

Hydroformylation of Monosubstituted Alkenes Catalyzed by W–Rh Bimetallic Complex

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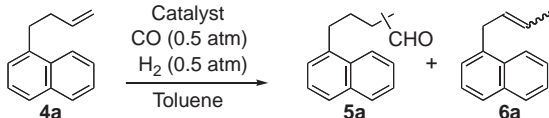
By using a heterobimetallic catalyst, $(\text{CO})_4(\text{PEtPh}_2)\text{W}(\mu\text{-PPh}_2)\text{Rh}(\text{CO})(\text{PPh}_3)$, chemoselective hydroformylation of monosubstituted alkenes proceeds efficiently at room temperature under atmospheric pressure of CO/H_2 , without affecting functional groups such as disubstituted alkene moieties, aryl and alkenyl iodide moieties, and hydroxy and carboxy groups.

Hydroformylation of alkenes is an important process to produce aldehydes, where rhodium complexes are often used as catalysts due to their high catalytic ability.¹ One of the problems on alkene hydroformylation is competitive alkene hydrogenation and isomerization, which produce undesired products without incorporation of CO. It is supposed that rapid formation of acylrhodium intermediates via efficient CO insertion would suppress these side reactions.

Bimetallic catalysis has now been employed in organic synthesis,^{2,3} because it is expected that two metal centers take part in a reaction together. We have been interested in bimetallic catalysts including a rhodium nucleus. It is considered that rhodium bimetallic system would provide ideal catalysis in hydroformylation if the counter metal part assists the rhodium center for the incorporation of CO. Group 6 metal carbonyl complexes are known as good CO sources in palladium-catalyzed carbonylation for preparation of amides⁴ and esters,⁵ and in some cases CO is incorporated more efficiently rather than using atmospheric CO gas. Therefore, our attention was directed to use a rhodium–tungsten bimetallic complex, $(\text{CO})_4(\text{PEtPh}_2)\text{W}(\mu\text{-PPh}_2)\text{Rh}(\text{CO})(\text{PPh}_3)$ (**1**),⁶ for hydroformylation of alkenes in an expectation of rapid formation of the acylrhodium intermediate with an intramolecular assistance of the tungsten carbonyl part. In this article is described rhodium–tungsten bimetallic complex-catalyzed hydroformylation of alkenes and its chemoselectivity is discussed as compared to the reaction with $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ (**2**), which is recognized as one of the efficient catalysts for hydroformylation.⁷

First, the hydroformylation of 1-(but-3-en-1-yl)naphthalene (**4a**) was examined by using **1** (0.2 mol. amt.) at room temperature under 0.5 atm each of H_2 and CO partial pressure (Entry 1 in Table 1).⁸ The corresponding aldehydes **5a** were obtained as a mixture of *n*- and *iso*-isomers (*n*:*iso* = 2.5:1) in 92% total yield with only a trace amount of isomerized alkenes **6a**. The hydroformylation was monitored by ³¹P NMR analysis and the peak of $\mu\text{-PPh}_2$ was observed during the reaction course.⁹ This observation indicates that the bimetallic structure, $\text{W}(\mu\text{-PPh}_2)\text{Rh}$, is maintained in the reaction. Aldehydes **5a** were obtained in high yield even with a reduced amount of catalyst **1** (0.02 mol. amt.) (Entry 2). In the hydroformylation with $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ (**2**), a considerable amount of undesired inner alkenes **6a** (8%) were produced, even though aldehydes **5a** were obtained in 83% (Entry 3). Diphenylphosphido bisrhodium com-

Table 1. Hydroformylation of terminal alkene **4a** catalyzed by rhodium complexes



Entry	Catalyst	(mol. amt.)	Temp. /°C	Time /h	Yield/%	
					5a (<i>n</i> : <i>iso</i>) ^a	6a
1	$\begin{matrix} \text{Ph}_2 \\ \\ \text{P} \\ \\ \text{Rh} \end{matrix}$	1	(0.2)	25	20	92 (2.5:1) <0.5
2	$(\text{CO})_4(\text{PEtPh}_2)\text{W} \cdots \text{Rh}(\text{PPh}_3)(\text{CO})$	(0.02)	25	185		95 (2.5:1) <0.5
3	$\text{RhH}(\text{CO})(\text{PPh}_3)_3$	2	(0.2)	25	20	83 (2.5:1) 8
4	$[\text{Rh}(\mu\text{-PPh}_2)(\text{cod})]_2$	3	(0.2)	50	18	6 (3:1) 89

^aRatio of *n*- and *iso*-isomer estimated by ¹H NMR analysis.

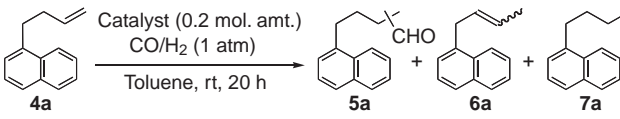
plex **3**,¹⁰ without tungsten part, was ineffective in hydroformylation (Entry 4).

The hydroformylation of alkene **4a** with **1** also proceeded efficiently even under lower partial pressure (1/8 or 1/16 atm) of CO (Entries 1 and 2 in Table 2). On the contrary, reactions catalyzed by $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ gave a significant amount of undesired isomerization and hydrogenation products (Entries 3 and 4). These results suggest that the tungsten carbonyl part assists incorporation of CO in the hydroformylation.

The bimetallic complex-catalyzed hydroformylation is sensitive to the substitution pattern of alkenes. The reactions of disubstituted alkenes required heating (50 °C) and a longer reaction time (Table 3, Entries 1 and 2). It is supposed that the steric bulkiness of bimetallic complex **1** suppressed the interaction of the multisubstituted alkene part to the rhodium center.


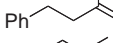

This property allowed a monosubstituted alkene-selective hydroformylation. In the hydroformylation of diene **4e**, monoaldehydes **5e** were selectively formed without affecting the inner alkene part (eq 1). In contrast, the reaction with $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ gave **5e** only in 60% yield and a mixture of side products

Table 2. Hydroformylation of **4a** under low partial pressure of CO

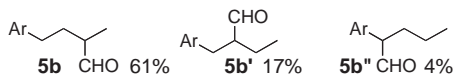


Entry	Catalyst	Partial Pressure		Yield/%		
		CO/atm	H ₂ /atm	5a	6a	7a
1	1	0.125	0.875	92	2	0
2	1	0.063	0.937	92	4	0
3	2	0.125	0.875	62	14	12
4	2	0.063	0.937	51	13	31

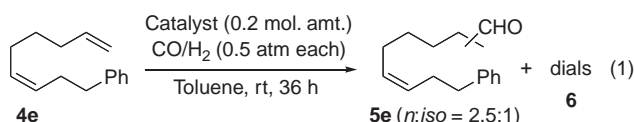
Table 3. Hydroformylation of multisubstituted alkenes **4b–4d** catalyzed by **1** at 50 °C^a

Entry	Alkene 4	Time/h	Yield of 5 /%	(<i>n</i> : <i>iso</i>) ^b
1	 4b	43	82	(—) ^c
2	 4c	50	94	(<i>n</i> only)
3	 4d	50	0	(—)

^aReaction conditions: **1** (0.2 mol. amt.), CO/H₂ (0.5 atm each), toluene, 50 °C. ^bRatio of *n*- and *iso*-isomer estimated by ¹H NMR analysis. ^cThree aldehydes **5b**, **5b'**, and **5b''** were obtained (Ar = naphthalen-1-yl).



including dialdehydes **6** (ca. 12%).



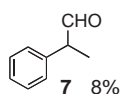
Catalyst: (CO)₄(PEtPh₂)W(μ-PPh₂)Rh(CO)(PPh₃) **1**: 89% –
RhH(CO)(PPh₃)₃ **2**: 60% ca. 12%

We investigated the functional group compatibility in this hydroformylation (Table 4 and eq 2). It is of interest that alkenes containing a hydroxy or carboxy were efficiently transformed to aldehydes (Entries 3 and 4). To the best of our knowledge, the hydroformylation of alkenes having an aryl or an alkenyl iodide moiety has not been reported. Although aryl and alkenyl iodides are potentially sensitive to oxidative addition, the iodo moiety was not affected in the reaction (Entry 6 and eq 2). On the other hand, the mononuclear rhodium catalyst **2** reacted with the iodo moiety to give a deiodination product **7** (Entry 7). The bulkiness

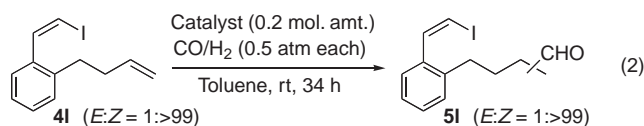
Table 4. Investigation on the functional group tolerance in the hydroformylation catalyzed by **1** or **2**

Entry	R	Catalyst	Time/h	Yield of 5 /%	<i>n</i> : <i>iso</i> ^b
1	OCOCH ₃	1	46	93 (98)	1:23
2	NMe ₂	1	57	82 (94)	1:12
3	OH	1	50	88 (96)	1:12
4	CO ₂ H	1	42	86	1:20
5	Br	1	36	92	1:30
6	I	1	34	95 (96)	1:29
7	I	2	34	83 ^c	1:21

^aNumber in parentheses shows yield estimated by GC analysis. ^bRatio of *n*- and *iso*-isomer estimated by ¹H NMR analysis. ^cAldehyde **7** was obtained.



of tungsten part in bimetallic complex **1** might prevent an approach of the iodo moiety to the rhodium center.



Catalyst: (CO)₄(PEtPh₂)W(μ-PPh₂)Rh(CO)(PPh₃) **1**: 92% (*n*:*iso* = 3:1)
RhH(CO)(PPh₃)₃ **2**: 68% (*n*:*iso* = 3:1)

In conclusion, the phosphido-bridged rhodium–tungsten complex **1** is an efficient catalyst for the chemoselective hydroformylation of monosubstituted alkenes. This catalytic system does not affect various functional groups under the hydroformylation conditions.

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- Typical procedure is as follows. A mixture of 1-(but-3-en-1-yl)-naphthalene (**4a**; 0.50 mmol) and catalyst **1** (0.10 mmol) in toluene (7.5 mL) was stirred at room temperature for 20 h under CO/H₂ (0.5 atm each). Aldehydes **5a** were obtained by purification using florisil column chromatography (hexane/ethyl acetate = 9:1).
- The peak, δ = 89.3 (ddd, ²J_{31P_μ-31P_{Rh}} = 177.8 Hz, ¹J_{31P_μ-103Rh} = 89.0 Hz, ²J_{31P_μ-31P_W} = 22.6 Hz, μ-PPh₂), which shows ¹⁸³W satellites (¹J_{31P_μ-183W} = 215.8 Hz), was observed as the bridged phosphorous atom.
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