An Effective Pd-Catalyzed Regioselective Hydroformylation of Olefins with Formic Acid

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S *Supporting Information*

ABSTRACT: An effective palladium-catalyzed regioselective hydroformylation of olefins with formic acid is described. The ligand plays a crucial role in directing the reaction pathway. Linear aldehydes can be obtained in up to 93% yield with >20:1 regioselectivity using 1,3-bis(diphenylphosphino)propane (dppp) as the ligand. The reaction process is operationally simple and requires no syngas.

Figure 1. Hydrocarbonylation with HCOOH.

Aldehydes are an important class of organic compounds and synthetically versatile intermediates for pharmaceuticals and fine chemicals. Hydroformylation provides a direct approach to aldehydes from olefins (Scheme 1).[1] Various transition metals

Scheme 1. Transition-Metal-Catalyzed Hydroformylation of Olefins
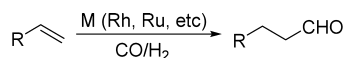
such as Co, Rh, Ru, Ir, and Pd have been used as catalysts. The reaction with Rh is probably the most extensively studied.[2] Hydroformylation is traditionally carried out with syngas (CO/H$_2$) (frequently at high pressure). Studies and applications of the hydroformylation process are hindered for laboratories that are not equipped to handle CO and H$_2$. Progress has been made in hydroformylation with syngas surrogates[3] such as formaldehyde[4] and alcohols.[5] Formic acid has also been used for hydroformylation with a Rh catalyst in the presence of CO.[6] In this case, formic acid served as the hydrogen source for the reaction.

We recently showed that carboxylic acids can be obtained in good yields via Pd-catalyzed hydrocarboxylation of olefins with formic acid in the presence of catalytic amounts of HCOOPh[7] or Ac$_2$O.[8,9] Pd complex **10** was proposed to be an intermediate for the formation of carboxylic acid **3** (Figure 1). From this intermediate, we envisioned that aldehyde **2** could be generated under proper reaction conditions via loss of CO$_2$ and reductive elimination of the resulting Pd hydride species **11** (Figure 1). To explore this possibility, various reaction parameters were subsequently investigated. It was found that the ligand has a dramatic effect on the reaction pathway. We now report that the envisioned hydroformylation process can be achieved with 1,3-bis(diphenylphosphino)propane (dppp) as the ligand using HCOOH and Ac$_2$O in the presence of Pd catalyst.[10] A variety of
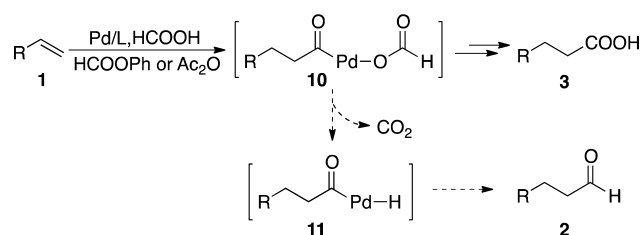
aryl and alkyl olefins can be effectively hydroformylated to give the corresponding aldehydes without using syngas. The high regioselectivity for linear aldehydes with aryl olefins is particularly worth noting. In general, branched aldehydes[2b,k–o,x] are favored in most of the hydroformylation processes with few exceptions,[2p,v] likely because of the formation of a stabilized benzyl metal complex.

Styrene (**1a**) was used as the test substrate for the studies. Various phosphine ligands were initially screened with 5 mol % Pd(OAc)$_2$, 2.0 equiv of HCOOH, and 1.0 equiv of Ac$_2$O in toluene at 80 °C for 24 h. As shown in Table 1, the reaction outcome was highly dependent on the ligand used. Little aldehyde was observed with monodentate ligands such as PPh$_3$, (entry 1). For most of the bidentate ligands except dppp and **L2**, little or no aldehydes were detected (entries 2–8). In the case of dppp, aldehydes **2a** and **2a′** were formed in 42% crude yield (entry 3). Encouraged by this result, additional reaction conditions were further investigated with dppp as the ligand. Several Pd catalysts were subsequently tested for the hydroformylation (see the Supporting Information (SI)), and the best result was obtained with Pd(OAc)$_2$. The solvent was also found to be an important factor for the competition between hydroformylation and hydrocarboxylation (entries 9 and 10; for more solvent studies, see the SI). The formation of acids **3a** and **3a′** was suppressed when the reactions were carried out in DCE (entry 10). Studies showed that the hydroformylation could be further improved by the addition of small amounts of an additive such as Bu$_4$NI, as aldehyde **2** was formed 77% yield with a linear:branched ratio (l:b) of ≥20:1 when 5 mol % Pd(OAc)$_2$, 10 mol % dppp, 2.0 equiv of HCOOH, and 1.0 equiv of Ac$_2$O were used in the presence of 2.5 mol % Bu$_4$NI (entry 11; for more additive studies, see the SI). The amount of Bu$_4$NI used appeared

Table 1. Studies of the Reaction Conditions[a]

entry	ligand	solvent	additive	yields (%)[b]			
				2a	**2a′**	**3a**	**3a′**
1	PPh$_3$	toluene		0	0	17	68
2	dppe	toluene		4	3	8	15
3	dppp	toluene		36	6	30	5
4	dppb	toluene		2	1	69	26
5	dppf	toluene		0	0	56	40
6	binap	toluene		5	2	36	10
7	**L1**	toluene		3	1	trace	trace
8	**L2**	toluene		24	3	26	6
9	dppp	THF		34	7	40	13
10	dppp	DCE		49	4	0	1
11	dppp	DCE	Bu$_4$NI	75	2	0	0
12[c]	dppp	DCE	Bu$_4$NI	35	0	0	0
13[d]	dppp	DCE	Bu$_4$NI	0	0	0	0
14[e]	dppp	DCE	Bu$_4$NI	83	2	0	0
15[f]	dppp	DCE	Bu$_4$NI	93	0	0	0
16[f]	dppf	DCE	Bu$_4$NI	0	0	80	20

[a]The reactions were carried out with **1a** (0.50 mmol), Pd(OAc)$_2$ (0.025 mmol), ligand (0.050 or 0.10 mmol, P:Pd = 4:1), HCOOH (1.0 mmol), Ac$_2$O (0.50 mmol), and additive (0.0125 mmol) in toluene (0.50 mL) at 80 °C for 24 h, unless otherwise stated. [b]The yields were determined from the crude reaction mixtures by ^{1}H NMR spectroscopy with BnOCH$_3$ as an internal standard. [c]With 10 mol % Bu$_4$NI. [d]With 20 mol % Bu$_4$NI. [e]With 3.0 equiv of HCOOH and 2.0 equiv of Ac$_2$O. [f]With 3.9 equiv of HCOOH and 3.0 equiv of Ac$_2$O.
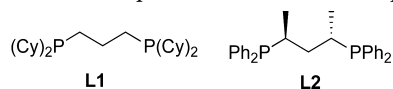
to be important for the reaction. The yield of aldehyde **2a** was reduced to 35% when 10 mol % Bu$_4$NI was used (entry 12). The reaction was completely suppressed with 20 mol % Bu$_4$NI (entry 13).[11] The yield was also found to be dependent on the amounts of HCOOH and Ac$_2$O (entries 14 and 15) and increased to 93% with 3.9 equiv of HCOOH and 3.0 equiv of Ac$_2$O (entry 15). To further investigate the effect of the ligand on the hydroformylation, the reaction was reexamined with other ligands such as dppf under the optimized reaction conditions (in the presence of 2.5 mol % Bu$_4$NI in DCE). In this case, acids were formed predominantly (entry 16), illustrating the crucial role of dppp in the hydroformylation.

With the optimized reaction conditions in hand, the generality of the reaction was subsequently investigated. As shown in Table 2, the hydroformylation can be extended to a variety of styrenes, giving the corresponding linear aldehydes in 67−93% yield (entries 1−11).[12] Various substituents on the phenyl groups were tolerated. The reaction proceeded with high regioselectivity (l:b ≥ 20:1) regardless of the substituent on the phenyl group. The hydroformylation was also effective for alkyl terminal olefins. The corresponding linear aldehydes were isolated in 52−83% yield (entries 12−15). The regioselectivity was somewhat dependent on the alkyl group on the olefin, with the ranging from l:b = 7:1 to >20:1. The reaction also proceeded smoothly with complex substrates such as sterol derivative **1p**, which gave the corresponding aldehyde in 81% yield with l:b > 20:1 (entry

## Table 2. Pd-Catalyzed Hydroformylation of Olefins[a]

entry	substrate	product	yield (%)(l:b)[b]
1	X = H, **1a**	**2a**	93 (> 20:1)
2	X = p-Cl, **1b**	**2b**	79 (> 20:1)
3	X = p-OMe, **1c**	**2c**	81 (> 20:1)
4	X = m-OMe, **1d**	**2d**	89 (> 20:1)
5	X = o-OMe, **1e**	**2e**	90 (> 20:1)
6	**1f**	**2f**	85 (> 20:1)
7	**1g**	**2g**	88 (> 20:1)
8	**1h**	**2h**	67 (> 20:1)
9	X = H, **1i**	**2i**	78 (> 20:1)
10	X = p-Cl, **1j**	**2j**	86 (> 20:1)
11	X = p-Me, **1k**	**2k**	80 (> 20:1)
12	**1l**	**2l**	65 (7:1)
13	R = Bn, **1m**	**2m**	52 (9:1)
14	R = TBDPS, **1n**	**2n**	65 (9:1)
15	**1o**	**2o**	83 (> 20:1)
16	**1p**	**2p**	81 (> 20:1)
17	n = 1, **1q**	**2q**	79
18	n = 2, **1r**	**2r**	65

[a]Reactions were carried out with substrate **1** (0.50 mmol), Pd(OAc)$_2$ (0.025 mmol), dppp (0.050 mmol), Bu$_4$NI (0.0125 mmol), 4 Å molecular sieves (10 mg), HCOOH (1.95 mmol), and Ac$_2$O (1.50 mmol) in DCE (0.50 mL) at 80 °C for 24 h. [b]Isolated yields. The l:b values were determined by ^{1}H NMR analysis of the crude reaction mixture.

16). Cycloalkenes were also effective substrates for the hydroformylation process, giving the aldehydes in 65−79% yield (entries 17 and 18).

A precise reaction mechanism is not clear at this moment, one plausible catalytic cycle is shown in Scheme 2. Pd(0) may be

**Scheme 2. Proposed Catalytic Cycle for Regioselective Hydroformylation**
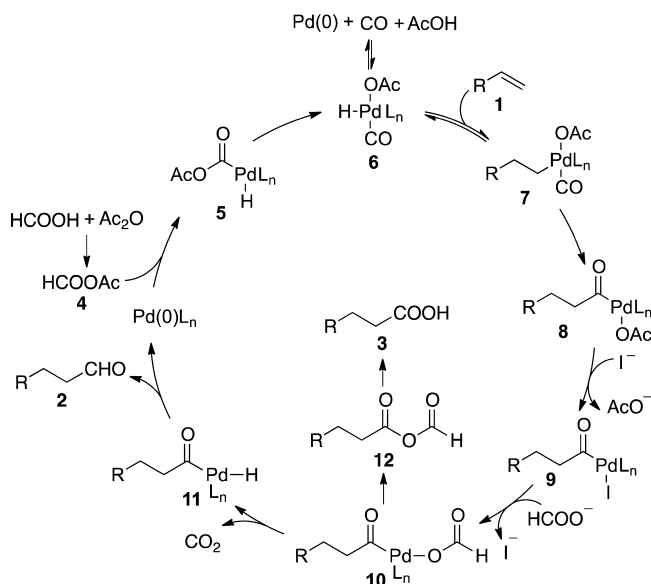
oxidatively inserted into HCOOAc (**4**) (generated from HCOOH and Ac_2O) to give palladium hydride complex **5**, which would rearrange to complex **6**. The olefin (**1**) would be hydropalladated by **6** to generate alkylpalladium complex **7**, which would undergo migratory insertion to give acylpalladium complex **8**. The OAc group of **8** would subsequently be replaced by the iodide to give Pd−I complex **9**, which would react with HCOOH to form complex **10**. The Pd−H complex **11** would be formed from complex **10** via release of CO_2. Reductive elimination of **11** would then lead to aldehyde **2** and regenerate the Pd(0) catalyst.

The additive and ligand were crucial for the hydroformylation process. Overall, the iodide could facilitate the acetate−formate exchange (from **8** to **10**) via Pd−I intermediate **9**. However, the addition of excess amounts of iodide relative to Pd was found to be detrimental to the hydroformylation process (Table 1, entries 12 and 13 vs entry 11), likely as a result of overcoordination of the iodide to Pd.[11] Among various ligands examined, only dppp was found to be effective for the current hydroformylation process. Complex **10** serves as a common intermediate for both acid **3** and aldehyde **2**. The reductive elimination of **10** could give anhydride **12**, subsequently leading to acid **3**. It appears that the unique bite angle of dppp[13,14] favors the CO_2 release process over the corresponding reductive elimination, thus favoring the formation of the aldehyde (**2**) over the corresponding carboxylic acid (**3**).

To investigate whether HCOOAc is involved in the reaction, isolated anhydride HCOOAc (**4**) (prepared from AcCl and HCOONa)[15] was used. As shown in Scheme 3, aldehyde **2a** was obtained in 87% yield when the reaction was carried out with 3.0 equiv of HCOOAc and 1.0 equiv of HCOOH in the presence of 5 mol % Pd(OAc)$_2$, 10 mol % dppp, and 2.5 mol % Bu$_4$NI. These results support the involvement of HCOOAc. When the reaction

Scheme 3. Hydroformylation with HCOOAc and HCOOH
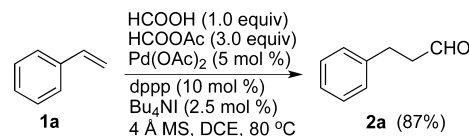
was carried out in the absence of HCOOH, only trace amounts of the aldehyde were observed, showing that HCOOH is also necessary for the reaction.

To further probe the reaction mechanism, the hydroformylation was carried out with 1-methoxy-4-vinylbenzene (**1c**), DCOOAc, and DCOOD in the presence of 5 mol % Pd(OAc)$_2$, 10 mol % dppp, and 2.5 mol % Bu$_4$NI (Scheme 4).

Scheme 4. Deuterium-Labeling Experiments
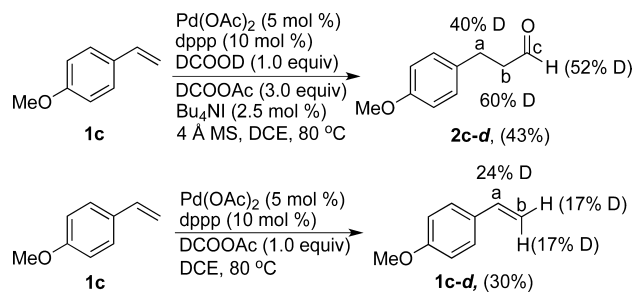
Aldehyde **2c-d** was isolated in 43% yield with 40% D, 60% D, and 52% D at carbons a, b, and c, respectively. When the reaction was carried out in the absence of DCOOD, 30% unreacted olefin was recovered with 24% D and 17% D at the two carbons. These results suggest that both linear and branched Pd complexes **7** and **7′** are formed during the hydropalladation of the olefin by Pd−H complex **6** and that the reaction process is reversible (Scheme 5). The linear aldehyde resulting from complex **7** is formed predominately under the reaction conditions.

Scheme 5. Reversible Hydropalladation
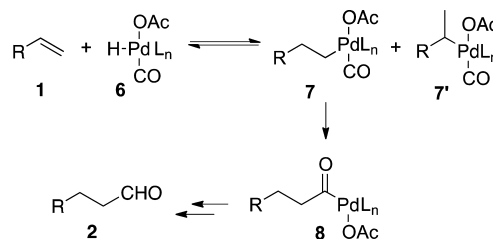
In summary, we have developed an effective Pd-catalyzed regioselective hydroformylation of olefins with dppp as the ligand using HCOOH/Ac$_2$O under mild reaction conditions. A wide variety of linear aldehydes have been obtained in good yields with high regioselectivity without using flammable and toxic syngas. The hydroformylation reaction is operationally simple and thus could be a useful method for the preparation of linear aldehydes. It was found that the ligand plays a crucial role in directing the reaction pathway (hydroformylation vs hydrocarboxylation). Further efforts will be devoted to understanding the reaction mechanism, expanding the substrate scope, and developing a reaction process for branched aldehydes.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b10297.

Experimental procedures, characterization data, crystallographic data for **2p**, and NMR spectra (PDF)
Crystallographic data for **2p** (CIF)

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Notes
The authors declare no competing financial interest.

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