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Direct Carbonylation of Benzyl Alcohol and Its Analogs Catalyzed by Palladium and HI in Aqueous Systems and Mechanistic Studies

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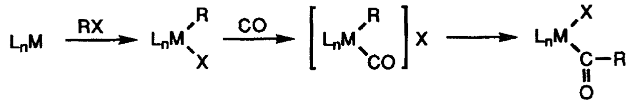
Carbonylation of benzyl alcohol, benzyl formate, dibenzyl ether, and benzyl phenylacetate catalyzed by palladium complexes and promoted by hydrogen iodide gives phenylacetic acid in moderate to excellent yields in aqueous systems. Application of the carbonylation process to other arylmethanol analogs provides convenient means to prepare 2-naphthaleneacetic acid, 3-isochromanone, 1,4-benzenediacetic acid, and *o*-hydroxybenzeneacetic acid. A mechanism for the catalytic reaction is proposed, which involves (1) formation of benzyl iodide by the reaction of benzyl alcohol with HI in situ, (2) oxidative addition of benzyl iodide to palladium(0) to form a benzylpalladium iodide species, (3) CO insertion into the Pd-benzyl bond to form a (phenylacetyl)palladium iodide species, (4) reductive elimination of phenylacetyl iodide, and (5) its hydrolysis into phenylacetic acid. Evidence supporting the mechanism was obtained by examining the properties of benzyl- and (phenylacetyl)palladium iodide and chloride complexes. Formation of benzyl(carbonyl)palladium species and migratory insertion of the benzyl group to CO was confirmed by means of NMR at low temperature under high pressure.

Transition metal-catalyzed carbonylation of organic halides provides a convenient means for synthesis of functionalized organic compounds.[1] There are two principal routes to give the carbonylated compounds. One is the palladium-catalyzed carbonylation of aryl and alkenyl halides using nucleophiles under basic conditions and the other is carbonylation of aliphatic alcohols in the presence of hydrogen halide, as represented by carbonylation of methanol catalyzed by rhodium complexes.[2] As common elementary steps in these catalytic reactions, both processes comprise oxidative addition of an organic halide to a low valent transition metal complex to give an organotransition metal halide and the subsequent CO insertion into the metal–carbon bond to give an acyltransition metal species (Eq. 1).

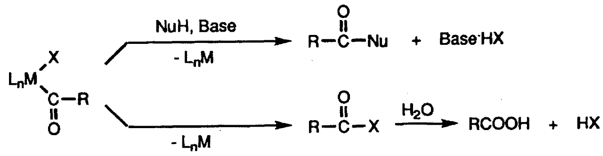


X = halide, R = alkyl or aryl, L = ligand

(1)

In the former approach, which has been extensively used with palladium catalysts, the acyltransition metal complex reacts with a nucleophile to release carbonyl derivatives, such as carboxylic acids, esters, and amides, depending on the nucleophiles employed (Eq. 2a). The process has been conveniently utilized in organic synthesis and the recently developed double carbonylation process provides further utility to produce α-keto acid derivatives.[3] The process, however, possesses an intrinsic problem in that the halide used in the reaction has to be eventually removed by using a base, making this process less desirable from economical and environmental viewpoints.

In the latter process, on the other hand, the organic halide is generated in situ and, subsequent to the CO insertion, the acyl ligand is liberated with the halide as an acyl halide (Eq. 2b).[4] The acyl halide is hydrolyzed into carboxylic acid with regeneration of hydrogen halide that converts alcohol to alkyl halide and drives the catalytic cycle (Eq. 3). The problem in the latter process is the requirement of acidic conditions that limits the utility in organic synthesis.



(2a)

(2b)

NuH = R'OH, R'$_2$NH, H$_2$O

$$ROH + HX \rightleftharpoons RX + H_2O \qquad (3)$$

The utility of the palladium-catalyzed carbonylation of aryl and alkenyl halides (Heck carbonylation process) is generally limited to these halides. Application to aliphatic halides has been hindered because of their reactivity with nucleophiles before the oxidative addition takes place and because of occurrence of β-hydrogen elimination from the alkylpalladium species formed by oxidative addition.[5] However, some allylic compounds such as allylic halides, esters, ethers, carbonates, and alcohols have been successfully carbonylated to give unsaturated carboxylic acid derivatives.[6] Recently a method to perform double carbonylation of certain allylic chlorides under mild conditions has been developed.[7] Conversion of a palladium-catalyzed allylic formates into carboxylic acids has also been realized.[7] We have also developed a direct method for converting allylic alcohols to the corresponding acids with the assistance of carbon dioxide without involving halides.[8] As an extension of the palladium-catalyzed carbonylation and double carbonylation processes of allylic compounds, we have attempted the carbonylation of benzylic compounds. Palladium- and cobalt-catalyzed carbonylations of benzyl halides in homogeneous systems and biphasic systems using phase-transfer catalysts have been widely investigated.[1,9] The carbonylation of benzylic alcohols and their derivatives has been attracting considerable attention from industrial chemists because of the importance of their carbonylated products, arylacetic acid and its derivatives, in the pharmaceutical industry.[10] Palladium-catalyzed hydroxycarbonylation of 1-arylethyl esters has been developed to prepare optically active 2-arylpropionic acids,[11] and HCl-promoted carbonylation of 1-arylethanols to 2-arylpropionic acids has been reported in a patent form.[10] Recently Toniolo studied the palladium-catalyzed carbonylation of *para*-hydroxy-substituted benzyl alcohols promoted by HCl.[12] Another recent development is carbonylation of 5-(hydroxymethyl)furfural and benzyl alcohol using water-soluble palladium complexes in acidic conditions.[13] On the other hand, cobalt-catalyzed carbonylation of benzyl alcohols into phenylacetic acids under basic conditions has been reported.[14]

In our attempts at carbonylating benzylic compounds under basic and acidic conditions, we found that benzyl alcohol can be converted into phenylacetic acid in the presence of palladium catalysts and hydrogen iodide in water-containing systems; we reported the results in a communication form.[15] Here we report the full details of the carbonylation processes under acidic conditions. The results of mechanistic studies dealing with the behavior of model compounds assumed in the catalytic systems are also described.

Results

Carbonylation of Benzyl Alcohol. After examination of the various conditions needed to carbonylate benzyl alcohol (**1**), we found that heating benzyl alcohol containing HI at 90 °C in the presence of [Pd(PPh$_3$)$_4$] in water-containing solvent such as acetone under CO gives satisfactory results to form phenylacetic acid (**2**) as shown in Table 1. In addition to **2**, benzyl phenylacetate (**3**) and toluene (**4**) were formed as side products (Eq. 4).

$$\underset{\mathbf{1}}{\mathrm{PhCH_2OH}} + \mathrm{CO} \xrightarrow[\text{HI (0.1 mol amt.)}]{[\mathrm{Pd(PPh_3)_4}]\text{ (0.01 mol amt.)}} \underset{\mathbf{2}}{\mathrm{PhCH_2COOH}} + \underset{\mathbf{3}}{\mathrm{PhCH_2COOCH_2Ph}} + \underset{\mathbf{4}}{\mathrm{PhCH_3}} \qquad (4)$$

Addition of HI (0.1 molar amount) as a promoter is essential for the formation of **2**. Decreasing the amount of HI to 0.05 molar amount (Entry 2, Table 1) caused the decrease in the conversion of **1** to **2** with increase in the amount of **3**, whereas using too high concentration of HI (0.5 molar amount, Entry 3 in Table 1) had an adverse effect and caused the decrease in the yield of **2** with increase of toluene. A similar increase in the protonation product of the benzyl moiety was also reported in the carbonylation of p-HOC$_6$H$_4$CH$_2$OH catalyzed by [PdCl$_2$(PPh$_3$)$_2$]/HCl system.[12]

Heating the system at 90 °C seems to be necessary. Comparison of the results in Entry 1 with those in 4 and 7 shows that heating at 60 °C is not enough, whereas heating the system as high as 150 °C has a deteriorating effect, giving larger amounts of toluene and 1,2-diphenylethane. No reaction proceeded at room temperature (Entry 8). A rather high pressure of CO (90 atm) seems to be required for getting **2** in a high selectivity. At 50 atm, selectivity for **2** decreased with increase in the amount of toluene (Entry 5). Shortening the reaction time to one day from the usual two days led to a lower yield of **2** (Entry 6).

The presence of a certain amount of water is essential for significant carbonylation of **1** to **2**. Omission of water caused a significant drop in the selectivity for **2** (Entries 9 and 10, Table 1), and removal of a trace amount of water by addition of Molecular Sieves 4A caused suppression of the reaction (Entry 11). The carbonylation can be carried out in water containing n-Bu$_4$NBr (0.1 molar amount), although higher temperatures than 90 °C were required in the aqueous system (Entries 12—14). On the other hand, a lower pressure could be employed at higher temperatures in the aqueous systems (Entry 14). Addition of a quaternary salt was indispensable in the aqueous systems. Comparison of the results in Table 1 including Entries 16—18 shows that water-containing acetone solution or an aqueous system containing the quaternary salt seems to be a good choice of the solvent.

Having proved that addition of HI gives a favorable acceleration effect for conversion of benzyl alcohol into phenylacetic acid (**2**), we have examined the effect of other promoters used in combination with [Pd(PPh$_3$)$_4$]. Employment of other protic acids such as HCl and HBF$_4$·OMe$_2$ with [Pd(PPh$_3$)$_4$] gave no carbonylation products (Entries 21—22, Table 1). The ineffectiveness of HCl in carbonylation of benzyl alcohol is in contrast with what has been reported previously regarding HCl-promoted carbonylation of p-hydroxybenzyl alcohol.[12] Addition of lithium iodide showed no promotion effect (Entry 20), whereas adding benzyl iodide to the system containing benzyl alcohol and [Pd(PPh$_3$)$_4$] in the acetone/water mixture gave lower but considerable amounts of the carbonylation products, **2** (28%) and **3** (57%), at 90 °C under 90 atm of CO pressure (Entry 19).

Table 2 compares the effect of Pd(0) and Pd(II) catalysts for the carbonylation of benzyl alcohol.[16] Pd(II) compounds are as effective as the Pd(0) complexes such as [Pd(PPh$_3$)$_4$] and [Pd$_2$(dba)$_3$]·CHCl$_3$ when used in combination with two mols of PPh$_3$ per palladium in the presence of HI (Entries 2, 6, and 8, Table 2).

Whereas PPh$_3$ proved to be an appropriate ligand for the carbonylation, bidentate ligands 1,2-bis(diphenylphosphino)ethane (dppe) and 1,3-bis(diphenylphosphino)propane (dppp) used in combination with the η^3-allylpalladium chloride in its dimeric form served as much poorer ligands than

Table 1. Carbonylation of Benzyl Alcohol$^{a)}$

	Conditions				Products %$^{b)}$			**1**
Entry	T (°C)	P (atm)	Time (h)	Solvents	**2**	**3**	**4**	%$^{b)}$
1	90	90	44	Acetone/H_2O	90	3	6	0$^{c)}$
2$^{d)}$	90	90	44	As above	24	58	7	7
3$^{e)}$	90	90	46	As above	48	0	27	0$^{c)}$
4	60	90	44	As above	20	22	2	53
5	90	50	44	As above	74	5	14	2$^{c,f)}$
6	90	90	25	As above	72	11	7	5$^{c,f)}$
7	150	40	46	As above	39	2	18	0$^{g)}$
8	25	130	88	As above	0	0	0	100
9	90	90	46	Acetone	53	28	7	8$^{c)}$
10	110	90	72	Acetone	75	12	8	1$^{c)}$
11$^{h)}$	90	100	65	Acetone	0	18	Trace	70
12$^{i)}$	110	90	43	H_2O	88	1	4	Trace
13$^{i)}$	90	90	46	H_2O	9	2	1	80
14$^{i)}$	150	40	46	H_2O	87	0	9	0
15	150	40	45	H_2O	2	1	10	78$^{f)}$
16	120	80	41	Dioxane/H_2O	62	12	19	Trace$^{c)}$
17	80	100	70	THF	20	20	4	55
18	100	100	48	None	4	38	3	52
19$^{j)}$	90	90	45	Acetone/H_2O	28	57	3	9$^{c)}$
20$^{k)}$	100	100	46	As above	0	0	Trace	96
21$^{l)}$	90	90	48	As above	2	7	Trace	88
22$^{m)}$	90	90	69	As above	0	0	0	40

a) Reaction conditions: a mixture of $PhCH_2OH$ (5 mmol), HI (0.5 mmol), and $[Pd(PPh_3)_4]$ (0.05 mmol) in a solvent mixture (2 mL) was heated (solvent/H_2O=20/1) under CO pressure. b) Determined by GC and ^{1}H NMR. c) A trace of 1,2-diphenylethane was detected. d) 0.25 mmol of HI was used. e) 2.5 mmol of HI was used. f) A trace of dibenzyl ether was detected. g) 1,2-Diphenylethane (9%) was detected. h) MS 4A (1.0 g) was added and dibenzyl ether (12%) was formed. i) n-Bu_4NBr (0.1 molar amount) was added. j) $PhCH_2I$ (0.1 molar amount) was used instead of HI. k) LiI (0.2 molar amount) was used instead of HI. l) HCl (0.1 molar amount) was used instead of HI. m) $HBF_4 \cdot OMe_2$ (0.1 molar amount) was used instead of HI, and dibenzyl ether (58%) was formed.

Table 2. Comparison of the Results Catalyzed by Various Palladium Complexes$^{a)}$

	[Pd]	Ligand	Promoter	Products %$^{b)}$			**1**
Entry	(mol amt. × 10^2)	(mol amt. × 10^2)	(mol amt.)	**2**	**3**	**4**	%$^{b)}$
1	$[Pd(PPh_3)_4]$ (1)	None	HI (0.1)	75	Trace	20	0$^{c,d,e)}$
2	$[PdCl_2(PPh_3)_2]$ (1)	None	HI (0.1)	73	10	15	Trace$^{d)}$
3	$[PdCl_2(PPh_3)_2]$ (1)	None	LiI (0.2)	35	24	4	26
4	$[PdCl_2(PPh_3)_2]$ (1)	None	HCl (0.2)	Trace	Trace	3	95
5$^{f)}$	$[PdCl_2(PPh_3)_2]$ (1)	None	LiI (0.2)	0	0	0	100
6	$[\eta^3\text{-}C_3H_5PdCl]_2$ (0.5)	PPh_3 (2)	HI (0.1)	75	0	19	0$^{e)}$
7	$[\eta^3\text{-}C_3H_5PdCl]_2$ (0.5)	PPh_3 (2)	LiI (0.2)	30	31	13	21
8	$[Pd(OAc)_2]$ (1)	PPh_3 (2)	HI (0.1)	76	0	20	0$^{e)}$
9	$[Pd_2(dba)_3] \cdot CHCl_3$ (0.5)	PPh_3 (2)	HI (0.1)	73	0	22	0$^{e)}$
10	$[\eta^3\text{-}C_3H_5PdCl]_2$ (0.5)	Dppe (1)	HI (0.1)	19	17	18	26$^{e,g)}$
11	$[\eta^3\text{-}C_3H_5PdCl]_2$ (0.5)	Dppp (1)	HI (0.1)	25	12	19	20$^{e,g)}$
12	$[\eta^3\text{-}C_3H_5PdCl]_2$ (0.5)	None	HI (0.1)	45	0	31	0$^{e)}$

a) Reaction conditions: a mixture of $PhCH_2OH$ (5 mmol), the promoter, and the palladium complex in acetone/H_2O (2/0.1 mL) was heated under CO (100 atm) for 44 h at 100 °C. b) Determined by GC and ^{1}H NMR. c) $[PhCH_2PPh_3]^+I^-$ (4 mol%) and PdI_2 were found in the reaction mixture. d) CO_2 was detected in the gas phase by GC. e) A trace of 1,2-diphenylethane was detected. f) $HNEt_2$ (0.1 molar amount) was added and a trace of diethyl oxamide was detected. g) A trace of dibenzyl ether was detected.

PPh_3 for the carbonylation of benzyl alcohol (Entries 10 and 11, Table 2). The carbonylation reaction can take place, giving **2** in a moderate yield, even in the absence of a phosphine ligand, although in this case the formation of by-product toluene was increased (Entry 12, Table 2).

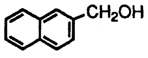
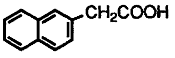
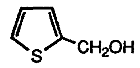
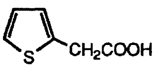
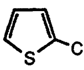
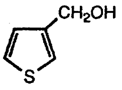
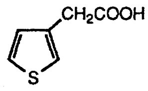
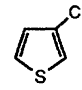
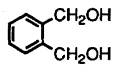
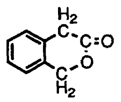
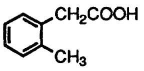
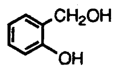
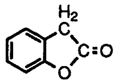
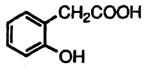
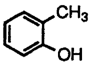
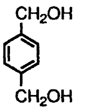
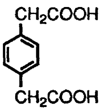
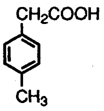
Although addition of LiI instead of HI did not give any carbonylation product when $[Pd(PPh_3)_4]$ was used as the catalyst, addition of LiI in combination with $[PdCl_2(PPh_3)_2]$ or with $[(\eta^3\text{-allyl})PdCl]_2$ had some promotion effect of the carbonylation of benzyl alcohol (Entries 3 and 7, Table 2). Addition of $HNEt_2$ in the presence of LiI completely blocked the carbonylation reaction catalyzed by $[PdCl_2(PPh_3)_2]$ (Entry 5). It is also noteworthy that addition of HCl in combination with $[PdCl_2(PPh_3)_2]$ gave no carbonylation product (Entry 4).

Formation of CO_2 was confirmed in the carbonylation when $[Pd(PPh_3)_4]$ or $[PdCl_2(PPh_3)_2]$ was used as the catalyst with the HI promoter (Entries 1 and 2, Table 2). It is noted that $[PhCH_2PPh_3]^+I^-$ and PdI_2 were recovered from the system using $[Pd(PPh_3)_4]$, whereas no palladium metal deposition was observed (Entry 1).

Carbonylation of Other Arylmethanols. The successful carbonylation of benzyl alcohol has stimulated us to explore the carbonylation of other arylmethanols and bifunctional alcohols. The results are summarized in Table 3.

2-Naphthalenemethanol (**5**) gave 2-naphthaleneacetic acid

Table 3. Carbonylation of Arylmethanols[a)]

Entry	Alcohol	Products, yield% (isolated yield%)[b)]
1[c)]	 **5**	 **6**, 97(90)
2	 **7**	 **8**, 18 +  **9**, 12
3	 **10**	 **11**, 34 +  **12**, 11
4[c)]	 **13**	 **14**, 88(56) +  **15**, 9
5[c,d)]	**13**	**14** 13 + **15** 52
6[d)]	 **16**	 **17**, 9 +  **18**, 56(36) +  **19**,7
7	**16**	**17** 10 + **18** 2 + **19** 8
8[c,e)]	 **20**	 **21**,(48) +  **22**, 16

a) Reaction conditions: a mixture of alcohol (4 mmol), HI (0.4 mmol), and $[Pd(PPh_3)_4]$ (0.04 mmol) in acetone/H_2O (3/0.1 mL) under CO (90 atm) was heated at 90 °C for 42 h. b) Determined by GC and ^1H NMR. c) A trace of 2-methylnaphthalene (Entry 1), *o*-xylene (Entries 4 and 5), and *p*-xylene (Entry 8) was detected, respectively. d) Dioxane/H_2O (3/0.2 mL) was used as a solvent mixture instead of acetone/H_2O and the reaction was carried out at 120 °C. e) HI (0.8 mmol) and $[Pd(PPh_3)_4]$ (0.08 mmol) were used.

(**6**) in an excellent yield when the carbonylation was performed with [Pd(PPh_3)$_4$] as the catalyst in the presence of HI (Entry 1, Table 3). That the reactivities of naphthylmethyl derivatives are higher than those of the corresponding benzyl compounds has been already observed in other systems.[11,17] Carbonylation of 2- and 3-thiophenemethanols (**7** and **10**) was also examined, but the yields of 2- and 3-thiopheneacetic acids (**8** and **11**) were poor and the reactions were accompanied by formation of small amounts of 2- and 3-methylthiophenes (**9** and **12**), respectively (Entries 2 and 3, Table 3). Successful carbonylation of 5-(hydroxymethyl)furfural to 5-formylfuran-2-acetic acid catalyzed by water-soluble palladium catalyst containing trisulfonated triphenylphosphine ligands has been recently reported.[13,18]

3-Isochromanone (**14**) was obtained in a good yield in the carbonylation of 1,2-bis(hydroxymethyl)benzene (**13**) catalyzed by [Pd(PPh_3)$_4$] and promoted by HI (Entry 4, Table 3). A small amount of *o*-methylphenylacetic acid (**15**) and a trace of *o*-xylene were detected as side reaction products. When dioxane/water mixture was used instead of the acetone/water mixture, the partly protonated carbonylation product **15** was formed as the main product (Entry 5, Table 3). The one-step formation of 3-isochromanone (**14**) provides a novel method to synthesize a δ-lactone directly from a diol. The other route leading to **14** in a 71% yield utilizing the carbonylation of 2-(bromomethyl)benzyl alcohol was previously reported by J. K. Stille.[19] A significant effect of the nature of the solvent mixture used for the carbonylation of 2-hydroxybenzyl alcohol (**16**) was observed. Whereas the carbonylation of **16** in the acetone/water mixture containing HI gave poor results (Entry 7), employment of a solvent mixture of dioxane/H_2O gave *o*-hydroxyphenylacetic acid (**18**) in a considerably better yield (Entry 6). Attempts to obtain γ-lactone **17** in a higher yield by change of solvents or raise of temperature were unsuccessful. Selective conversion of 2-allylphenols to lactones of different ring sizes has been recently reported by Alper.[20] Another route leading to aromatic γ-lactone by a three-component coupling of naphthol, aldehydes, and CO catalyzed by [Pd(PPh_3)$_4$] has been recently reported, where a route through carbonylation of arylethanol was suggested.[21]

1,4-Bis(hydroxymethyl)benzene (**20**) was doubly carbonylated at two alcoholic functions to give 1,4-benzenediacetic acid (**21**) in a 48% yield together with a singly carbonylated product, *p*-methylphenylacetic acid (**22**, Entry 8).

Carbonylation of Benzylic Derivatives. Benzyl formate, dibenzyl ether, and benzyl phenylacetate can be also carbonylated to phenylacetic acid (**2**) with palladium catalysts in the presence of HI or LiI as a promoter. The results are given in Table 4.

As in the carbonylation of benzyl alcohol, HI showed higher promotion activities in carbonylation of these benzyl derivatives than LiI, which had little to meager activity when used in combination with [$PdCl_2$(PPh_3)$_2$].

Attempts to carbonylate 1-phenylethanol in acetone/H_2O catalyzed by [Pd(PPh_3)$_4$]/HI under CO (90 atm) at 90 °C gave poor results. Formation of $PhCH(CH_3)COOH$ (15%), $PhCH_2CH_2COOH$ (6%), $PhCH_2CH_3$ (4%), and a mixture of various skeletal isomers of $(PhC_2H_4)_2$ were confirmed by the analysis of GC, GC-MS, and ^1H NMR.

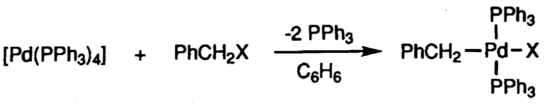
Mechanistic Studies. For obtaining information concerning the mechanism of the carbonylation of benzyl alcohol and for exploring the possibilities of accomplishing double carbonylation of benzylic compounds, we studied the reactions concerning the oxidative addition of benzyl iodide to Pd(0) complex and further CO insertion into the Pd–benzyl bond to give a (phenylacetyl)palladium complex. In addition, η^3-benzylpalladium complexes were prepared and their reactivities toward CO were examined. Comparison of the reactivities of the (phenylacetyl)palladium iodide and chloride complexes revealed considerable differences between the behaviors of these two halide complexes.

The oxidative addition of benzyl chloride to [Pd(PPh_3)$_4$] in a benzene solution to give *trans*-[Pd(CH_2Ph)Cl(PPh_3)$_2$] (**23**) was already reported in 1969 (Eq. 5).[22] We have confirmed that a similar reaction of [Pd(PPh_3)$_4$] with benzyl iodide also proceeded smoothly in benzene as well as in chloroform solution at room temperature within 10 min to give *trans*-[Pd(CH_2Ph)I(PPh_3)$_2$] (**24**) having an η^1-bonded benzyl ligand with palladium, as was characterized by elemental analysis and spectroscopic analysis of the isolated complex (Eq. 5).

Table 4. Carbonylation of Benzylic Derivatives[a)]

Entry	Substrate	Catalyst[b)]	Promoter (mol amt.)	Products %[c)] **2**	**3**	**4**	Conversion %[c)]
1[d)]	$PhCH_2OC(O)H$	A	HI (0.1)	70	6	18	100
2[e,f)]	$PhCH_2OC(O)H$	B	LiI (0.2)	22	15	19	70
3[g)]	$PhCH_2OCH_2Ph$	A	HI (0.2)	68	3	20	64
4[g)]	$PhCH_2OCH_2Ph$	B	LiI (0.4)	0	0	0	0
5[d)]	$PhCH_2COOCH_2Ph$	A	HI (0.1)	98	—	17	71
6[e,f)]	$PhCH_2COOCH_2Ph$	B	LiI (0.2)	11	—	1	10

a) Reaction conditions: a mixture of substrate (5 mmol), promoter, and palladium complex in acetone/H_2O (2/0.1 mL) was heated under CO (100 atm) for 42 h at 100 °C. b) Catalyst A: [Pd(PPh_3)$_4$] (0.01 molar amount); B: [$PdCl_2$(PPh_3)$_2$] (0.01 molar amount). c) Determined by GC and ^1H NMR in mol%/mol substrate. d) A trace of 1,2-diphenylethane was detected. e) A trace of benzyl iodide was detected. f) A trace of dibenzyl ether was detected. g) 0.02 molar amount of catalyst was used.

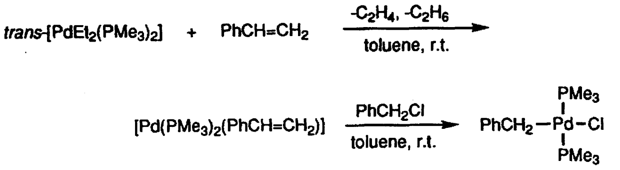


$$[Pd(PPh_3)_4] + PhCH_2X \xrightarrow[C_6H_6]{-2\,PPh_3} PhCH_2-\overset{PPh_3}{\underset{PPh_3}{Pd}}-X$$

(5)

23, X = Cl
24, X = I

For comparison, a PMe_3-coordinated benzyl complex *trans*-$[Pd(CH_2Ph)Cl(PMe_3)_2]$ (**25**) was prepared by the reaction of benzyl chloride with $[Pd(PMe_3)_2(styrene)]$, prepared in situ by thermolysis of *trans*-$[PdEt_2(PMe_3)_2]$ in the presence of styrene (Eq. 6).[23]

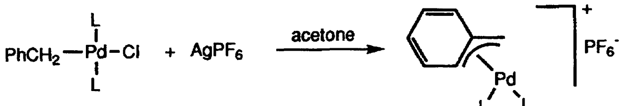


$$trans\text{-}[PdEt_2(PMe_3)_2] + PhCH{=}CH_2 \xrightarrow[toluene,\ r.t.]{-C_2H_4,\ -C_2H_6}$$
$$[Pd(PMe_3)_2(PhCH{=}CH_2)] \xrightarrow[toluene,\ r.t.]{PhCH_2Cl} PhCH_2-\overset{PMe_3}{\underset{PMe_3}{Pd}}-Cl$$

25

(6)

Both η^1-bonded benzylpalladium complexes **23** and **25** were converted into the corresponding cationic η^3-benzylpalladium complexes **26** and **27** with two PPh_3 and PMe_3 ligands, respectively, on treatment with $AgPF_6$ (Eq. 7).[24]

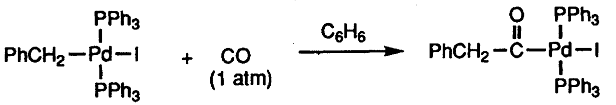


23, L = PPh_3
25, L = PMe_3

26, L = PPh_3
27, L = PMe_3

(7)

The PPh_3-coordinated benzylpalladium complex **24** underwent the CO insertion rapidly under ambient conditions to give *trans*-$[Pd(COCH_2Ph)I(PPh_3)_2]$ (**28**) within 10 min (Eq. 8).

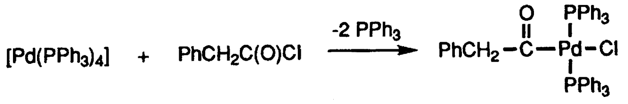


$$PhCH_2-\overset{PPh_3}{\underset{PPh_3}{Pd}}-I + \underset{(1\ atm)}{CO} \xrightarrow{C_6H_6} PhCH_2-\overset{O}{\overset{\|}{C}}-\overset{PPh_3}{\underset{PPh_3}{Pd}}-I$$

24 **28**

(8)

For comparison, the (phenylacetyl)palladium complex *trans*-$[Pd(COCH_2Ph)Cl(PPh_3)_2]$ (**29**) has been prepared through a different route by the reaction of phenylacetyl chloride with $[Pd(PPh_3)_4]$ (Eq. 9).[25]

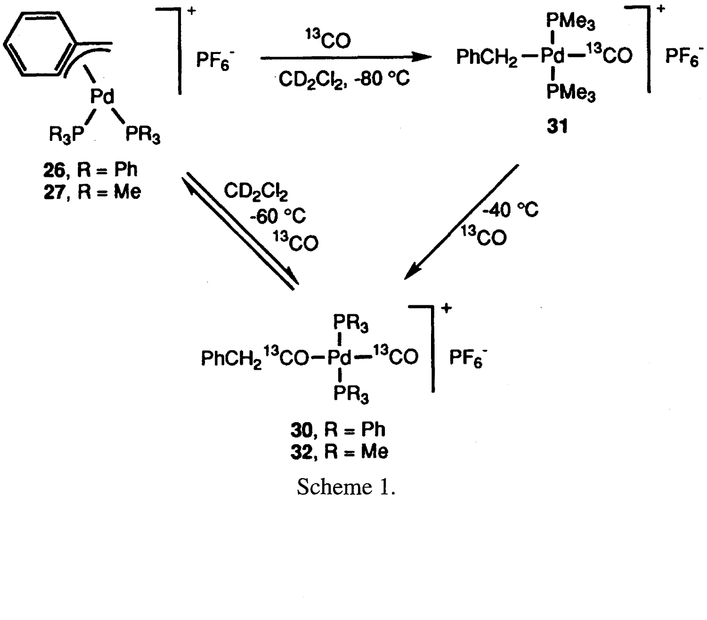


$$[Pd(PPh_3)_4] + PhCH_2C(O)Cl \xrightarrow{-2\,PPh_3} PhCH_2-\overset{O}{\overset{\|}{C}}-\overset{PPh_3}{\underset{PPh_3}{Pd}}-Cl$$

29

(9)

Heck previously studied the CO insertion of a PPh_3-coordinated benzylpalladium bromide complex and found that the reaction was first-order with a rate constant of 0.01 s^{-1} at 2.3 °C.[26] The reaction of the PPh_3-coordinated η^3-benzylpalladium complex **26** with ^{13}CO proceeded rapidly and only ^{13}CO-coordinated (phenylacetyl)palladium complex **30** was produced at −60 °C, while about 30% of the starting complex **26** remained in the system (Scheme 1). Since the CO insertion into the PPh_3-coordinated benzylpalladium complexes takes place too rapidly to provide information regarding the CO insertion intermediate, the reaction of the PMe_3-coordinated benzylpalladium complexes with CO was examined. The reaction of *trans*-$[Pd(CH_2Ph)Cl(PMe_3)_2]$ (**25**) with CO (1 atm) in CD_2Cl_2 at 25 °C proceeded slowly, following the first-order rate law with $k_{25°}=7.6\pm0.1\times10^{-5}$ s^{-1}, and was complete in 9 h to give *trans*-$[Pd(COCH_2Ph)Cl(PMe_3)_2]$.[23b] When the cationic η^3-benzylpalladium complex **27** having two PMe_3 ligands was treated with ^{13}CO (isotopic purity=99%, 10 atm) at −80 °C, we first observed the coordination of ^{13}CO to the cationic η^1-benzylpalladium center, giving **31** (Scheme 1). The $^{13}C\{H\}$ NMR spectrum of **31** showed a triplet at 179.1 ppm with a coupling constant of 18 Hz. The signal can be assigned to the coordinated-^{13}CO which is coupled with adjacent two phosphines in mutually *trans* positions.[27] Upon raising the temperature to −40 °C, smooth insertion of ^{13}CO followed to afford ^{13}CO-coordinated (phenylacetyl)palladium complex **32** having the ^{13}C-labeled phenylacetyl ligand, as evidenced by the observation of new signals in the $^{13}C\{H\}$ NMR. A doublet at 234.0 ppm (J=34 Hz) and a doublet of triplets at 180.0 (J=33, 19 Hz)



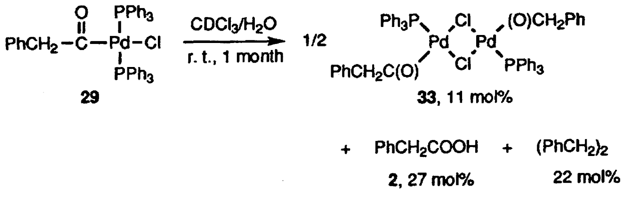
Scheme 1.

can be attributed to the resonances of the ^{13}C in the phenylacetyl group and terminal carbon monoxide, respectively.[27] Treatment of the CO-coordinated (phenylacetyl)palladium complex **32** with diethylamine under CO (10 atm) gave α-keto amide, $PhCH_2COCONEt_2$, and amide, $PhCH_2CONEt_2$, in yields of 71 and 29%. The result is reminiscent of the behavior of *trans*-$[Pd(COPh)(CO)(PMePh_2)_2]^+ClO_4^-$ toward amines.[27b] The details of the kinetic study of CO insertion and properties of the CO-coordinated (phenylacetyl)-palladium complexes will be reported separately.[28] The CO insertion into methylpalladium complexes having bidentate and monodentate tertiary phosphine ligands have been reported recently.[29]

These results on the oxidative addition of benzyl iodide to Pd(0) complexes and the subsequent CO insertion into the benzyl–palladium bond indicate that these reactions proceed very quickly above room temperature and can not be the rate-determining process in the actual catalytic cycle. Thus we examined next the reactivities of *trans*-$[Pd(COCH_2Ph)I(PPh_3)_2]$ (**28**) and *trans*-$[Pd(COCH_2Ph)Cl(PPh_3)_2]$ (**29**).

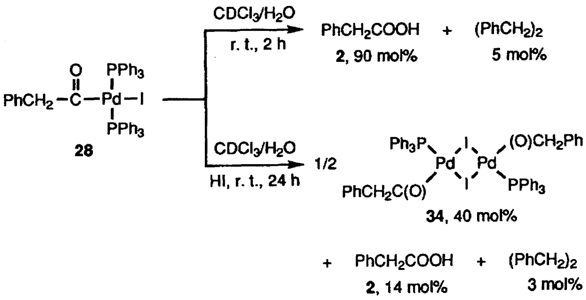
Reactivities of *trans*-$[Pd(COCH_2Ph)I(PPh_3)_2]$ (28) and *trans*-$[Pd(COCH_2Ph)Cl(PPh_3)_2]$ (29) toward Water: These (phenylacetyl)palladium complexes are quite stable in the solid state but are decomposed on reaction with water and on thermolysis. We examined the decomposition courses of **28** and **29** in the presence as well as in the absence of water.

The (phenylacetyl)palladium chloride complex **29** was found quite resistant to hydrolysis at room temperature in a $CDCl_3$ solution containing water. It took 10 days at room temperature to decompose 40 mol% of **29** to liberate 12 mol% of **2** together with 14 mol% of $(PhCH_2)_2$. During this period, 31 mol% of **29** was transformed into a chloride-bridged (phenylacetyl)palladium dimer $[Pd(COCH_2Ph)Cl(PPh_3)]_2$ (**33**)[30] having one PPh_3 ligand per palladium. It took one month for further decomposition of **29** to give **2** (27 mol%), $(PhCH_2)_2$ (22 mol%), **33** (11 mol%), and several unidentified compounds (Eq. 10).



(10)

In contrast to the behavior of the chloride complex **29**, the iodide analog **28** was much more susceptible to decomposition (Eq. 11a). It was completely decomposed in 2 h at room temperature in a $CDCl_3$ solution saturated with H_2O to give 90% of **2** and a small amount of $(PhCH_2)_2$. In the presence of LiOH (20 molar amounts), it was similarly decomposed, yielding 85% of $PhCH_2COO^-$. In contrast, decomposition of **28** in the presence of HI (5 molar amounts) was quite slow and only 14 mol% of **2** and 3 mol% of $(PhCH_2)_2$ were formed at room temperature in 24 h (Eq. 11b). Most of the phenylacetyl moiety remained undecomposed in a dimeric form $[Pd(COCH_2Ph)I(PPh_3)]_2$ (**34**, 40 mol%). The iodide-bridged complex **34** was identified by comparison of its NMR spectrum with that prepared by treatment of the known chloride dimer **33** with an excess of LiI in CD_2Cl_2.



(11a)

(11b)

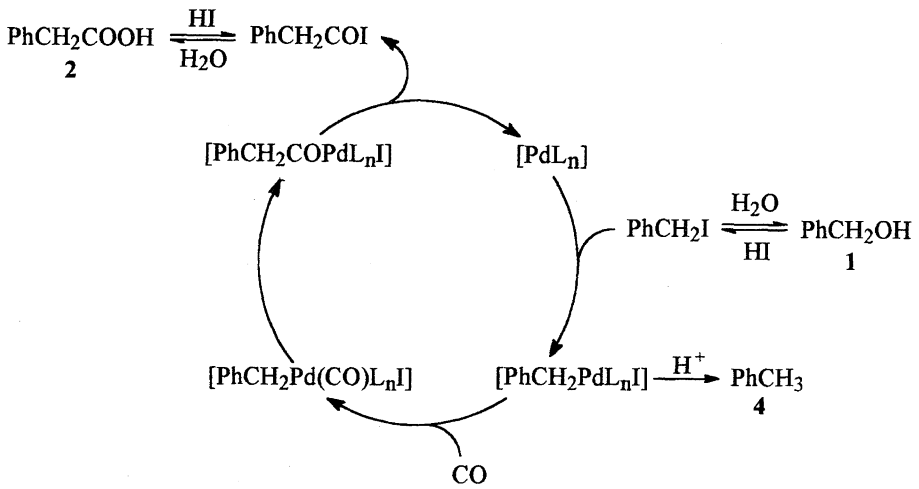
These results indicate that (phenylacetyl)palladium complexes are quite resistant to hydrolysis in acidic conditions.

Thermolysis of 28 and 29 in Water-Free System. Thermal decompositions of **28** and **29** were performed in acetone solution at 100 °C for two days under CO (50 atm) in the presence of Molecular Sieves 4A. Small amounts of $[PhCH_2COPPh_3]^+$ ($M^+=381$) and $[(PhCH_2CO)_2PPh_3]$ moieties ($M^+-1=499$) were found in the FAB-MS spectra in the reaction systems of both complexes. Examination of the product of the separately performed reaction of a 1 : 1 mixture of $PhCH_2COCl$ with PPh_3 in a CH_2Cl_2 solution showed a similar spectrum to that obtained in the thermolysis experiments.[31] The formation of the acylphosphonium compounds indicates occurrence of the reductive elimination of phenylacetyl halides which were trapped by free PPh_3 dissociated from the palladium complexes at high temperature.

Examination of the Reaction Intermediate in the Catalytic Carbonylation of Benzyl Alcohol. For obtaining clues regarding active species in the catalytic system, a mixture of benzyl alcohol in acetone-d_6/H_2O (2/0.5 mL) with $[Pd(PPh_3)_4]$ (0.05 molar amount) and HI (0.2 molar amount) was heated for 2 h at 90 °C under the pressure of CO (90 atm) in an autoclave. After cooling the system and releasing CO, we obtained a red-brown solution containing an orange precipitate. Isolation of the precipitate and its examination with ^1H and ^{31}P NMR revealed the solid as $[PdI_2(PPh_3)_2]$ (59%/Pd). The solution was found to contain phenylacetic acid (**2**, 2 mol%/alcohol), benzyl phenylacetate (**3**, 2 mol%), toluene (1 mol%), $[PhCH_2PPh_3]^+I^-$ (6 mol%), $[Pd(COCH_2Ph)I(PPh_3)]_2$ (**34**, 0.5 mol%), a trace of $(PhCH_2)_2$, and unreacted benzyl alcohol. The results indicate that most of $[Pd(PPh_3)_4]$ added as the catalyst precursor was transformed into $[PdI_2(PPh_3)_2]$ in the catalytic system and (phenylacetyl)palladium species was observed as the major organopalladium species. Formation of $[PdI_2(PPh_3)_2]$ was confirmed in the mixture of $[Pd(PPh_3)_4]$ with HI reacted at room temperature in 1 to 2 molar ratio.

Discussion

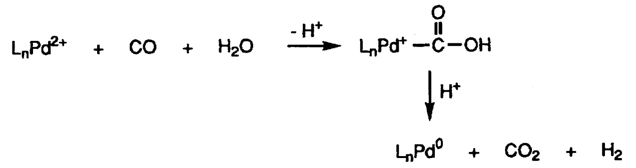
On the basis of the experimental results we propose a catalytic cycle for the carbonylation of benzyl alcohol to phenylacetic acid as shown in Scheme 2, which is similar to the Rh-catalyzed carbonylation of methanol to acetic acid.[4]



Scheme 2. Catalytic cycle for the carbonylation of $PhCH_2OH$ (L=PPh_3).

The model studies separately performed indicate that benzyl iodide, once formed, can rapidly oxidatively add to a Pd(0) complex to give a benzylpalladium species (Eq. 5).

The results shown in Table 2, indicating that Pd(II) complexes used in combination with PPh_3 and HI are as effective as $[Pd(PPh_3)_4]$ and $[Pd_2(dba)_3]\cdot CHCl_3/PPh_3$, are in line with the assumption of the reduction of the Pd(II) complexes to a Pd(0) active species in the catalytic carbonylation reaction in the water-containing system, probably by a process like that shown in Eq. 12 (the water gas shift reaction).[32] On the other hand, formation of $[PdI_2(PPh_3)_2]$ and CO_2 was confirmed in the catalytic carbonylation system containing $[Pd(PPh_3)_4]$, benzyl alcohol, and HI. The ready formation of $[PdI_2(PPh_3)_2]$ in the system may arise by oxidative addition of HI to the Pd(0) complex to give $[PdHI(PPh_3)_2]$ which may be further decomposed to give $[PdI_2(PPh_3)_2]$, liberating H_2.[33] Alternatively, $[PdI_2(PPh_3)_2]$ may be formed by disproportionation of $[PdHI(PPh_3)_2]$.



$$L_nPd^{2+} + CO + H_2O \xrightarrow{-H^+} L_nPd^+-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{H^+} L_nPd^0 + CO_2 + H_2 \qquad (12)$$

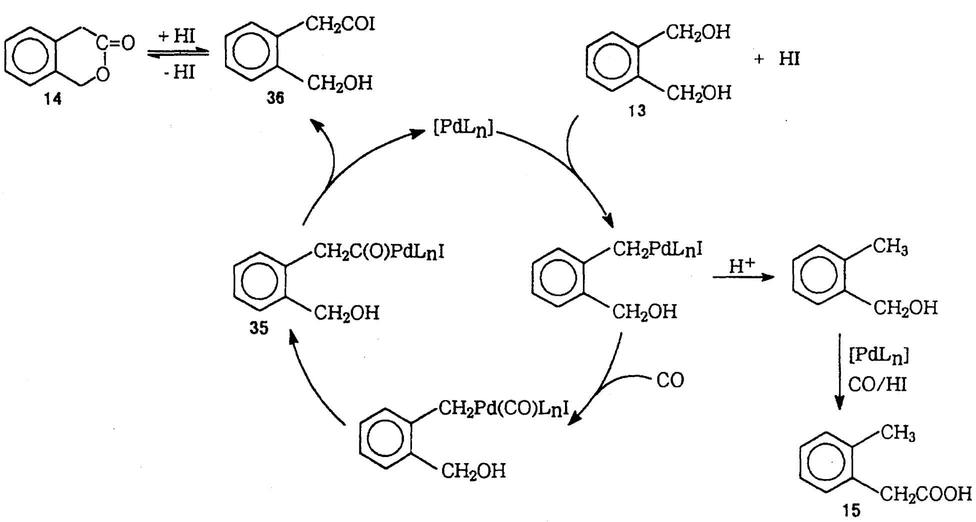
Oxidative addition of HI and benzyl iodide to Pd(0) species will be competing in the actual catalytic system. Since the oxidative addition of benzyl iodide to a Pd(0) complex and the succeeding CO insertion into benzylpalladium complex to afford the (phenylacetyl)palladium complex are rapid processes and since complex **28** was proved to be resistant to hydrolysis in the acidic solution (Eq. 11b), the organopalladium complexes can remain in the acidic system for some time before the reductive elimination of $PhCH_2COI$. Formation of toluene as the side product implies a partial protonolysis of the benzylpalladium species (Scheme 2). In fact, the formation of toluene was enhanced when higher concentration of HI was employed (Entry 3 in Table 1) and under the lower pressure of CO (Entries 5 and 7 in Table 1). Formation of toluene and $(PhCH_2)_2$ under lower CO pressure and at higher temperature suggests an equilibrium between the phenylacetyl and benzyl species in the catalytic system (Entry 7, Table 1). Formation of a higher amount of $(PhCH_2)_2$ implies that disproportionation of the benzylpalladium species is enhanced under the conditions.

The benzylpalladium ligand can take η^1- as well as η^3-benzyl forms, but the CO insertion takes place readily into both the η^1- and η^3-benzylpalladium bonds and the difference in the behavior of the η^1- and η^3-benzylpalladium forms would not affect the actual catalytic process.

The reaction of ^{13}CO with the PMe_3-coordinated η^3-benzylpalladium complex, **27**, revealed that coordination of CO on benzylpalladium(II) complex takes place first to afford a benzyl(carbonyl)palladium(II) complex, *trans*-$[Pd(CH_2Ph)(^{13}CO)(PMe_3)_2]^+PF_6^-$ (**31**, Scheme 1). Insertion of CO into the Pd–C(benzyl) bond occurs subsequently to give a (phenylacetyl)palladium(II) complex *trans*-$[Pd(^{13}COCH_2Ph)(^{13}CO)(PMe_3)_2]^+PF_6^-$ (**32**).

The dimeric (phenylacetyl)palladium complex having one phosphine ligand, $[Pd(COCH_2Ph)I(PPh_3)]_2$ (**34**), was detected as an exclusive organopalladium complex containing benzyl moiety in the course of carbonylation reaction. The observation suggests that the key step in the catalytic carbonylation cycle of benzyl alcohol (Scheme 2) is in the final process, which involves reductive elimination of $PhCH_2COI$ from the (phenylacetyl)palladium iodide species. Subsequent hydrolysis of $PhCH_2COI$ liberates **2** with generation of HI that is used to convert benzyl alcohol into benzyl iodide according to Scheme 2. The results of the thermal decomposition of (phenylacetyl)palladium halides demonstrate that the reductive elimination of phenylacetyl iodide is possible under CO pressure at high temperature. The reaction of acylpalladium(II) and -platinum(II) complexes with halogens to induce the reductive elimination of carboxylic acid halides has been reported.[25]

The results that the dimeric complex $[Pd(COCH_2Ph)I(PPh_3)]_2$ (**34**) was formed in the reaction of **28** with HI (Eq. 11b) and detected in the catalytic carbonylation solution show that either this dimer or a 3-coordinate species formed by dissociation of a PPh_3 ligand from **28** may be in-



Scheme 3. Mechanism for the carbonylation of 1,2-bis(hydroxymethyl)benzene (L=PPh_3).

volved as a key intermediate to undergo the reductive elimination of $PhCH_2COI$. The fact that $[PhCH_2PPh_3]^+I^-$ was produced in the catalytic carbonylation of benzyl alcohol using Pd(0) complex and PPh_3 ligands suggests that $PhCH_2I$ generated in situ reacts with PPh_3 to remove part of the PPh_3 ligands in the intermediate organopalladium complexes having two PPh_3 ligands. Reductive elimination induced by phosphine dissociation from a d^8-diorganotransition metal complex has been documented[34)] and a course of reductive elimination through a three-coordinated diorganopalladium complex having a phosphine ligand was supported theoretically.[35)] Reductive elimination of an alkyl bromide from a Br-bridged dimeric complex and suppression of the reductive elimination by adding PPh_3 have been observed.[36)] Halide-bridged dimeric acylpalladium complexes **33** and $[Pd(COAr)I(PPh_3)]_2$ were also proposed as intermediates in the carbonylation of benzyl and aryl halides in two phase systems under basic conditions.[37)]

Alcoholysis of phenylacetyl iodide with benzyl alcohol gives rise to the benzyl ester **3**, which can be further converted into phenylacetic acid in the catalytic system by extension of the reaction time or by increasing the amount of HI added (see Table 1). In fact, the ester **3** can be catalytically carbonylated to acid **2** by using an iodide-promoted palladium catalyst, as shown in Entry 5 in Table 4.

The big difference in effectiveness between HI and HCl as promoters in the carbonylation of benzyl alcohol merits some comment. The much slower decomposition of *trans*-$[Pd(COCH_2Ph)Cl(PPh_3)_2]$ (**29**) than that of *trans*-$[Pd(COCH_2Ph)I(PPh_3)_2]$ (**28**) in $CDCl_3$ solutions saturated with water demonstrates that the formation of $PhCH_2COOH$ is considerably hindered by the replacement of the iodide with chloride in the (phenylacetyl)palladium halide complex. It seems to be reasonable to ascribe the effect to the difference in the rate of reductive elimination of phenylacetyl chloride vs. iodide.

The carbonylation of various benzylic derivatives ($PhCH_2Y$, Y=OC(O)H, OCH_2Ph, and $OC(O)CH_2Ph$) into phenylacetic acid (**2**) under acidic conditions may be analogously accounted for by the first formation of benzyl iodide on their reactions with HI. The subsequent processes should proceed as in Scheme 2.

The carbonylation of 1,2-bis(hydroxymethyl)benzene (**13**) may be accounted for by Scheme 3, which consists of oxidative addition of benzylic iodide and CO insertion to give an acyl intermediate **35**. Scheme 3 shows a tentative mechanism assuming the operation of a mechanism similar to Scheme 2, involving reductive elimination of an acyl iodide **36** from the acylpalladium complex and the subsequent lactonization giving **14**. Nucleophilic attack of the OH group in the acylpalladium complex **35** on the acyl carbonyl group to liberate the lactone **14** with liberation of HI should be considered as another possible route.

Conclusion

Direct carbonylation of benzyl alcohol and its analogs to carboxylic acids or lactones could be achieved by using palladium catalysts in the presence of HI. In contrast to the previous reports using HCl, the catalytic activity was developed only by using HI. The fundamental studies on the elementary processes involving oxidative addition of benzyl iodide to a Pd(0) complex, the CO insertion to give a (phenylacetyl)palladium iodide, and reductive elimination of $PhCH_2COI$ that is hydrolyzed to phenylacetic acid provided the evidence accounting for the reasons why use of HI, not HCl, is essential to drive the catalytic cycle. The proposed mechanism is similar to that proposed for the well-known rhodium catalyzed carbonylation of methanol promoted by HI, but no such process utilizing HI as the promoter has been realized, to our knowledge, with use of a palladium catalyst.

Experimental

General Considerations. All manipulations were carried out under an atmosphere of argon. Infrared spectra were recorded on a Hitachi 295 spectrometer using KBr pellets. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a JEOL EX-270 spectrometer. Chemical shifts are reported in δ units (parts per million, ppm) downfield from Me_4Si for ^1H and ^{13}C, and H_3PO_4 (85% in aqueous solution, external reference) for ^{31}P. Carbon, hydrogen, and nitrogen analyses were carried out on a Perkin–Elmer PE 2400II Elemental Analyzer. Mass spectra were analyzed on a JEOL AUTOMASS or an SX-102A spectrometer. Gas chromatographic (GC) analyses were performed on a Hitachi 263-50 or Hitachi 263-30 equipped with an SE-30 or Unibeads C column for either solution or gas phase detection, respectively, using N_2 as carrier gas.

Solvents were dried and distilled before use by standard methods. Alcohols, other benzylic derivatives, phosphines, $AgPF_6$, $[PdCl_2(PPh_3)_2]$, and $[Pd(OAc)_2]$ were commercially available and were used without further purification. Benzyl iodide was prepared from the reaction of benzyl chloride with excess of LiI. Palladium complexes, $[Pd(PPh_3)_4]$, $[\eta^3\text{-}C_3H_5PdCl]_2$, and $[Pd_2(dba)_3]\cdot CHCl_3$, were synthesized as reported in the literature.[38] *Trans*-$[Pd(CH_2Ph)Cl(PPh_3)_2]$[22] and *trans*-$[PdEt_2(PMe_3)_2]$[39] were prepared according to the previous reports.

General Procedure for the Carbonylation Reactions. In a typical experiment, palladium complex (0.05 mmol), substrate (5 mmol), acetone/H_2O (2/0.1 mL), and HI (0.05 mmol, an aqueous solution containing 57% of HI) were charged into a 100 mL stainless steel autoclave under an atmosphere of argon. The reactor was pressurized to the desired value with CO at room temperature and then heated in an oil bath for a set time. After that time, the autoclave was cooled to room temperature and the gas phase of the carbonylation reaction was analyzed, if necessary, by GC before its release (for analysis of CO_2 a column containing Unibeads C 60/80 was used). The liquid phase was analyzed by GC (Column: SE-30) using $C_{16}H_{34}$ or $C_{10}H_{22}$ as an internal standard. After the solvent in the reaction mixture was removed by using a rotary evaporator, organic compounds in the residue were characterized by comparison of ^{1}H NMR and GC-mass spectra with corresponding authentic samples. When necessary, the products were isolated by using a chromatographic column with ether as an eluent. Among the products shown in Table 3, the dibasic acid **21** was precipitated from the reaction solution and identified. The phosphonium salt $[PhCH_2PPh_3]^+I^-$ and PdI_2 were separated from organic compounds by precipitation from acetone or ether solution. The phosphonium salt was identified by ^{1}H, ^{31}P NMR, IR, and elemental analysis, and comparison with the reaction product of PPh_3 and $PhCH_2I$.

Preparation of *trans*-$[Pd(CH_2Ph)I(PPh_3)_2]$ (24). To a benzene (50 mL) solution of $[Pd(PPh_3)_4]$ (1.000 g, 0.865 mmol) was added $PhCH_2I$ (0.105 mL, 0.865 mmol) dropwisely at room temperature under argon. After stirring the mixture for 20 min at room temperature and concentrating the solution, we obtained an orange oily residue, which we triturated with ether (40 mL) and pentane (40 mL) to give an orange precipitate. The orange solid of **24** was obtained after filtration, washing with pentane, and drying (0.668 g, 91%). ^{1}H NMR (CD_2Cl_2, 270 MHz, 293 K) δ=7.7—7.3 (m, 30H, 2 PPh_3), 7.06 (t, J=6 Hz, 1H, p-C_6H_5), 6.97 (t, J=6 Hz, 2H, m-C_6H_5), 6.33 (d, J=7 Hz, 2H, o-C_6H_5), 2.89 (s, 2H, CH_2). ^{31}P NMR (CD_2Cl_2, 109.4 MHz, 293 K) δ=24.4 (s.br). Anal. Found: C, 60.09; H, 4.38%. Calcd for $C_{43}H_{37}IP_2Pd$: C, 60.83; H, 4.39%.

The reaction of $[Pd(PPh_3)_4]$ with $PhCH_2I$ in a 1 to 1 ratio was also examined in $CDCl_3$ as monitored by ^{1}H and ^{31}P NMR at room temperature. The reaction was complete after 10 min to form *trans*-$[Pd(CH_2Ph)I(PPh_3)_2]$ (**24**).

Preparation of *trans*-$[Pd(CH_2Ph)Cl(PMe_3)_2]$ (25). To a Schlenk tube containing *trans*-$[PdEt_2(PMe_3)_2]$ (1.10 g, 3.5 mmol) and toluene (10 mL) cooled to −30 °C was added styrene (0.80 mL, 7 mmol). The mixture was stirred for 5 h at room temperature to give a pale yellow homogenous solution. To the system was added $PhCH_2Cl$ (3.2 mL, 28 mmol) and the reaction mixture was stirred for 4 h at room temperature. Concentration and addition of hexane gave a white precipitate, which was filtered, washed with hexane, and dried in vacuo. The product was recrystallized from CH_2Cl_2–hexane to give a white powder of **25** (1.01 g, 75%). ^{1}H NMR ($CDCl_3$, 270 MHz, 293 K) δ=7.34 (d, J=7 Hz, 2H, o-C_6H_5), 7.13 (t, J=7 Hz, 2H, m-C_6H_5), 7.03 (t, J=7 Hz, 1H, p-C_6H_5), 2.72 (t, J=8 Hz, 2H, CH_2), 1.35 (vt (virtual triplet), J=3 Hz, 18H, 2 PMe_3). ^{31}P NMR ($CDCl_3$, 109.4 MHz, 293 K) δ=−15.0 (s). Anal. Found: C, 40.90; H, 6.61%. Calcd for $C_{13}H_{25}ClP_2Pd$: C, 40.54; H, 6.54%.

Preparation of (η^3-Benzyl)bis(triphenylphosphine)palladium Hexafluorophosphate (26). To an acetone solution (8 mL) of *trans*-$[Pd(CH_2Ph)Cl(PPh_3)_2]$ (1.03 g, 1.36 mmol) was added $AgPF_6$ (0.345 g, 1.36 mmol) in 2 mL of acetone at −20 °C. A white suspension was immediately formed. The reaction mixture was stirred for 2 h at −20 °C. Removal of AgCl by filtration gave a clear yellow solution. After its concentration followed by addition of ether, a yellow precipitate was formed. Filtration of the precipitate and the subsequent washing with ether and drying in vacuo gave a pale yellow powder of **26** (1.014 g, 86%). ^{1}H NMR ($CDCl_3$, 270 MHz, 293 K) δ=7.44—6.85 (m, 35H, Ph and 2 PPh_3), 3.08 (s.br., 2H, CH_2). ^{31}P NMR ($CDCl_3$, 109.4 MHz, 293 K) δ=32.2 (d, J=41 Hz), 22.7 (d, J=40 Hz), −144.4 (sept., J=710 Hz, PF_6^-). Anal. Found: C, 59.30; H, 4.42%. Calcd for $C_{43}H_{37}F_6P_3Pd$: C, 59.56; H, 4.30%.

Preparation of (η^3-Benzyl)bis(trimethylphosphine)palladium Hexafluorophosphate (27). A similar procedure to the above was used for the preparation of the PMe_3-coordinated complex **27**. Treatment of the *trans*-$[Pd(CH_2Ph)Cl(PMe_3)_2]$ (0.518 g, 1.34 mmol) with $AgPF_6$ (0.340 g, 1.34 mmol) gave a white powder of **27** (0.524 g, 79%). ^{1}H NMR ($CDCl_3$, 270 MHz, 243 K) δ=7.59 (t, J=7 Hz, 2H, m-C_6H_5), 7.46 (s.br., 1H, p-C_6H_5), 6.64 (s.br., 2H, o-C_6H_5), 2.96 (d, J=9 Hz, 2H, CH_2), 1.63 (d, J=11 Hz, 9H, PMe_3), 1.13 (d, J=9 Hz, 9H, PMe_3). ^{31}P NMR ($CDCl_3$, δ, 109.4 MHz, 243 K): −6.2 (d, J=47 Hz), −26.9 (d, J=47 Hz), −143.8 (sept., J=713 Hz, PF_6^-). Anal. Found: C, 31.68; H, 5.11%. Calcd for $C_{13}H_{25}F_6P_3Pd$: C, 31.56; H, 5.09%.

Preparation of *trans*-$[Pd(COCH_2Ph)I(PPh_3)_2]$ (28). To a benzene (20 mL) solution of $[Pd(PPh_3)_4]$ (0.500 g, 0.433 mmol) was added $PhCH_2I$ (0.052 mL, 0.433 mmol) dropwisely at room temperature under argon. After 20 min stirring at room temperature, the solution was cooled and argon gas was replaced with CO (1 atm). The resulting solution became orange when it was allowed to be warmed to room temperature. The orange solution which formed was stirred for 10 min and then concentrated to 5 mL. Addition of pentane (10 mL) gave a yellow precipitate of **28**, which was filtered and washed with pentane (2×5 mL) (0.300 g, 79%). ^{1}H NMR (CD_2Cl_2, 270 MHz, 243 K) δ=7.7—7.3 (m, 30H, 2 PPh_3), 7.01 (t, J=7 Hz, 1H, p-C_6H_5), 6.89 (t, J=7 Hz, 2H, m-C_6H_5), 5.59 (d, J=7 Hz, 2H, o-C_6H_5), 3.51 (s, 2H, CH_2). ^{31}P NMR (CD_2Cl_2, 109.4 MHz, 243 K) δ=18.6 (s). IR: $\nu_{C=O}$=1694 cm^{-1}. Anal. Found: C, 61.08; H, 4.15%. Calcd for $C_{44}H_{37}IOP_2Pd$: C, 60.26; H, 4.25%.

The direct reaction of **24** with CO (1 atm) was also examined in a $CDCl_3$ solution as monitored by ^{1}H and ^{31}P NMR at room temperature. After 10 min, *trans*-$[Pd(COCH_2Ph)I(PPh_3)_2]$ (**28**) was formed exclusively.

Reaction of *trans*-$[Pd(CH_2Ph)Cl(PMe_3)_2]$ (25) with CO (1 atm). To a CD_2Cl_2 solution of **25** (0.020 g, 0.052 mmol) in an NMR tube was bubbled CO (1 atm) for 1 min at room temperature. The following reaction was monitored by ^{1}H and ^{31}P NMR, which indicated the formation of *trans*-$[Pd(COCH_2Ph)Cl(PMe_3)_2]$. The reaction was followed by observing the increase in the intensity of the acetyl protons in *trans*-$[Pd(COCH_2Ph)Cl(PMe_3)_2]$. It was found that the carbonylation process obeyed the first-order rate law in the palladium complex and was complete in 9 h at room temperature.

Formation of Complexes *trans*-$[Pd(CH_2Ph)(^{13}CO)(PMe_3)_2]^+PF_6^-$ (31) and *trans*-$[Pd(^{13}COCH_2Ph)(^{13}CO)(PMe_3)_2]^+PF_6^-$ (32). A CD_2Cl_2 (0.5 mL) solution of (η^3-benzyl)bis(trimethylphosphine)palladium hexafluorophosphate (0.020 g, 0.04 mmol) was placed in a high pressure NMR tube and was cooled in a liquid nitrogen bath. To the cooled solution, ^{13}CO gas (13 mL) was added by using a syringe so that the internal pressure reached 10 atm at room temperature, as estimated by measuring the space in the NMR tube. The mixture was warmed to -80 °C and the reaction was monitored by ^1H, ^{13}C, and ^{31}P NMR. After 2.5 h at this temperature, **31** was detected as a single product, together with the starting palladium complex which remained unreacted, in a molar ratio of 1 to 2.5. The temperature was further increased to -40 °C and the migratory insertion of the benzyl group to CO in complex **31** was observed to proceed smoothly to afford *trans*-$[Pd(^{13}COCH_2Ph)(^{13}CO)(PMe_3)_2]^+PF_6^-$ (**32**). NMR data assigned for **31**: ^1H NMR (CD_2Cl_2, 270 MHz, 233 K) $\delta=7.5$—7.1 (m, Ph, overlapped with the signal of complex **32**), 2.67 (td, $^4J_{P-H}=9$, $^2J_{CO-H}=2$ Hz, 2H, CH_2), 1.4 (vt, $J=3$ Hz, overlapped with the signal of complex **32**, 18H, $2PMe_3$). ^{13}C NMR (CD_2Cl_2, 67.9 MHz, 233 K) $\delta=179.1$ (t, $^2J_{P-CO}=18$ Hz, ^{13}CO). ^{31}P NMR (CD_2Cl_2, 109.4 MHz, 233 K) $\delta=-12.9$ (d, $^2J_{P-CO}=18$ Hz). NMR data assigned for **32**: ^1H NMR (CD_2Cl_2, 270 MHz, 233 K) $\delta=7.6$—7.2 (m, 5H, Ph), 3.97 (d, $J=5$ Hz, 2H, Ph-CH_2), 1.42 (vt, $J=4$ Hz, 18H, PMe_3). ^{13}C NMR (CD_2Cl_2, 67.9 MHz, 233 K) $\delta=233.7$ (d, $J=34$ Hz, $^{13}COCH_2Ph$), 180.3 (dt, $J=34$ and 18 Hz, ^{13}CO), 129.7 (s, Ph), 128.8 (s, Ph), 127.6 (s, Ph), 124.7 (s, Ph), 60.5 (m, CH_2Ph), 15.0 (vt, $J=17$ Hz, PMe_3). ^{31}P NMR (CD_2Cl_2, 109.4 MHz, 233 K) $\delta=-19.1$ (d, $^2J_{C-P}=18$ Hz), -144.2 (sept., $J=713$ Hz, PF_6^-).

The reaction of **26** with ^{13}CO was examined in a similar manner to that described above and formation of *trans*-$[Pd(^{13}COCH_2Ph)(^{13}CO)(PPh_3)_2]^+PF_6^-$ (**30**) was confirmed. The characterization of **30** and the reaction of **32** with Et_2NH will be reported separately.[28)]

Reactivities of *trans*-$[Pd(COCH_2Ph)X(PPh_3)_2]$ (X=Cl,I) toward H_2O. Three NMR tubes were charged with **28** (0.010 g, 0.0114 mmol) in $CDCl_3$ (0.6 mL) solutions saturated with H_2O, respectively. To one of them was added HI (57% in aqueous solution, 0.008 mL, 0.057 mmol), to a second was added LiOH (0.0055 g, 0.228 mmol), and to the third was not added any additive. The reactions were monitored by ^1H and ^{31}P NMR. Complex **28** reacted with water to give $PhCH_2COOH$ (90 mol%/Pd) and $(PhCH_2)_2$ (5 mol%/Pd) in 2 h at room temperature. The reaction of **28** with LiOH–H_2O at room temperature released 85% of $PhCH_2COO^-$. In the experiment where HI was added, the dimeric complex, $[Pd(COCH_2Ph)I(PPh_3)]_2$ (**34**), was detected as a main compound (40 mol%/Pd) in the solution together with $PhCH_2COOH$ (14 mol%/Pd) and $(PhCH_2)_2$ (3 mol%/Pd) after 24 h at room temperature. The dimeric iodide complex **34** was separately prepared by mixing $[Pd(COCH_2Ph)Cl(PPh_3)]_2$ (**33**)[30)] (0.020 g, 0.019 mmol) with LiI (0.025 g, 0.19 mmol) in CD_2Cl_2 (0.6 mL) at room temperature. After 2 d, **33** was totally converted into a red solution of iodide-bridged dimer, with small amounts of $PhCH_2COOH$ and $(PhCH_2)_2$. NMR data for **34**: ^1H NMR (CD_2Cl_2, 270 MHz, 293 K) $\delta=7.7$—7.4 (m, 30H, 2 PPh_3), 7.09 (d.br., $J=6$ Hz, 6H, *m,p*-Ph), 6.58 (d, $J=5$ Hz, 4H, *o*-Ph), 3.78 (s, 4H, 2 CH_2). ^{31}P NMR (CD_2Cl_2, 109.4 MHz, 293 K) $\delta=23.7$ (s).

The reaction of **29** (0.015 g, 0.019 mmol) with water in $CDCl_3$ (0.6 mL) solution was examined by ^1H and ^{31}P NMR. After 10 d, 40 mol%/Pd of **29** was converted into $PhCH_2COOH$ (12 mol%/Pd) and $(PhCH_2)_2$ (14 mol%/Pd), and 31 mol% of **29** was found to be transformed into its dimer. After one month, the mixture was analyzed to contain $PhCH_2COOH$ (27 mol%/Pd), $(PhCH_2)_2$ (22 mol%/Pd), $[Pd(COCH_2Ph)Cl(PPh_3)]_2$ (11 mol%/Pd), and small amounts of unidentified compounds.

Thermal Decomposition of *trans*-$[Pd(COCH_2Ph)X(PPh_3)_2]$ (X=Cl,I). In a 100 mL stainless steel autoclave, complex **29** (0.100 g, 0.127 mmol) was mixed with Molecular Sieves 4A (1.0 g) and acetone (3 mL) under an argon atmosphere. The system was then pressurized with CO (50 atm). The reactor was heated in an oil bath at 100 °C for two days. After cooling the system to room temperature, the gas was released and the reaction mixture was filtered to give an orange solution. After evaporation of the volatile matter in the solution, the residue was dissolved in acetone-d_6 and was subjected to analysis by MS (FAB mode), GC-MS, ^1H, and ^{31}P NMR. The formation of $(PhCH_2)_2$, small amounts of $[PhCH_2COPPh_3]^+Cl^-$, and $PhCH_2COOH$ was confirmed.

The same procedure was employed for the analysis of the thermal decomposition products of **28**. The reaction gave $(PhCH_2)_2$ as the main product together with a small amount of $PhCH_2COOH$ and a trace of $[PhCH_2COPPh_3]^+I^-$.

Detection of the Intermediates in the Carbonylation of Benzyl Alcohol. In a 100 mL stainless steel autoclave, benzyl alcohol (0.5 mL, 5 mmol) in acetone-d_6/H_2O (2/0.5 mL) was mixed with $[Pd(PPh_3)_4]$ (0.290 g, 0.25 mmol) and HI (0.132 mL, 1 mmol, and aqueous solution containing 57% of HI) under an argon atmosphere. The system was then pressurized with CO (90 atm) and heated in an oil bath at 90 °C for 2 h. After cooling the system to room temperature, the gas was released and an orange precipitate and a red-brown solution were obtained. After filtration, the filtrate was analyzed by ^1H and ^{31}P NMR to contain a mixture of **2** (2 mol%/alcohol), **3** (2 mol%), **4** (1 mol%), $[PhCH_2PPh_3]^+I^-$ (6 mol%), **34** (0.5 mol%), a trace of $(PhCH_2)_2$, and unreacted benzyl alcohol. The orange crystalline solid, which was washed with acetone and dried, was identified as $[PdI_2(PPh_3)_2]$ (0.13 g, 59%/Pd) by means of NMR and elemental analysis.

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