

Selective Hydroformylation of Internal Acetylenes by PdCl₂(PCy₃)₂: Remarkable Synergistic Effect of Cobalt¹

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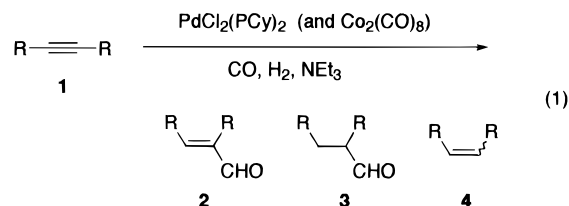
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We have long been interested in development of homogeneous heterobimetallic catalyst systems composed of two different metal complexes which might be used for unique organic synthesis. During our continuing study toward this direction, we have developed several mixed-metal catalyst systems for various types of carbonylation reactions including the homologation of methanol,² hydroformylation of olefins,³ formylation of iodoarenes,⁴ and silylative carbonylation reactions of iodoarenes.¹ Such mixed-metal complex systems have now become recognized as a promising tool in organic synthesis. Actually, rates and/or selectivities of some synthetic reactions have been significantly enhanced by effective cooperation of two or more metal centers.⁵

The hydroformylation of olefins is one of the most important industrial processes catalyzed by transition metal complexes, and has therefore been extensively studied.⁶ On the other hand, the hydroformylation of acetylenes to the α,β -unsaturated aldehydes has met with little success.⁷ Most catalysts so far reported have suffered from low selectivity and/or low yield of the unsaturated aldehydes, primarily because the formation of the corresponding saturated aldehydes and noncarbonylated olefins can hardly be suppressed. However, Buchwald and co-workers have reported very recently an effective catalyst composed of Rh(CO)₂(acac) (acac = pentane-2,4-dionate) and a special bisphosphite ligand.⁸ As an extension of our study on hydroformylation of olefins catalyzed by Co–Ru mixed systems,³ we have now surveyed various combinations of transition metal complexes to achieve the hydroformylation of acetylenes. Here we report that (i) PdCl₂(PCy₃)₂ (Cy =

cyclohexyl) catalyzes the selective hydroformylation of internal acetylenes to give the corresponding α,β -unsaturated aldehydes and (ii) the use of the PdCl₂(PCy₃)₂–Co₂(CO)₈ bimetallic catalyst system significantly improves the catalytic activity without lowering the selectivity.

Preliminary examination of the hydroformylation of 4-octyne (**1a**, R = C₃H₇) with the catalyst systems composed of PdCl₂–(PPh₃)₂ and/or metal carbonyls resulted in low selectivity (up to 49% yield) of the unsaturated aldehyde **2a**. In contrast, the PdCl₂(PCy₃)₂ catalyst exhibited very high selectivity and moderate activity in the presence of NEt₃. The yield of **2a** reached 83% after 6 h (eq 1), and the formation of the saturated



aldehyde **3a** and the simple hydrogenation product **4a** was almost negligible. Although the reaction proceeds at a relatively high temperature (150 °C), this finding is of special interest, because palladium complexes have received little attention as catalysts for hydroformylation of olefins. Furthermore, the combined use of PdCl₂(PCy₃)₂ and Co₂(CO)₈ remarkably improved the catalytic activity with little change of the selectivity. Thus, by use of the Pd–Co bimetallic catalyst (Pd/Co atomic ratio 1/1), the reaction was complete within 1 h, and **2a** was obtained in 95% yield (Table 1). The stereochemistry of the aldehyde was 95% *E*, which is compatible with the common hydrometalation–carbonylation mechanism. Since both Co₂(CO)₈ alone and Co₂(CO)₈–PCy₃ are of low catalytic activity and selectivity, it is obvious that palladium and cobalt metals participate cooperatively in the selective production of the unsaturated aldehyde. Table 1 also shows the effects of other metal carbonyls as the second component of the catalyst. Among them, Co₂(CO)₈ accelerated the reaction most effectively, but Fe₃(CO)₁₂ and W(CO)₆ also brought about unexpected enhancement of the reaction rate without lowering the selectivity. In contrast, Rh₄(CO)₁₂ gave rise to formation of a considerable amount of **3a**, and other transition metal carbonyls such as Cr(CO)₆, Mo(CO)₆, Mn₂(CO)₁₀, Re₂(CO)₁₀, and Ru₃(CO)₁₂ exhibited no or small effects on the yields and selectivities of the products.

Changing the phosphine ligand of the palladium complex was also found to dramatically influence the catalytic activity and the product distribution. The use of bulky trialkylphosphines such as PCy₃ and P(*i*-Pr)₃ was found to be essential to achieve satisfactory activity, the former exhibiting the higher selectivity. Catalysts with arylphosphines including PMe₂Ph, PPh₂, and bisphosphines of the type Ph₂P(CH₂)_{*n*}PPh₂ (*n* = 1–4) were much inferior in both activity and selectivity (13–62% yield of **2a** under the reaction conditions shown in Table 1). P(OPh)₃ was totally ineffective as the ligand for the present Pd–Co catalyst system. This makes a sharp contrast to the rhodium-based catalyst reported by Buchwald, in which a bisphosphite ligand was adopted.⁸

The PdCl₂(PCy₃)₂ and PdCl₂(PCy₃)₂–Co₂(CO)₈ catalyst systems were applicable to the hydroformylation of various internal acetylenes. The results are summarized in Table 2. It should be pointed out that the Pd–Co bimetallic catalyst is of high efficiency and selectivity for the hydroformylation of aliphatic acetylenes, but the reaction of diphenylacetylene (**1e**) was accompanied by significant formation of stilbene (**4e**). The hydrogenation product **4e** seems to be caused mainly by cobalt species, and this drawback could be avoided simply by

(1) Homogeneous Multimetallic Catalysts. 12. Part 11: Misumi, Y.; Ishii, Y.; Hidai, M. *Organometallics* **1995**, *14*, 1770.

(2) Hidai, M.; Orisaku, M.; Ue, M.; Koyasu, Y.; Kodama, T.; Uchida, Y. *Organometallics* **1983**, *2*, 292.

(3) (a) Hidai, M.; Fukuoka, A.; Koyasu, Y.; Uchida, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 516. (b) Hidai, M.; Fukuoka, A.; Koyasu, Y.; Uchida, Y. *J. Mol. Catal.* **1986**, *35*, 29. (c) Hidai, M.; Matsuzaka, H. *Polyhedron* **1988**, *7*, 2369. (d) Ishii, Y.; Sato, M.; Matsuzaka, H.; Hidai, M. *J. Mol. Catal.* **1989**, *54*, L13.

(4) Misumi, Y.; Ishii, Y.; Hidai, M. *J. Mol. Catal.* **1993**, *78*, 1.

(5) (a) Braunstein, P.; Rose, J. In *Stereochemistry of Organometallic and Inorganic Compounds*; Bernal, I., Ed.; Elsevier: Amsterdam, 1989; Vol. 3, pp 3–138. (b) Roberts, D. A.; Geoffroy, G. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 6, pp 763–877. For other pertinent examples, see: (c) Sawamura, M.; Sudoh, M.; Ito, Y. *J. Am. Chem. Soc.* **1996**, *118*, 3309. (d) Wang, D.; Alper, H. *J. Am. Chem. Soc.* **1992**, *114*, 7018. (e) Brunet, J.-J.; de Montauzon, D.; Taillefer, M. *Organometallics* **1991**, *10*, 341. Heterometallic clusters also serve as potential heterobimetallic catalyst precursors. For such examples, see: (f) Wakabayashi, T.; Ishii, Y.; Ishikawa, K.; Hidai, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2123. (g) Murata, T.; Mizobe, Y.; Gao, H.; Ishii, Y.; Wakabayashi, T.; Nakano, F.; Tanase, T.; Yano, S.; Hidai, M.; Echizen, I.; Nanikawa, H.; Motomura, S. *J. Am. Chem. Soc.* **1994**, *116*, 3389. (h) Adams, R. D.; Barnard, T. S.; Li, Z.; Wu, W.; Yamamoto, J. H. *J. Am. Chem. Soc.* **1994**, *116*, 9103.

(6) Parshall, G. W.; Ittel, S. D. In *Homogeneous Catalysis*, 2nd ed.; Wiley-Interscience: New York, 1992; pp 106–111.

(7) (a) Doyama, K.; Joh, T.; Shiohara, T.; Takahashi, S. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 4353. (b) Campi, E. M.; Jackson, W. R. *Aust. J. Chem.* **1989**, *42*, 471. (c) Nombel, P.; Lugan, N.; Mulla, F.; Lavigne, G. *Organometallics* **1994**, *13*, 4673.

(8) Johnson, J. R.; Cuny, G. D.; Buchwald, S. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1760.

Table 1. Hydroformylation of 4-Octyne Catalyzed by PdCl₂(PCy₃)₂ and/or Metal Carbonyls^a

catalyst	conv/%	GLC yield/%		
		2a	3a	4a
PdCl ₂ (PCy ₃) ₂	20	16	<1	0
PdCl ₂ (PCy ₃) ₂ ^b	84	83	<1	<1
Co ₂ (CO) ₈	12	0	<1	1
Co ₂ (CO) ₈ -PCy ₃ ^c	25	21	2	2
Co ₂ (CO) ₈ -PCy ₃ ^{b,c}	89	50	24	15
PdCl ₂ (PCy ₃) ₂ -Co ₂ (CO) ₈	100	95	2	3
PdCl ₂ (PCy ₃) ₂ -W(CO) ₆	92	85	tr	tr
PdCl ₂ (PCy ₃) ₂ -Fe ₃ (CO) ₁₂	76	68	tr	tr
PdCl ₂ (PCy ₃) ₂ -Rh ₄ (CO) ₁₂	65	46	16	3

^a Reaction conditions: 4-octyne, 5 mmol; H₂, 35 atm; CO, 35 atm; PdCl₂(PCy₃)₂, 0.1 mmol; metal carbonyl, 0.1 mmol as metal atom; benzene 5 mL; NEt₃, 3 mmol; 150 °C; 1 h. ^b Reaction time, 6 h. ^c PCy₃, 0.2 mmol.

Table 2. Hydroformylation of Internal Acetylenes Catalyzed by PdCl₂(PCy₃)₂ or PdCl₂(PCy₃)₂-Co₂(CO)₈^a

acetylene	cat. ^b	conv/%	GLC yield/%		
			2	3	4
1a (R = <i>n</i> -C ₃ H ₇)	A	100	95 (81) ^c	2	3
1b (R = C ₂ H ₅)	A	96	88 (47) ^c	3	3
1c (R = <i>n</i> -C ₄ H ₉)	A	97	90 (70) ^c	2	5
1d (R = <i>n</i> -C ₅ H ₁₁)	A	95	95 (89) ^c	2	2
1e (R = Ph)	A	99	53 ^d	0	30 ^e
1e ^f	B	94	77 ^g (70) ^c	0	15 ^h

^a For reaction conditions, see Table 1. ^b A: PdCl₂(PCy₃)₂-Co₂(CO)₈, B: PdCl₂(PCy₃)₂. ^c Isolated yield in parentheses. ^d 90% *E*. ^e PhCH₂CH₂Ph was formed in 16% yield. ^f Reaction time, 5 h. ^g 92% *E*. ^h PhCH₂CH₂Ph was formed in 2% yield.

using the monometallic PdCl₂(PCy₃)₂ catalyst, which produced α -phenylcinnamaldehyde (**2e**) in 77% GLC yield. A similar reaction of 1-phenyl-1-propyne (PdCl₂(PCy₃)₂ catalyst, 155 °C, 6 h) resulted in the formation of a 3/2 mixture of 2-methyl-3-phenyl-2-propenal and 2-phenyl-2-butenal in 83% total GLC yield (>96% *E*) along with a small amount (<10%) of propenylbenzenes.

One interesting feature of the PdCl₂(PCy₃)₂ and PdCl₂(PCy₃)₂-Co₂(CO)₈ catalysts is their chemoselectivity. Thus, when a 1:1 mixture of styrene and **1a** was allowed to undergo hydroformylation in the presence of the PdCl₂(PCy₃)₂ catalyst (150 °C, 6 h), **1a** was cleanly transformed into the unsaturated aldehyde **2a** (80% conversion, 78% yield), while styrene was recovered almost quantitatively. No more than trace amounts of hydrogenation and hydroformylation products of styrene were observed. Furthermore, when a mixture of cyclooctene and **1c** was hydroformylated with the Pd-Co catalyst (150 °C, 1 h),

2c was obtained in 92% yield and cyclooctene was recovered quantitatively. The chemoselectivity observed with these catalysts leads to the selective hydroformylation of enynes. When the hydroformylation of (*Z*)-1,4-diphenyl-1-buten-3-yne was performed with the PdCl₂(PCy₃)₂ catalyst (155 °C, 6 h), (*2E,4Z*)-2,5-diphenyl-2,4-pentadienal was obtained as the exclusive carbonylation product (ca. 80% conversion, 39% isolated yield).

The origin of the synergistic effect observed for the Pd-Co system is of special interest. On the basis of fact that the product selectivity of the bimetallic catalyst was similar to that observed with the monometallic PdCl₂(PCy₃)₂ catalyst, we consider that chemical transformation of acetylenes mainly proceeds on a palladium metal center and a cobalt species plays an important role in accelerating at least a part of the palladium-catalyzed cycle. We have previously observed that, in the reaction of PdPh(PMe₃)₂(O₃SCF₃) with [Co(CO)₄]⁻ anion, facile CO insertion into the Pd-C bond occurs to give the dinuclear benzoyl complex (PMe₃)₂(PhCO)PdCo(CO)₄.⁹ More recently Fukuoka and Komiyama reported that the CO insertion into the Pd-C bond in (dppe)MePdCo(CO)₄ (dppe = Ph₂PCH₂CH₂PPh₂) is much faster than that in PdMeCl(dppe).¹⁰ These facts suggest that the cobalt metal in the present hydroformylation promotes the CO insertion into the Pd-C bond of a vinylpalladium intermediate to form an acylpalladium species. On the other hand, a preliminary kinetic study showed that both the PdCl₂(PCy₃)₂ and PdCl₂(PCy₃)₂-Co₂(CO)₈ catalysts exhibited some dependency of the reaction rates on the H₂ pressure. This indicates a mechanism in which the rate-determining step is the hydrogenolysis of an acylpalladium intermediate to produce the aldehyde, and the cobalt catalyst has a function to accelerate the hydrogenolysis of the acyl-Pd bond. Indeed, this type of rate enhancement has been revealed to operate in carbonylation reactions with heterobimetallic catalyst systems^{3,4,11} or a homodinuclear complex catalyst.¹² Although we must await further investigation to elucidate the cooperative effects of the palladium and cobalt metal centers, it is noteworthy that the combined use of Co₂(CO)₈ with PdCl₂(PCy₃)₂ showed remarkably favorable effects on the hydroformylation of acetylenes. Further study on the mechanism and application of the novel catalyst systems is actively underway.

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(9) Misumi, Y.; Ishii, Y.; Hidai, M. *J. Chem. Soc., Dalton Trans.* **1995**, 3489.

(10) Fukuoka, A.; Fukugawa, S.; Hirano, M.; Komiyama, S. *Chem. Lett.* **1997**, 377.

(11) Koyasu, Y.; Fukuoka, A.; Uchida, Y.; Hidai, M. *Chem. Lett.* **1985**, 1083.

(12) Broussard, M. E.; Juma, B.; Train, S. G.; Peng, W.-J.; Laneman, S. A.; Stanley, G. G. *Science* **1993**, 260, 1784.