrix-assisted laser desorption ionization Fourier transform ion cyclotron resonance mass spectrometry (MALDI-FT-ICR-MS), and $[Pd(DPPP)(H)]^+$ was observed at m/z 519.06241 (Fig. S20). The D_2 labeling test proved that the H^+ of the $[Pd(DPPP)(H)]^+$ was from the matrix dithranol rather than H_2 (Fig. S21). At 0.5 h, minor $[Pd(DPPP)(CH_3)]^+$ and $[Pd(DPPP)(OAc)]^+$ were also detected at m/z 533.07807 and m/z 577.06799, respectively (Fig. S20). No catalytic species containing CO was observed, which suggested that the release of CO from the species was a quick step. After 4 h of reaction, $[Pd(DPPP)(CH_3)]^+$ disappeared, which suggested the completion of the catalytic cycle for Ac_2O decomposition (Fig. S22).

According to the results in Table S12, the necessary catalytic components to decompose Ac_2O were $Pd(acac)_2$ and **L1**. Based on this fact and the literature,[42,46,47] we proposed the possible pathway of Ac_2O decomposition (Fig. 7). The rationality of the pathway as well as the related transition states was further verified by DFT calculations of solvated free energy (ΔG) (Fig. 8 and S23–S25). The initial active species **IM2** of the catalytic cycle was Pd(DPPP), formed by coordination of the Pd precursor and the **L1** ligand. Firstly, Ac_2O underwent oxidative addition to Pd(DPPP) *via* the transition state (**TS2-4**), forming a four-coordinated intermediate **IM4**, Pd(DPPP)(Ac)(OAc). Secondly, the C–C bond of the acetyl group (Ac) broke, and a subsequent rearrangement occurred *via* the transition state (**TS4-6**), forming a five-coordinated intermediate **IM6**, Pd(DPPP)(OAc)(Me)(CO). Thirdly, CO was generated by dissociation from **IM6**, giving a four-coordinated species **IM7**, namely, Pd(DPPP)(OAc)(Me). Subsequently, in the presence of H_2, the –OAc group dissociated from **IM7** *via* the transition state (**TS7-11**), where AcOH was produced and the four-coordinate species **IM11** formed, namely, Pd(DPPP)(Me)(H). Finally, CH_4 dissociated from **IM11** through the transition state (**TS11-2**), where the initial active species **IM2** was regenerated and the next catalytic cycle began. In Fig. 8, the proposed pathway (green curves) was also
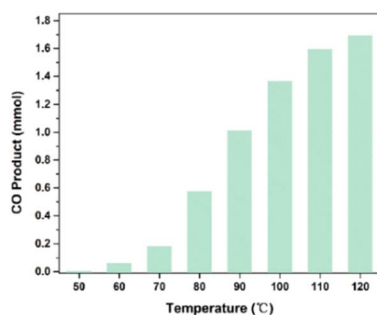

Fig. 6 Effect of temperature on Ac_2O decomposition. Reaction conditions: 30 μmol $Pd(acac)_2$, 60 μmol **L1**, 4 mmol Ac_2O, 1 mL 2-MTHF, 6 MPa H_2, 4 h.
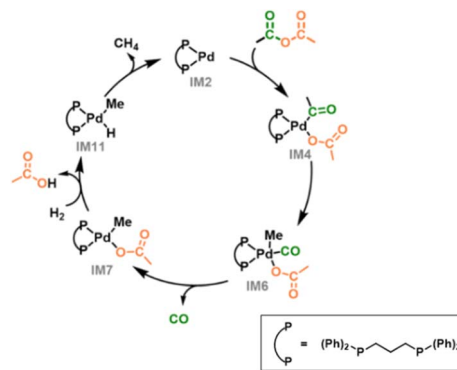

Fig. 7 The proposed pathway of Ac_2O decomposition. In the figure, the structural formula of the bidentate phosphine ligand DPPP is simplified and presented within the box.
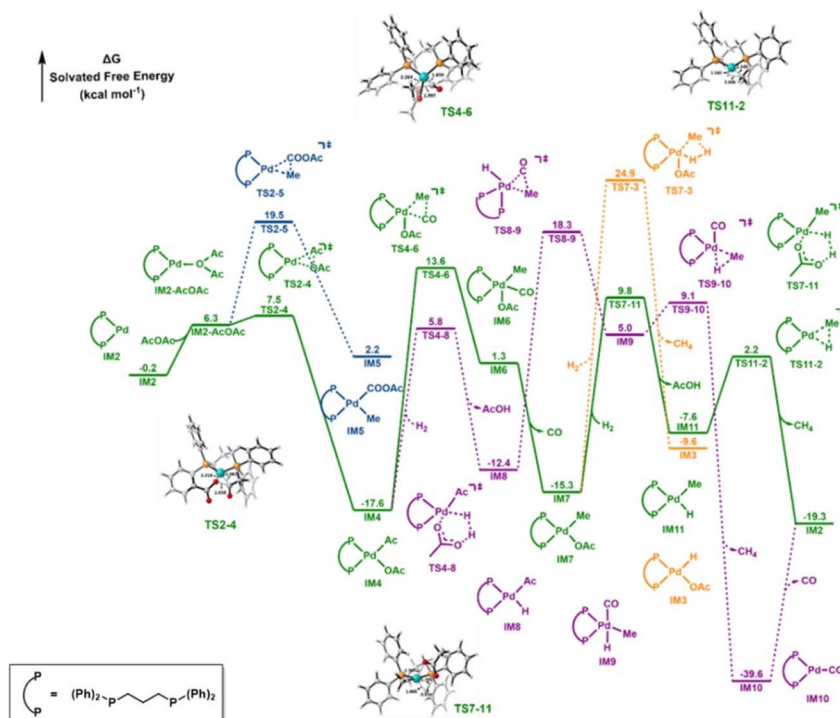
Fig. 8 The DFT calculation of solvation free-energy changes of different pathways for Ac$_2$O decomposition (see the SI for computational details). The green curves represent the reasonable pathway. In the figure, the structural formula of the bidentate phosphine ligand DPPP is simplified and presented within the box.

compared with various other possible decomposition routes, such as different modes of oxidative addition of Ac$_2$O (dark blue curves), and different detachment orders of groups on the intermediates (purple curves and brown curves). The results demonstrated that the pathway in Fig. 7 was reasonable. Besides Pd(DPPP) (**IM2**), other common initial Pd species such as Pd(DPPP)(OAc)$^-$ (**IM1**) and Pd(DPPP)(OAc)(H) (**IM3**) were also evaluated by DFT calculations (Fig. S23). The results suggested that Pd(DPPP) was the more favorable initial active species of the reaction. In a word, the proposed pathway of the Ac$_2$O decomposition was reasonable.

Conclusions

In summary, we have discovered that Ac$_2$O can be used as a CO surrogate and a versatile carbon source in carbonylation reactions. A Pd-based catalytic system was designed to selectively synthesize aldehydes, acetate esters and carboxylic acids from olefins, Ac$_2$O and H$_2$, where the type of the main product could be tuned by simply changing the reaction solvent or regulating the iodide additive. The yields of acetate esters, aldehydes and carboxylic acids could be as high as 95%, 86% and 69%, respectively. The catalytic system could be applied to various olefin substrates, including linear olefins (terminal and internal) and cyclic olefins. In addition, both terminal and internal alkenes could serve as substrates, yielding acetates or aldehydes with good regioselectivity. In some cases, the linear-to-branched ratio reached up to 10 : 1. The outstanding results of acetate esters synthesis displayed good atom economy and

successful cascade reactions. Notably, Ac$_2$O not only participated in these carbonylation reactions as a feedstock, but also provided the necessary acidic solvent environment. The mechanism of Ac$_2$O decomposition was proposed based on a series of control experiments and DFT calculations. We believe this discovery represents a novel paradigm for carbonylation reactions and will trigger more research in this area.

Author contributions

Y. R. Z. and Y. W. contributed equally. Y. R. Z., Y. W., Q. L. Q. and B. X. H. proposed the project, designed the experiments, and wrote the manuscript. Y. R. Z. performed all the experiments. J. F. X. and J. C. conducted the high-pressure NMR studies and offered the operation guidance for the *in situ* NMR test. Y. Y. W., L. B. Z., J. H., C. L. Y., J. G., X. T., Z. W. Z. and T. B. W. conducted some characterization studies and assisted in analyzing the experimental data. Q. L. Q. and B. X. H. supervised the whole project.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary

information: experimental methods, figures, tables, and DFT calculations. See DOI: https://doi.org/10.1039/d5sc06323j.

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