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Rhodium-Catalyzed Highly Regioselective Hydroformylation-Hydrogenation of 1,2-Allenyl-Phosphine Oxides and -Phosphonates

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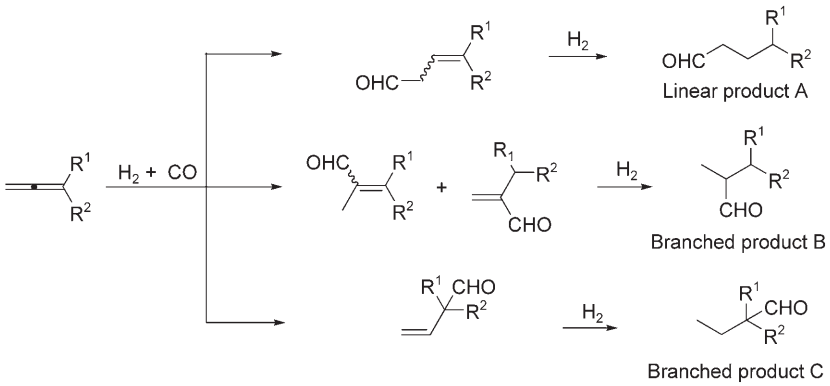
Abstract: The rhodium-catalyzed hydroformylation-hydrogenation of 1,2-allenyl-phosphine oxides and -phosphonates is reported in this paper. The regioselectivity was well controlled, affording only saturated linear γ-phosphinyl aldehydes under the standard conditions: (carbonyl)tris(triphenylphosphine)-rhodium hydride [$RhH(CO)(PPh_3)_3$] (3 mol%), triphenylphosphine (PPh_3) (10 mol%), carbon monoxide (CO) (2.4×10^6 Pa), hydrogen (H_2) (subsequently charged to 4.8×10^6 Pa), toluene, 100 °C, 24 h.

Keywords: aldehydes; allenes; hydroformylation; hydrogenation; phosphorus; rhodium

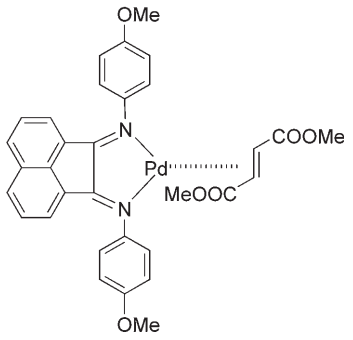
The hydroformylation of alkenes, discovered first by Roelen in 1938,[1,2] is a powerful method for the synthesis of aldehydes and has been widely explored and has become an extremely important industrial process.[3,4,5] As we know, the unsaturated C–C bonds that exist in alkenes, alkynes, and allenes, in principle, may all undergo hydroformylation to afford different aldehydes. The hydroformylation of alkenes and alkynes has already been well explored,[3,4] however, the hydroformylation reaction of allenes still remains undeveloped. Only one experimental study in this field was carried out by Fell and Beutler in 1976 with very poor selectivities giving a mixture of mono- and dialdehydes.[6] In 2005, the [$HCo(CO)_3$]-catalyzed hydroformylation of allene and propyne was investigated at the B3LYP level of density functional theory by Jiao et al.[7] Even now, the hydroformylation of allenes still furnishes challenges in controlling the chemo-, regio-, and stereoselectivities. As shown in Scheme 1, several different aldehydes such as β,γ- or α,β-unsaturated enals and saturated aldehydes A/B/C may be formed. On the other hand, allenes have recently been demonstrated to be a class of important chemicals with high reactivities and selectivities.[8,9,10] Following our recent report on the semihydrogenation of 1,2-allenyl-phosphonate, 1,2-allenyl-phosphine oxide, 1,2-allenyl-sulfone, and 2,3-allenoate,[10f] we became interested in the hydroformylation of allenes.



Scheme 1. The hydroformylation-hydrogenation of allenes.

Here, we report the first example of the Rh-catalyzed, highly regioselective hydroformylation-hydrogenation of 1,2-allenyl-phosphine oxides and -phosphonates yielding only saturated linear γ-phosphinyl aldehydes, which are difficult to prepare by other methods.

In the beginning, we chose 1,2-allenyl-phosphine oxide **1a** as the model substrate to study the hydroformylation reaction. At first, we used Pd(Ar-BIAN)(dimethyl fumarate)[10f] (Scheme 2) as the catalyst, disappointingly, only 77% of the starting material was recovered (entry 1, Table 1). Then we used $RuHCl(CO)(PPh_3)_3$ (3 mol%) as the catalyst. After careful analysis, it was observed that a 2% yield of a new product, the linear hydroformylation-hydrogenation aldehyde **2a**, was formed. However, it was formed together with some other unidentified aldehydes (entry 2, Table 1). Further screening indicated that $RhH(CO)(PPh_3)_3$ is a better catalyst for this reaction with 3 mol% being the best, affording the linear saturated aldehyde **2a** as the only product in 72% isolated yield (entry 7, Table 1).



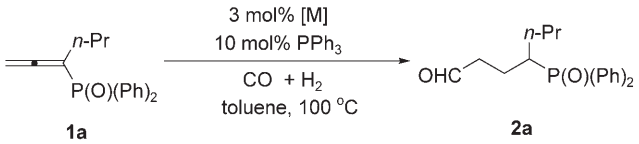
Scheme 2. Pd(Ar-BIAN)(dimethyl fumarate).

Then the effect of the pressure of CO and H_2 was examined (Table 2), suggesting that an initial charging of CO to a pressure of 2.4×10^6 Pa followed by charging to a total pressure of 4.8×10^6 Pa with H_2 was the best (entry 2, Table 2).

Furthermore, we also examined the solvent effect for the reaction at 60 °C (entries 1–8, Table 3). All the tested solvents gave **2a** as the only product in the NMR yield of 56–84% with toluene being the best (entry 8, Table 3). The reaction in the absence of free PPh_3 afforded **2a** in lower yield, which indicates that 10 mol% of free PPh_3 is necessary (entry 9, Table 3). Since the yield for the reaction at 100 °C was a little bit higher than that at 60 °C (entries 8 and 10, Table 3), 100 °C was applied for the following studies.

Thus, conditions A [$RhH(CO)(PPh_3)_3$ (3 mol%), PPh_3 (10 mol%), CO (2.4×10^6 Pa) followed by charging to a final combined pressure of 4.8×10^6 Pa with H_2, toluene, and 100 °C for 24 h] were applied for the Rh-catalyzed highly regioselective hydroformylation-hydrogenation of 1,2-allenyl-phosphine oxides and -phosphonates. Some typical results are shown in Table 4. Alkyl, cyclopropyl, and phenyl groups could be introduced into the α-position of the substrates. All the substrates gave the linear saturated aldehydes as the only products.

Table 1. The hydroformylation-hydrogenation of **1a** under different catalysts and reaction parameters.[a]



1a **2a**

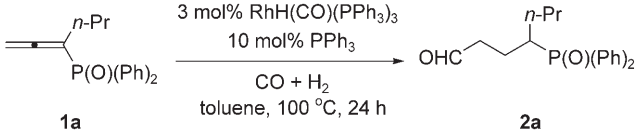
M = Ru or Rh

Entry	[M]	Time [h]	NMR Yield of **2a** [%][b]
1	Pd(Ar-BIAN)(dimethyl fumarate)[c]	2	NR[d]
2	$RuHCl(CO)(PPh_3)_3$	48	2[e,f]
3	$[RhCl(CO)_2]_2$	48	13[f]
4	$Rh(acac)(CO)_2$	48	75
5	$RhH(CO)(PPh_3)_3$[g]	24	51[f]
6	$RhH(CO)(PPh_3)_3$[h]	24	85
7	$RhH(CO)(PPh_3)_3$	24	89 (72)[i]

[a] The reaction was carried out at 100 °C using **1a** (0.2 mmol), [Rh] (3 mol%), and PPh_3 (10 mol%) in 3 mL of toluene under CO (2.4×10^6 Pa) followed by charging to a final combined pressure of 4.8×10^6 Pa with H_2.
[b] The regioselectivity and yield were determined for the crude reaction mixture by 300 MHz ^1H NMR analysis using CH_2Br_2 as the internal standard.
[c] The reaction was carried out at 100 °C using **1a** (0.2 mmol) and [Pd] (3 mol%) in 3 mL of toluene under CO (2.4×10^6 Pa) followed by charging to a final combined pressure of 4.8×10^6 Pa with H_2.
[d] 77% of **1a** was recovered.
[e] 41% of **1a** was recovered.
[f] Other unidentified aldehydes were formed.
[g] [Rh] (1 mol%) and PPh_3 (3 mol%) were applied.
[h] [Rh] (5 mol%) and PPh_3 (15 mol%) were applied.
[i] Isolated yield of **2a**.

Based on these results, a possible mechanism was proposed (Scheme 3).[11] Dissociation of one PPh_3 ligand from $RhH(CO)(PPh_3)_3$ yields the square-planar Rh intermediate **3**, which may coordinate with the electron-rich C=C bond in the allene moiety to give complex **4**. Subsequent hydrorhodiation afforded the square-planar allylic rhodium intermediate **5**. Then another molecule of CO coordinates with rhodium center forming the trigonal bipyramidal complex **6**. Subsequent migrative-insertion leads to the formation of acylrhodium intermediate **7**, which may further react with H_2 *via* oxidative addition and reductive elimination to afford the β,γ-unsaturated enal **8**. On the other hand, the Rh species **3** could coordinate with the β,γ-C=C bond in **8**[12] and undergo a second

Table 2. $RhH(CO)(PPh_3)_3$-catalyzed hydroformylation-hydrogenation of **1a** under different conditions.[a]



1a **2a**

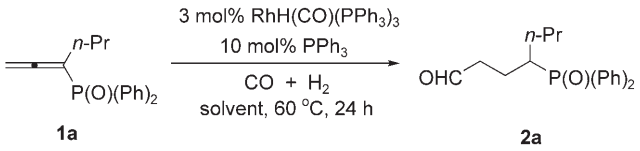
Entry	Initial pressure of CO [Pa]	Final pressure of $CO+H_2$ [Pa]	Yield of **2a** by ^1H NMR [%][b]
1	1.4×10^6	2.8×10^6	70
2	2.4×10^6	4.8×10^6	89 (72)[c]
3	5.2×10^6	10.3×10^6	77
4	1.4×10^6	4.1×10^6	67
5	2.8×10^6	4.1×10^6	80

[a] The reaction was carried out at 100 °C for 24 h using **1a** (0.2 mmol), $RhH(CO)(PPh_3)_3$ (3 mol%), and PPh_3 (10 mol%) in 3 mL of toluene under the initial pressure of CO followed by charging to the final combined pressure with H_2.

[b] The regioselectivity and yield were determined for the crude reaction mixture by 300 MHz ^1H NMR analysis using CH_2Br_2 as the internal standard.

[c] Isolated yield of **2a**.

Table 3. $RhH(CO)(PPh_3)_3$-catalyzed hydroformylation-hydrogenation of **1a** using different solvents.[a]



1a **2a**

Entry	Solvent	Yield of **2a** by ^1H NMR [%][b]
1	DMF	56
2	DMSO	64
3	EtOH	67
4	CH_3CN	68
5	Dioxane	70
6	THF	77
7	Benzene	77
8	Toluene	84 (67)[c]
9	Toluene[d]	65
10	Toluene[e]	89 (72)[c]

[a] The reaction was carried out at 60 °C for 24 h using **1a** (0.2 mmol), $RhH(CO)(PPh_3)_3$ (3 mol%), and PPh_3 (10 mol%) in 3 mL of solvent under CO (2.4×10^6 Pa) followed by charging to a final combined pressure of 4.8×10^6 Pa with H_2.

[b] The regioselectivity and yield were determined for the crude reaction mixture by 300 MHz ^1H NMR analysis using CH_2Br_2 as the internal standard.

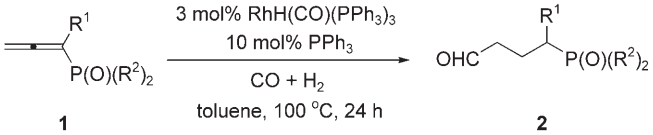
[c] Isolated yield of **2a**.

[d] No PPh_3 was applied.

[e] Reaction temperature: 100 °C.

hydrorhodiation to form the carbo-rhodium intermediate **9** or **10**,[12] which may further react with H_2 *via* oxidative addition[12] followed by reductive elimination[13] to afford the saturated linear aldehydes **2** and regenerate the catalytic species **3**.

Table 4. The hydroformylation-hydrogenation of 1,2-allenyl-phosphine oxides and -phosphonates under conditions A.[a,b]



1 **2**

Entry	**1** R^1	R^2	Isolated yield of **2** [%]
1	*n*-Pr	Ph (**1a**)	72 (**2a**)
2	*n*-Bu	Ph (**1b**)	68 (**2b**)
3	*n*-Hex	Ph (**1c**)	64 (**2c**)
4	Cyclopropyl	Ph (**1d**)	61 (**2d**)
5	*n*-Pr	OEt (**1e**)	54 (**2e**)
6	*n*-Bu	OEt (**1f**)	59 (**2f**)
7	*n*-Hex	OEt (**1g**)	53 (**2g**)
8	Cyclopropyl	OEt (**1h**)	50 (**2h**)
9	Ph	OEt (**1i**)	54 (**2i**)

[a] The reaction was carried out at 100 °C for 24 h using **1** (0.4 mmol), $RhH(CO)(PPh_3)_3$ (3 mol%), and PPh_3 (10 mol%) in 4 mL of toluene under CO (2.4×10^6 Pa) followed by charging to a final combined pressure of 4.8×10^6 Pa with H_2.

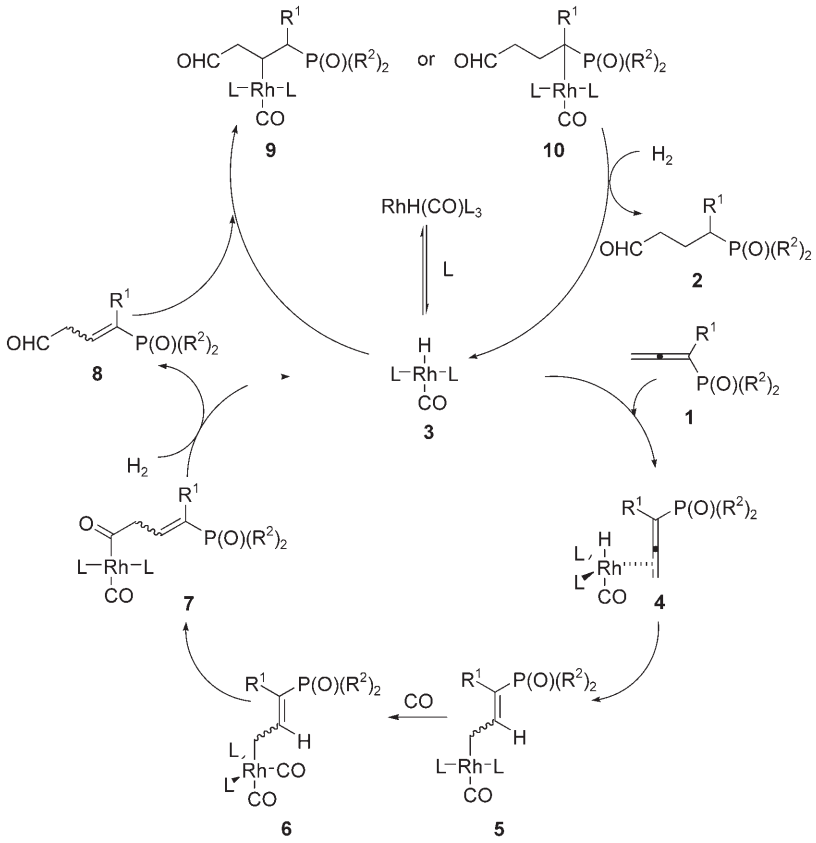
[b] The regioselectivity was determined for the crude reaction mixture by 300 MHz ^1H NMR analysis.

In conclusion, we have reported a Rh-catalyzed highly regioselective hydroformylation-hydrogenation of 1,2-allenyl-phosphine oxides and -phosphonates, forming only saturated linear γ-phosphinyl aldehydes. A possible mechanism was proposed. Due to the easy availability of the starting materials[13,14] and potential of the products with two functionalities, this reaction will be useful in organic synthesis. Further studies in this field including the hydroformylation of other allenes and the synthetic applications of this reaction are being carried out in our laboratories.

Experimental Section

Typical Procedure for the Hydroformylation-Hydrogenation of 1,2-Allenyl-Phosphine Oxides and -Phosphonates; Synthesis of 4-(Diphenylphosphinyl)-heptanal (2a)

PPh_3 (10 mg, 0.038 mmol), $RhH(CO)(PPh_3)_3$ (11 mg, 0.012 mmol), **1a** (113 mg, 0.40 mmol), and 4 mL of anhydrous toluene were added sequentially into a reaction vessel in the open air. Then the mixture was transferred into an autoclave containing 20 mL of anhydrous toluene, which was then charged with CO to a pressure of 6.9×10^5 Pa for three times to replace the air completely. Then it was charged with CO to a pressure of 2.4×10^6 Pa, which was followed by charging the autoclave to a final pressure of 4.8×10^6 Pa with



Scheme 3. The proposed mechanism for this reaction (L = PPh_3).

H_2. The resulting reaction mixture was stirred at 100 °C (oil bath). After 24 h, the reaction was cooled to room temperature, and the pressure was carefully released in a well-ventilated hood. After evaporation of the solvent to dryness, the resulting mixture was analyzed by 300 MHz ^{1}H NMR study showing **2a** was the only product. The residue was purified by flash chromatography on silica gel (eluent : ethyl acetate) to afford **2a** as a solid; yield: 91 mg (72%); mp 129–131 °C (ethyl acetate/petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.55 (s, 1H), 7.80–7.65 (m, 4H), 7.47–7.30 (m, 6H), 2.71–2.55 (m, 1H), 2.53–2.38 (m, 1H), 2.37–2.25 (m, 1H), 2.06–1.69 (m, 2H), 1.65–1.31 (m, 3H), 1.29–1.04 (m, 1H), 0.71 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 201.4, 132.4 (d, J_{PC} = 94.4 Hz), 132.1 (d, J_{PC} = 94.9 Hz), 131.4 (d, J_{PC} = 2.9 Hz), 131.3 (d, J_{PC} = 2.9 Hz), 130.6 (d, J_{PC} = 4.0 Hz), 130.5 (d, J_{PC} = 4.1 Hz), 128.5 (d, J_{PC} = 8.7 Hz), 128.3 (d, J_{PC} = 8.6 Hz), 40.8 (d, J_{PC} = 6.3 Hz), 35.1 (d, J_{PC} = 70.8 Hz), 28.6, 20.5 (d, J_{PC} = 10.4 Hz), 19.2, 13.7; ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 37.3; MS (m/z) 315 (M^+ + 1, 2.63), 314 (M^+, 0.48), 229 (100); IR (neat): ν = 1717, 1591, 1485, 1456, 1438, 1408, 1153, 1118 cm^{-1}; anal. calcd. for $C_{19}H_{23}O_2P$: C 72.59, H 7.37; found: C 72.25, H 7.35.

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