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Carbonylation reactions catalyzed by homogeneous Pd–Co bimetallic systems

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Abstract

The $PdCl_2(PPh_3)_2$–$Co_2(CO)_8$ bimetallic catalyst was found to be effective for the carbonylation of ArI with CO/$HSiEt_3$ to give benzyl silyl ethers as the major product, although neither $PdCl_2(PPh_3)_2$ nor $Co_2(CO)_8$ alone was catalytically active. Addition of NEt_3 to the reaction system changed the distribution of the carbonylation products, where 1,2-diaryl-1,2-disiloxyethanes were obtained predominantly. The former reaction is suggested to proceed via the aldehyde intermediate, while a mechanism involving the aroylcobalt complex $(ArCO)Co(CO)_3(PPh_3)$ formed by way of a Pd–Co bimetallic complex is proposed for the latter reaction. On the other hand, $PdCl_2(PCy_3)_2$ was found to work as a selective catalyst for the hydroformylation of internal alkynes to give the corresponding α,β-unsaturated aldehydes, and the combined use of $PdCl_2(PCy_3)_2$ and $Co_2(CO)_8$ remarkably improved the catalytic activity with little change of the selectivity. Regio- and chemoselective hydroformylation of alkynes was achieved by using the $PdCl_2(PCy_3)_2$ and $PdCl_2(PCy_3)_2$–$Co_2(CO)_8$ catalysts. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Carbonylation; Hydroformylation; Catalyst

1. Introduction

Homogeneous bimetallic or multimetallic catalysis has now been recognized as a promising tool in organic synthesis, because it is expected that cooperative or successive interaction of two (or more) different metal centers with the substrate molecule(s) gives rise to enhanced catalytic activities and selectivities, and in some cases, to new reactions which cannot be achieved by monometallic catalyst systems [1–5]. We have been interested in development of homogeneous heterobimetallic catalyst systems which consist of two different metal complexes, and reported several bimetallic catalysts including the $Co_2(CO)_8$–$RuCl_3$ system for homologation of methanol [6], the $Co_2(CO)_8$–$Ru_3(CO)_{12}$ system for hydroformylation of alkenes [7–10], and the $PdCl_2(PPh_3)_2$–$Ru_3(CO)_{12}$ system for formylation of aryl iodides [11]. In these carbonylation reactions, the specific combination of the metal complexes remarkably improved the catalytic activity. More recently, we disclosed that catalyst systems made up of the combination of Pd–phosphine complexes and $Co_2(CO)_8$ are effective for the silylative carbonylation of aryl iodides to give benzyl silyl ethers or 1,2-diaryl-1,2-disiloxyethanes [12] as well as for the hydroformylation of alkynes to give α,β-unsaturated aldehydes [13]. Here we summarize our recent studies on the synergistic effects of the Pd–Co bimetallic catalysts and discuss the origin of the synergism.

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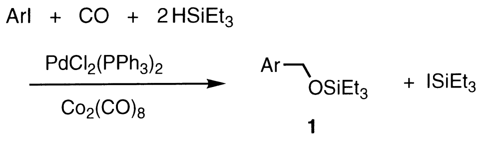
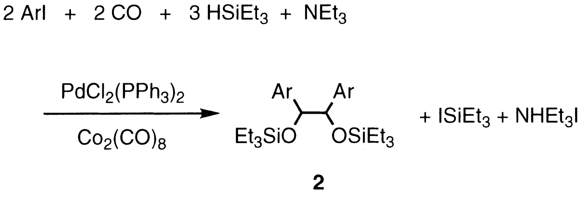
2. Carbonylation of aryl iodides with CO/$HSiEt_3$

It is well known that palladium complexes catalyze the formylation of aryl and vinyl halides with CO/H_2 [14]. In contrast, the attempted reaction of *p*-TolI with CO (50 atm)/$HSiEt_3$ in the presence of $PdCl_2(PPh_3)_2$ at 80°C gave no more than 5% total yield of the carbonylation products in spite of the formal similarity in the reactivities toward organometallic compounds between H_2 and hydrosilanes [15]. This fact prompted us to examine the catalytic activity of the bimetallic catalysts composed of $PdCl_2(PPh_3)_2$ and metal carbonyls for the carbonylation of *p*-TolI with CO/$HSiEt_3$ [12]. Interestingly, when $Co_2(CO)_8$ was used in combination with $PdCl_2(PPh_3)_2$, *p*-TolI was effectively and selectively carbonylated to afford *p*-$TolCH_2OSiEt_3$ (**1a**) in 76% yield (85% conversion), although $Co_2(CO)_8$ alone was totally ineffective as the catalyst. Furthermore, the addition of NEt_3 to the reaction system dramatically changed the distribution of the carbonylation products, where 1,2-di(*p*-tolyl)-1,2-bis(triethylsiloxy)ethane (**2a**) was obtained as the major product (57% yield at 70% conversion), and other products ((**1a**) and *p*-tolualdehyde (**3a**)) were formed in no more than marginal yields. These results are summarized in Table 1. $Ru_3(CO)_{12}$ was also found to be effective as the second component of the catalyst, but the selectivity was not high. Use of other carbonyls including $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, $Mn_2(CO)_{10}$, and $Fe(CO)_5$ in combination with $PdCl_2(PPh_3)_2$ showed no improvement in the catalytic activity. In the Pd–Co-catalyzed reactions, the formation of $ISiEt_3$ was confirmed; its yield based on the *p*-TolI used was almost equal to that of **1a** in the reaction without NEt_3, while in the presence of NEt_3 it was about half that of **2a**. On the basis of these observations, the above catalytic reactions are concluded to follow the stoichiometry shown in Eqs. (1) and (2) (Ar = *p*-Tol).



(1)



(2)

Table 2 summarizes the results of the silylative carbonylation of some aryl iodides (ArI) by using the $PdCl_2(PPh_3)_2$–$Co_2(CO)_8$ catalyst. Similarly to the reaction of *p*-TolI, benzyl silyl ether (**1**) or 1,2-diaryl-1,2-disiloxyethane (**2**) was selectively obtained in the absence or presence of NEt_3, respectively, although the reaction rate exhibited some dependence on the aryl group of the substrate. These carbonylation reactions are especially interesting in the point that the specific combination of two catalytically ineffective complexes displays a remarkable synergistic

Table 1
Silylative carbonylation of *p*-TolI catalyzed by $PdCl_2(PPh_3)_2$ and/or metal carbonyls[a]

Catalyst	NEt_3 (mmol)	Conversion (%)	GLC yield (%)		
			1a	**2a**	**3a**
$PdCl_2(PPh_3)_2$	–	10	0	0	3
$PdCl_2(PPh_3)_2$	3	4	0	0	2
$Co_2(CO)_8$	–	4	0	0	0
$Co_2(CO)_8$	3	5	0	0	0
$PdCl_2(PPh_3)_2$–$Co_2(CO)_8$	–	85	76	0	0
$PdCl_2(PPh_3)_2$–$Co_2(CO)_8$	3	70	6	57	2
$PdCl_2(PPh_3)_2$–$Ru_3(CO)_{12}$	–	79	40	4	10

[a] Reaction conditions: *p*-TolI, 2.5 mmol; $HSiEt_3$, 7.5 mmol; metal complex, 0.05 mmol as metal atom; benzene, 5 ml; CO, 50 atm; 80°C; 3 h.

Table 2
Silylative carbonylation of ArI catalyzed by $PdCl_2(PPh_3)_2$–$Co_2(CO)_8$[a]

ArI	NEt_3 (mmol)	Conversion (%)	GLC yield (%)		
			1	**2**	**3**
PhI	–	62	61	0	1
PhI	3	67	4	52	0
p-TolI	–	85	76	0	0
p-TolI	3	70	6	57	2
p-$MeOC_6H_4I$	–	83	81	0	0
p-$MeOC_6H_4I$	3	80	2	57	0
p-FC_6H_4I	–	54	38	0	1
p-FC_6H_4I	3	54	0	28	3

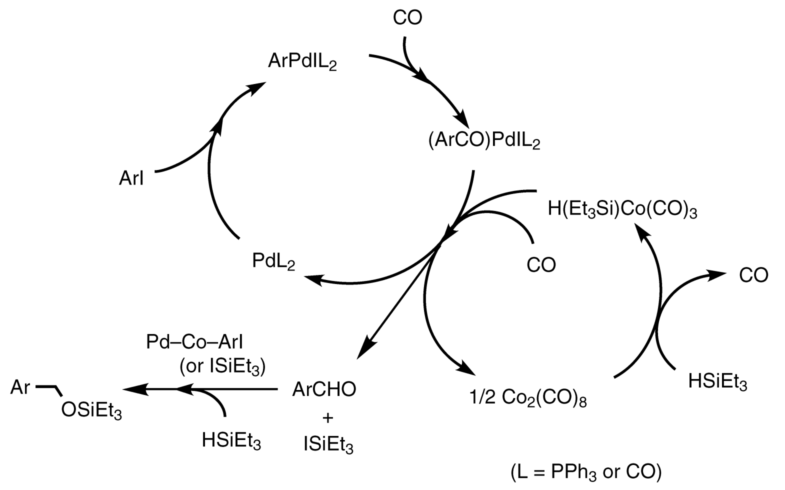
[a] Reaction conditions are the same as shown in Table 1 except ArI (2.5 mmol) was used instead of *p*-TolI.

effect, and in addition the product selectivity is completely changed upon the addition of NEt_3. We set out to investigate the reaction mechanisms of these reactions to elucidate the origin of the synergism.

Since one possible intermediate for the above reactions is the aldehyde (ArCHO, **3**), hydrosilylation of **3a** under the conditions adopted for the catalytic carbonylation reactions was examined in detail. Although both $PdCl_2(PPh_3)_2$ and $Co_2(CO)_8$ in the presence of *p*-TolI serve as active catalysts for the hydrosilylation of **3a** to give **1a** under N_2, high CO pressure (50 atm) seriously decreased their activities. However, the $PdCl_2(PPh_3)_2$–$Co_2(CO)_8$ bimetallic catalyst was revealed to be quite effective for the formation of **1a** from **3a** even under CO pressure in the presence of a catalytic amount of *p*-TolI. It should also be noted that the hydrosilylation of **3a** was strongly inhibited by the addition of NEt_3. These results indicate that **3** is a highly plausible intermediate for the reaction to give **1** (Eq. (1)), but cannot be the intermediate for the production of **2** (Eq. (2)).

Scheme 1 depicts the proposed mechanism for the formation of **2**. Oxidative addition of ArI to a Pd(0)–PPh_3 species followed by CO insertion yields an aroylpalladium complex $(ArCO)PdI(PPh_3)_2$ (**4**) [16]. On the other hand, the reaction of $Co_2(CO)_8$ with $HSiEt_3$ is supposed to give a hydridosilylcobalt complex $H(Et_3Si)Co(CO)_3$ as the primary product [17]. Since neither palladium nor cobalt monometallic catalyst exhibited activity for the silylative carbonylation of ArI, it is reasonable to assume that the bimetallic reaction between the acylpalladium and hydridocobalt complexes to produce the corresponding aldehyde is included in the catalysis. In fact, we have previously reported that hydrido complexes such as $[NEt_4][HRu_3(CO)_{11}]$ and $[NEt_4][HMo_2(CO)_{10}]$ readily react with complex **4** to give **3** [11].

On the other hand, $[Co(CO)_4]^-$ anion is considered to be generated from $Co_2(CO)_8$ and $HSiEt_3$ under the basic conditions of the reaction of Eq. (2) [17]. We have also observed that $Pd(PPh_3)_4$ catalyzes the reaction of ArI and $[Co(CO)_4]^-$ anion in the



Scheme 1.

Table 3
Palladium-catalyzed formation of aroylcobalt complexes (**5**) from ArI and $K[Co(CO)_4]$[a]

ArI	Time (h)	Conversion (%)	Isol. yield (%)
PhI	4	98	73
p-TolI	4	100	79
o-TolI	6	75	32
p-FC_6H_4I	6	93	36
p-ClC_6H_4I	4	98	68
p-$MeOC_6H_4I$	4	100	81

[a] Reaction conditions: ArI, 0.5 mmol; $K[Co(CO)_4]$, 0.8 mmol; PPh_3, 0.55 mmol; $Pd(PPh_3)_4$, 0.05 mmol; THF, 10 ml; 50°C.

presence of PPh_3 to form the aroylcobalt complex $(ArCO)Co(CO)_3(PPh_3)$ (**5**) (Eq. (3)) [18,19]. Typical results are shown in Table 3. This reaction is supposed to proceed via the initial oxidative addition of the ArI to a Pd(0) center and the subsequent migration of the aryl (or aroyl) group from the palladium atom to cobalt, where a Pd–Co dinuclear complex is involved as a key intermediate. As a related reaction, it has been reported that several Pt–W, Pt–Mo, and Pt–Fe dinuclear complexes with an alkyl group on the platinum center undergo alkyl migration to the other metal to afford the corresponding alkyl–W, –Mo, and –Fe complexes [20,21].

$$\mathrm{ArI + K[Co(CO)_4] + PPh_3 \xrightarrow{Pd(PPh_3)_4} \underset{\textbf{5}}{(ArCO)Co(CO)_3(PPh_3)} + KI} \quad (3)$$

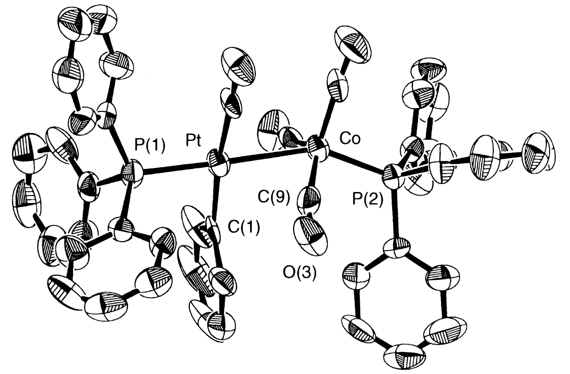
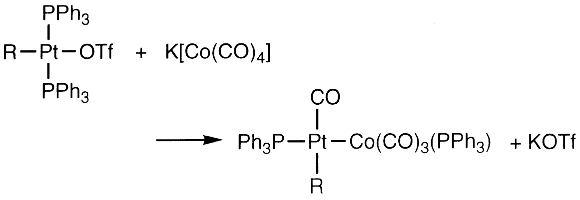


Fig. 1. An ORTEP drawing for complex **6b** drawn at the 50% probability level. Selected bond distances (Å) and angles (deg): Pt–Co, 2.645 (2); Pt–C(1), 2.062 (8); Co–Pt–P(1), 178.6 (1); Co–Pt–C(1), 92.6 (3); Pt–Co–P(2), 152.1 (1).

Although attempts to obtain the Pd–Co bimetallic intermediate with PPh_3 ligands were unsuccessful, a series of Pt–Co complexes $(PPh_3)(CO)(R)PtCo(CO)_3(PPh_3)$ (**6a**: R = *p*-Tol; **6b**: R = Ph; **6c**: R = Me) were obtained from the reaction of $Pt(R)(OTf)(PPh_3)_2$ (OTf = OSO_2CF_3) with $K[Co(CO)_4]$ (Eq. (4)) [18,19,22]. The molecular structure of **6b** is depicted in Fig. 1, which shows that the cobalt atom occupies the *cis* position to the phenyl group, and one of the carbonyl ligands on the cobalt center (C(9)–O(3)) is located at a semibridging position ($Pt \cdots C(9)$ = 2.58 (1) Å) [19]. It should also be noted that one of the PPh_3 ligands has migrated from the platinum center to the cobalt, and one CO ligand from the cobalt to the platinum. As expected, thermolysis of **6a** in C_6D_6 under a CO atmosphere at 50°C for 3 h afforded $(p\text{-}TolCO)Co(CO)_3(PPh_3)$ (**5a**) in 47% yield, which unambiguously indicate the involvement of a Pd–Co dinuclear species analogous to **6** as an intermediate in the catalytic reaction of Eq. (3) [19].

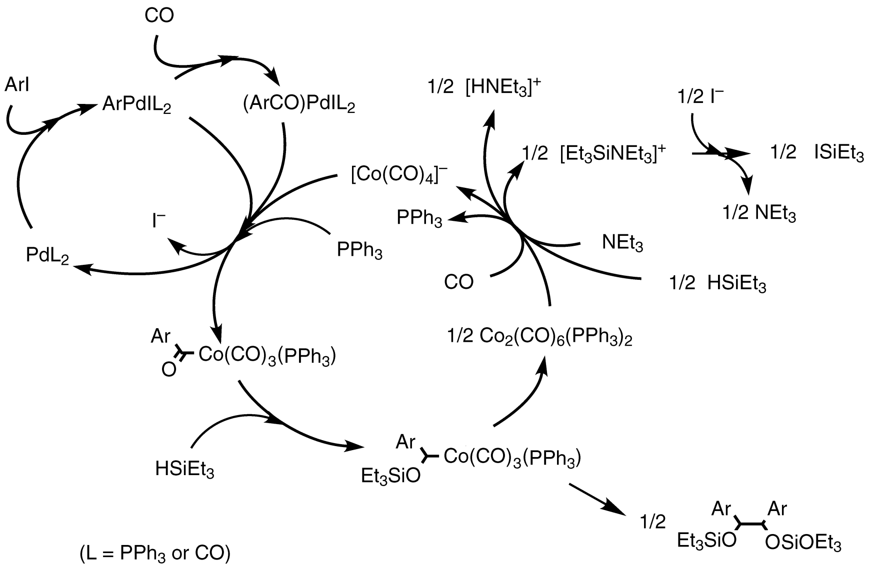


$$\mathrm{R{-}\underset{PPh_3}{\overset{PPh_3}{Pt}}{-}OTf + K[Co(CO)_4] \longrightarrow Ph_3P{-}\underset{R}{\overset{CO}{Pt}}{-}Co(CO)_3(PPh_3) + KOTf}$$

6

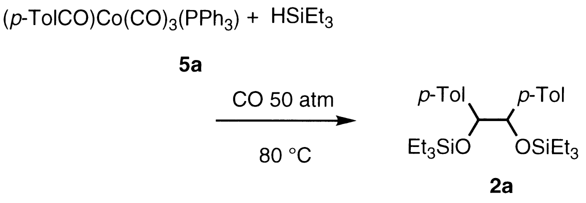
(4)

Further investigation of complex **5a** revealed that treatment of **5a** with $HSiEt_3$ under high CO pressure results in the formation of **2** as the major product (Eq. (5)) [12]. For example, **5a** reacted with $HSiEt_3$ at 80°C under 50 atm of CO to give **1a** and **2a** in 20 and 68% yield, respectively. Addition of NEt_3 and/or a catalytic amount of $Co_2(CO)_8$ to the reaction mixture significantly suppressed the formation of **1a**. Thus, when the reaction was carried out in the presence of NEt_3, **1a** and **2a** were formed in 1 and 67% yield, respectively. In contrast, a similar reaction of $(p\text{-}TolCO)Co(CO)_4$ with $HSiEt_3$ under CO pressure gave *p*-TolCHO as the major product (41% yield), and only a marginal amount of **2a** was obtained. These observations indicate that complex **5** is a highly probable intermediate for the catalytic formation of **2** in the carbonylation of



Scheme 2.

ArI with CO/HSiEt$_3$ in the presence of NEt$_3$.



(5)

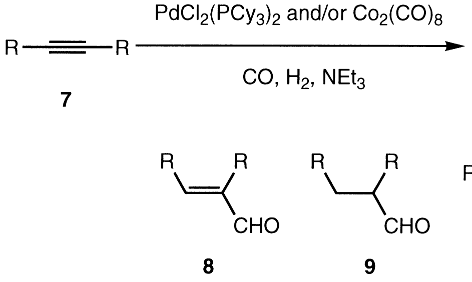
Catalyzed and uncatalyzed reactions of acyl complexes with hydrosilanes have so far been reported to afford siloxyalkyl complexes [23–26]. On the other hand, certain siloxyalkyl complexes such as Mn$\{$CHPh(OSiEt$_3$)$\}$(CO)$_5$ undergo thermolysis to give 1,2-disiloxyethanes via the homolytic fission of the metal–siloxyalkyl bond followed by the coupling of the siloxyalkyl radical [27]. We consider that the reaction of Eq. (5) proceeds through three steps including the formation of the siloxybenzylcobalt complex Co$\{$CHAr(OSiEt$_3$)$\}$(CO)$_3$(PPh$_3$), the homolytic cleavage of the Co–C bond to liberate the siloxybenzyl radical (Et$_3$SiO)ArCH$^\bullet$, and the coupling of the radical to form **2**.

On the basis of the findings described above, the reaction mechanism for the catalytic formation of **3** is proposed in Scheme 2. In this mechanism, ArI is first activated by a Pd(0) species through oxidative addition, and the aryl or aroyl group is then transferred from the palladium to the cobalt center by way of the reaction of ArPdIL$_2$ or (ArCO)PdIL$_2$ (L = PPh$_3$ or CO) with [Co(CO)$_4$]$^-$ anion to form the aroylcobalt complex **5**. These steps form the Pd-catalyzed cycle. In the cobalt-catalyzed cycle, the hydrosilylation of the aroylcobalt species **5** yields the siloxybenzylcobalt complex, whose homolytic Co–C bond cleavage leads to the formation of **2**. The Co(0) species generated is transformed into [Co(CO)$_4$]$^-$ anion by the action of HSiEt$_3$, NEt$_3$, and CO to complete the Co-catalyzed cycle. It should be emphasized that this mechanism involves the transfer of an organic group from one metal center (Pd) to another (Co) during the catalysis, and this is the origin of the synergistic effects between palladium and cobalt. Such a process has been expected to be operative in reactions using bimetallic catalysts but has rarely been confirmed in actual catalytic reactions.

3. Selective hydroformylation of internal alkynes

The hydroformylation of alkenes is one of the most important industrial processes catalyzed by transition metal complexes and has been studied extensively. In contrast, the hydroformylation of alkynes to the α,β-unsaturated aldehydes has been poorly exploited. Most catalysts so far reported have suffered from low selectivity and low yield of the unsaturated aldehydes, and this is primarily because it is difficult to suppress the formation of the corresponding saturated aldehydes and noncarbonylated hydrocarbons. Only recently it has been reported that the $Rh(CO)_2(acac)$-bisphosphite (acac = pentane-2,4-dionate) catalyst is effective for such a reaction [28]. We have turned our attention to development of novel mixed-metal catalyst systems for the hydroformylation of alkynes [13].

Preliminary examination of the hydroformylation of 4-octyne (**7a**, R = ^{n}Pr) (Eq. (6)) with the catalyst systems composed of $PdCl_2(PPh_3)_2$ and/or metal carbonyls resulted in low selectivity, but the bimetallic $PdCl_2(PPh_3)_2$–$Co_2(CO)_8$ catalyst showed some synergistic effect to give the desired unsaturated aldehyde **8a** in up to 49% yield by the reaction for 24 h. In contrast, the monometallic $PdCl_2(PCy_3)_2$ (Cy = cyclohexyl) catalyst exhibited very high selectivity in the presence of NEt_3, although its catalytic activity was moderate. The yield of **8a** reached 83% after 6 h at 150°C, and the formation of the saturated aldehyde **9a** and the simple hydrogenation product **10a** was almost negligible. Although the reaction requires a relatively high temperature, this result is of special interest, because palladium complexes have received little attention as catalysts for hydroformylation of alkenes. Furthermore, the combined use of $PdCl_2(PCy_3)_2$ and $Co_2(CO)_8$ remarkably improved the catalytic activity with little change of the selectivity. With the $PdCl_2(PCy_3)_2$–$Co_2(CO)_8$ catalyst (Pd/Co atomic ratio = 1/1) the reaction completed within 1 h, and **8a** was obtained in 95% yield. These results are summarized in Table 4. It is obvious that the palladium and cobalt metals participate cooperatively in the selective production of the unsaturated aldehyde. The stereochemistry of the aldehyde formed by the reaction with the $PdCl_2(PCy_3)_2$–$Co_2(CO)_8$ catalyst was 95% *E*, which is compatible with the common hydrometallation–carbonylation mechanism.



(6)

As the second component of the catalyst coupled with $PdCl_2(PCy_3)_2$, $Co_2(CO)_8$ accelerated the reaction most effectively, but unexpected enhancement of the reaction rate was also observed with $Fe_3(CO)_{12}$ and $W(CO)_6$, which gave **8a** in 85% yield (92% conversion) and 68% yield (76% conversion), respectively, by the reaction for 1 h. In contrast, $Rh_4(CO)_{12}$ gave rise to formation of a considerable amount of **9a**, and other transition metal carbonyls such as $Cr(CO)_6$,

Table 4
Hydroformylation of 4-octyne by Pd–Co catalysts[a]

Catalyst	Time (h)	Conversion (%)	GLC yield (%)		
			8a	**9a**	**10a**
$PdCl_2(PPh_3)_2$	24	85	7	0	4
$Co_2(CO)_8$	24	74	2	0	39
$PdCl_2(PPh_3)_2$–$Co_2(CO)_8$	24	100	39	14	19
$PdCl_2(PPh_3)_2$–$Co_2(CO)_8$[b]	24	80	49	8	4
$PdCl_2(PCy_3)_2$[c]	1	20	16	<1	0
$PdCl_2(PCy_3)_2$[c]	6	84	83	<1	<1
$PdCl_2(PCy_3)_2$–$Co_2(CO)_8$[c]	1	100	95	2	3

[a] Reaction conditions: 4-octyne, 5 mmol; $PdCl_2(PR_3)_2$, 0.1 mmol; $Co_2(CO)_8$, 0.05 mmol; CO, 25 atm; H_2, 25 atm; C_6H_6, 5 ml; 150°C.
[b] NEt_3, 5 mmol.
[c] NEt_3, 3 mmol; CO, 35 atm; H_2, 35 atm.

Table 5
Hydroformylation of internal alkynes catalyzed by $PdCl_2(PCy_3)_2$ or $PdCl_2(PCy_3)_2$–$Co_2(CO)_8$[a]

Alkyne	Catalyst	Conversion (%)	GLC yield (%)		
			8	**9**	**10**
7a (R = ^{n}Pr)	$PdCl_2(PCy_3)_2$–$Co_2(CO)_8$	100	95	2	3
7b (R = Et)	$PdCl_2(PCy_3)_2$–$Co_2(CO)_8$	96	88	3	3
7c (R = ^{n}Bu)	$PdCl_2(PCy_3)_2$–$Co_2(CO)_8$	97	90	2	5
7d (R = ^{n}Pen)	$PdCl_2(PCy_3)_2$–$Co_2(CO)_8$	95	95	2	2
7e (R = Ph)	$PdCl_2(PCy_3)_2$–$Co_2(CO)_8$	99	53	0	30[b]
7e[c]	$PdCl_2(PCy_3)_2$	94	77	0	15[d]

[a] Reaction conditions: alkyne, 5 mmol; $PdCl_2(PCy_3)_2$, 0.1 mmol; $Co_2(CO)_8$, 0.05 mmol; NEt_3, 3 mmol; CO, 35 atm; H_2, 35 atm; C_6H_6, 5 ml; 150°C; 1 h.

[b] $PhCH_2CH_2Ph$ was formed in 16% yield.

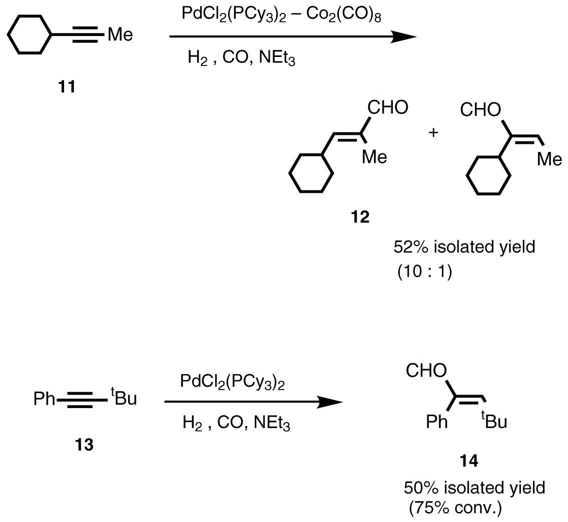
[c] Reaction time, 5 h.

[d] $PhCH_2CH_2Ph$ was formed in 2% yield.

$Mo(CO)_6$, $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, and $Ru_3(CO)_{12}$ exhibited no or small effects on the yields and selectivities of the products.

It should be mentioned that the use of bulky trialkylphosphines as the ligand of the palladium complex was essential to achieve satisfactory results. PCy_3 was particularly effective to obtain the unsaturated aldehyde selectively, while catalysts with arylphosphines such as PPh_3 and bisphosphines such as dppe ($Ph_2PCH_2CH_2PPh_2$) were much inferior both in activity and selectivity. $P(OPh)_3$ was totally ineffective as the ligand for the present Pd–Co catalyst system, making a sharp contrast to the results with the Rh-based catalyst where a phosphite ligand was adopted [28].

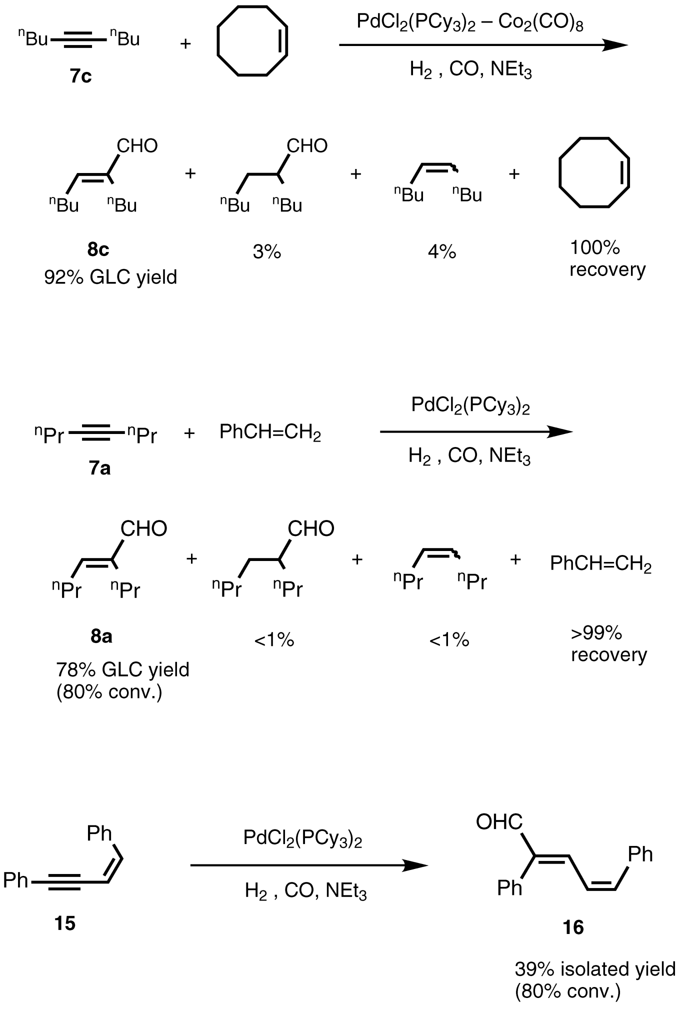
The $PdCl_2(PCy_3)_2$ and $PdCl_2(PCy_3)_2$–$Co_2(CO)_8$ catalyst systems were applicable to the hydroformylation of various internal alkynes. The results are summarized in Table 5. It should be pointed out that the Pd–Co bimetallic catalyst is of high efficiency and selectivity for the hydroformylation of aliphatic alkynes, but the reaction of diphenylacetylene (**7e**) was accompanied by significant formation of *cis*-stilbene (**10e**). The hydrogenation seems to be caused mainly by cobalt species, and the yield of (*E*)-α-phenylcinnamaldehyde (**8e**) was improved up to 77% by using the monometallic $PdCl_2(PCy_3)_2$ catalyst.



Scheme 3.

When an unsymmetric alkyne is used as a substrate, one may expect the regioselective formation of one of the aldehyde isomers. In fact, the hydroformylation of 1-cyclohexyl-1-propyne (**11**) by the $PdCl_2(PCy_3)_2$–$Co_2(CO)_8$ catalyst produced (*E*)-3-cyclohexyl-2-methyl-2-propenal (**12**) predominantly with good regioselectivity (Scheme 3). Similarly, the hydroformylation of 3,3-dimethyl-1-phenyl-1-butyne (**13**) by the $PdCl_2(PCy_3)_2$ catalyst led to exclusive formation of (*E*)-4,4-dimethyl-2-phenyl-2-pentenal (**14**). In these reactions, the more sterically demanding Cy and ^{t}Bu groups effectively control the CO insertion to occur at the remote acetylenic carbon.

Another interesting feature of the present hydroformylation is its chemoselectivity. When a 1:1



Scheme 4.

mixture of 5-decyne (**7c**) and cyclooctene was hydroformylated with the $PdCl_2(PCy_3)_2$–$Co_2(CO)_8$ catalyst, the unsaturated aldehyde **8c** was obtained in 92% yield and cyclooctene was recovered quantitatively (Scheme 4). Analogously, in the hydroformylation of a mixture of **7a** and styrene by the $PdCl_2(PCy_3)_2$ catalyst, **7a** was cleanly transformed into the unsaturated aldehyde **8a**, while styrene was recovered almost quantitatively. These results clearly demonstrate that the $PdCl_2(PCy_3)_2$ and $PdCl_2(PCy_3)_2$–$Co_2(CO)_8$ catalysts promote only the hydroformylation of alkynes. Furthermore, the good chemoselectivity enables the selective hydroformylation of enynes. Thus, when the hydroformylation of (*Z*)-1,4-diphenyl-1-buten-3-yne (**15**) was performed with the $PdCl_2(PCy_3)_2$ catalyst, (2*E*,4*Z*)-2,5-diphenyl-2,4-pentadienal (**16**) was obtained as the exclusive carbonylation product.

Finally, some comments should be added concerning the origin of the synergistic effect observed for the hydroformylation by the Pd–Co system. Since the product selectivity shown by the bimetallic $PdCl_2(PCy_3)_2$–$Co_2(CO)_8$ catalyst was similar to that by the monometallic $PdCl_2(PCy_3)_2$ catalyst, we consider that chemical transformation of alkynes mainly proceeds on a palladium metal center and a cobalt species plays a role in accelerating a part of the

Pd-catalyzed cycle. We have previously observed that the reaction of $PdPh(PMe_3)_2(OTf)$ with $[Co(CO)_4]^-$ anion induces facile CO insertion into the Pd–C bond to give eventually the dinuclear benzoyl complex $(PMe_3)_2(PhCO)PdCo(CO)_4$ [19]. It has more recently been reported that the CO insertion into the Pd–C bond in $(dppe)MePdCo(CO)_4$ is much faster than that in PdMeCl(dppe) [29]. These facts are suggestive of a mechanism where cobalt metal promotes the CO insertion into the Pd–C bond of a vinylpalladium intermediate. On the other hand, preliminarily kinetic study showed that both $PdCl_2(PCy_3)_2$ and $PdCl_2(PCy_3)_2$–$Co_2(CO)_8$ catalysts exhibited some dependence of the reaction rates on the H_2 pressure. This indicates that the cobalt catalyst has a function to accelerate the hydrogenolysis of the acyl–Pd bond to produce the aldehyde which is the rate determining step. Indeed, this type of rate enhancement has been revealed to operate in carbonylation reactions with heterobimetallic catalyst systems [6–8,10,30] or a homodinuclear complex catalyst [31]. Although the cooperative effects of the palladium and cobalt still remains to be elucidated, it is noteworthy that the combined use of $Co_2(CO)_8$ with $PdCl_2(PCy_3)_2$ showed remarkably favorable effects on the hydroformylation of alkynes.

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