Bull. Chem. Soc. Jpn., 72, 1851—1855 (1999) 1851

Palladium(II)-Catalyzed Aryl Coupling of Triarylbismuthines under Air

Toshiyuki Ohe, Takumi Tanaka, Masashi Kuroda, Chan Sik Cho, Kouichi Ohe, and Sakae Uemura*

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University,
Sakyo-ku, Kyoto 606-8501

(Received February 8, 1999)

Triarylbismuthines readily reacted with a catalytic amount of palladium(II) acetate in methanol under air to give the corresponding biaryls in high yields. The presence of oxygen was indispensable for this catalytic coupling, biaryl formation being quite slow under nitrogen. Oxygen absorption was observed during the reaction and a Pd-oxygen complex prepared separately worked effectively as a reagent for this coupling even under inert gas.

Organic transformations using bismuth compounds are of current interest. Several examples of conversion of C–Bi bond to C–C bond[1] have been reported, such as Pd(II)-mediated Heck-type reaction of triphenylbismuthine (Ph_3Bi) with alkenes,[2] Pd(0)-mediated biaryl formation by a self-coupling of triarylbismuthines (Ar_3Bi),[3] Pd(0)-catalyzed ketone formation from Ar_3Bi and acyl chlorides,[3] Pd(0)- and Rh(I)-catalyzed carbonylation of Ar_3Bi,[4] and base-induced phenylation of aromatics with organobismuth(V) compounds.[5] Here, in the biaryl formation reaction, it has been reported that Ar_3Bi reacted with an equimolar amount of palladium(II) acetate [$Pd(OAc)_2$] and triethylamine to form biaryls quantitatively in tetrahydrofuran (THF) under argon.[3] On the other hand, in our laboratory, biaryls were formed as by-products in Pd(0) or Rh(I) complex-catalyzed carbonylation of Ar_3Bi in methanol (MeOH) or acetonitrile, giving esters and ketones under carbon monoxide.[4] We carried out further experiments by focusing on this by-product (biaryl) formation and disclosed that Ar_3Bi (except those having a substituent at *ortho*-position) readily gave the corresponding biaryls in high yields by stirring them in MeOH in the presence of a *catalytic amount* of $Pd(OAc)_2$ *under air*. The presence of oxygen was revealed to be indispensable for this catalytic coupling, biaryl formation being quite slow under nitrogen or argon. As one of our series of studies in organic transformations using organoheteroatom compounds of Group 15 (Sb,[6] Bi[4]), we report here the details of this new catalytic reaction.

Results and Discussion

$Pd(OAc)_2$-Catalyzed Phenyl-Coupling of Ph_3Bi in MeOH. Treatment of Ph_3Bi (**1a**) (0.5 mmol) with a catalytic amount of $Pd(OAc)_2$ in MeOH under air at 25 °C for 2 h afforded biphenyl (**2a**) in quite high yield. At first, 0.025 mmol of $Pd(OAc)_2$ (0.05 molar amount of **1a**) was used, but it was revealed that only 0.005 mmol of $Pd(OAc)_2$ (0.01 molar amount of **1a**) was effective enough in this catalytic reaction (Scheme 1). On the other hand, this catalytic reaction was quite slow under N_2. Under pure oxygen, a similar treatment of **1a** with 0.01 molar amount of $Pd(OAc)_2$ also afforded **2a**, but the yield was somewhat lower than that obtained under air and the prolonged reaction time was needed for the completion. Typical results are listed in Table 1. In this coupling, MeOH was revealed to be the solvent of choice, other solvents such as ethanol (EtOH), acetonitrile, THF and dichloromethane (CH_2Cl_2) being not effective at all.

$$\underset{\substack{(\mathbf{1a})\\(0.5\ \mathrm{mmol})}}{\mathrm{Ph_3Bi}}\ \xrightarrow[\mathrm{MeOH(20\ mL),\ 25\ ^\circ C,\ 2\ h}]{\mathrm{Pd(OAc)_2\ (0.005\ mmol)}}\ \underset{(\mathbf{2a})}{\mathrm{Ph\text{-}Ph}}$$

Scheme 1.

$Pd(OAc)_2$-Catalyzed Aryl-Coupling of Other Ar_3Bi in MeOH. Various other triarylbismuthines were similarly treated in MeOH in the presence of a catalytic amount of $Pd(OAc)_2$ under air at 25 °C for 2 h (Scheme 2). Since the compound **1b** was less soluble in MeOH, a larger amount of MeOH was used. Each Ar_3Bi **1b**—**1f** afforded the corresponding biaryl **2b**—**2f** in high yield. In some cases, such as **1b**, **1e**, and **1h**, the formation of a slight amount of the corresponding arene **3** was observed. Triarylbismuthines having a substituent at *ortho*-position such as **1g** and **1h** were inert in this catalytic coupling reaction (Table 2), showing that this reaction was strongly influenced by the steric hindrance at the *ortho*-position of the aryl group.

When the coupling reaction using two kinds of Ar_3Bi was carried out, the product was a mixture of homo-coupling

Table 1. $Pd(OAc)_2$-Catalyzed Ph-Group of Ph_3Bi in MeOH

Atmosphere (1 atm)	GLC Yield (%)[a]
Air	89—92
Air	Trace[b]
O_2	69
O_2	93[c]
N_2	14

a) 0.75 mmol of Ph–Ph corresponds to 100 %. b) Without $Pd(OAc)_2$. c) Reaction time: 15 h.

$$\underset{\substack{(\mathbf{1})\\(0.5\ \text{mmol})}}{\text{Ar}_3\text{Bi}} \xrightarrow[\text{MeOH(20 mL), Air(1 atm), } 25\ ^\circ\text{C, 2 h}]{\text{Pd(OAc)}_2\ (0.005\ \text{mmol})} \underset{(\mathbf{2})}{\text{Ar-Ar}} + \underset{(\mathbf{3})}{\text{ArH}}$$

$$\begin{array}{ll} \text{Ar} = 4\text{-MeOC}_6\text{H}_4(\mathbf{b}) & 3\text{-MeC}_6\text{H}_4(\mathbf{f}) \\ \quad 4\text{-MeC}_6\text{H}_4(\mathbf{c}) & 2\text{-MeC}_6\text{H}_4(\mathbf{g}) \\ \quad 4\text{-FC}_6\text{H}_4(\mathbf{d}) & 2,4,6\text{-Me}_3\text{C}_6\text{H}_2(\mathbf{h}) \\ \quad 4\text{-ClC}_6\text{H}_4(\mathbf{e}) & \end{array}$$

Scheme 2.

Table 2. Coupling of the Ar-Group of Ar_3Bi

Ar_3Bi	GLC Yield (%)[a]	
	2	**3**
1a	89—92	
1b[b]	94	6
1c	99	
1d	81	
1e	92	4
1f	(89)	
1g	5	
1g[b]	15	
1g[c]	5	
1h	0	11

Isolated yield (%) is in parenthesis. a) 0.75 mmol of Ar–Ar and 1.5 mmol of ArH correspond to 100%, respectively. b) MeOH (50 mL). c) MeOH (20 mL) and CH_2Cl_2 (10 mL).

products and a cross-coupling product. Thus, the treatment of **1a** (0.25 mmol) and **1c** (0.25 mmol) in MeOH in the presence of $Pd(OAc)_2$ (0.005 mmol) at 25 °C for 2 h under air afforded a mixture of **2a** (0.18 mmol), 4-MeC_6H_4-Ph (0.30 mmol) and **2c** (0.20 mmol), as shown in Scheme 3.

$$\underset{(0.25\ \text{mmol})}{\mathbf{1a}} + \underset{(0.25\ \text{mmol})}{\mathbf{1c}} \xrightarrow[\text{MeOH(20mL), Air(1 atm), } 25\ ^\circ\text{C, 2 h}]{\text{Pd(OAc)}_2(0.005\ \text{mmol})} \underset{(0.18\ \text{mmol})}{\mathbf{2a}} + \underset{(0.30\ \text{mmol})}{4\text{-MeC}_6\text{H}_4\text{–Ph}} + \underset{(0.20\ \text{mmol})}{\mathbf{2c}}$$

Scheme 3.

Oxygen-Absorption during the Reaction. The absorption of oxygen was observed during this catalytic reaction. When **1a** was treated with 0.01 molar amount of $Pd(OAc)_2$ in MeOH, the amount of the absorbed oxygen corresponded to about a half molar amount of **2a** produced. For example, when 0.48—0.54 mmol of **2a** was produced, 0.22—0.28 mmol of oxygen was consumed. This fact clearly shows that the presence of oxygen was indispensable for this catalytic coupling and that the stoichiometry between reactants and products should be that shown in Scheme 4, although the formation of bismuth oxide was not confirmed.

Catalytic Efficiency of Other Pd Compounds. The effectiveness of various Pd compounds other than $Pd(OAc)_2$ was examined using **1a** in MeOH under air. As shown in Table 3, $PdCl_2$, $Pd(PPh_3)_4$, and Pd black were ineffective and Na_2PdCl_4 was moderately effective, while the activity of $Pd_2(dba)_3$ was revealed to be similar to that of $Pd(OAc)_2$ under both air and N_2. A Pd-oxygen complex $Pd(O_2)(PPh_3)_2$ was moderately effective and prolonged reaction time was needed for completion of the coupling. The catalysts such as $Pd(OAc)_2$, $Pd_2(dba)_3$, $Pd(O_2)(PPh_3)_2$, and Na_2PdCl_4 were soluble in MeOH, while the solubility of $PdCl_2$, $Pd(PPh_3)_4$, and Pd-black was low under similar conditions. It is worth noting here that the treatment of **1a** (0.5 mmol) with a stoichiometric amount (0.375 mmol) of $Pd(O_2)(PPh_3)_2$ in MeOH at 25 °C for 2 h afforded **2a** in high yield even under N_2 (84—87%, Table 3), the result being consistent with the fact that the oxygen was indispensable for this aryl coupling reaction.

Effect of the Additives. In order to obtain some information on the reaction scheme, the coupling reaction of **1a** was carried out in the presence of several radical scavengers such as hydroquinone (**4**), 2,2-diphenyl-1-picrylhydrazyl (**5**), galvinoxyl (**6**), and *m*-dinitrobenzene (**7**) as additives. As shown in Table 4, the compounds **4** and **5** showed strong effects for reducing the product yield, while the compounds

$$4\text{Ar}_3\text{Bi} + 3\text{O}_2 \rightarrow 6\text{Ar–Ar} + 2\text{Bi}_2\text{O}_3$$

Scheme 4.

Table 3. Effect of Pd Compound for the Ph-Coupling of **1a**[a]

Pd compound		Atmosphere	Reaction time	GLC Yield[b]
mmol		1 atm	h	%
$Pd(OAc)_2$	(0.005)	Air	2	89—92
$Pd(OAc)_2$	(0.005)	N_2	2	14
$PdCl_2$	(0.005)	Air	2	12
$Pd(PPh_3)_4$	(0.005)	Air	2	7
Na_2PdCl_4	(0.005)	Air	2	44
$Pd_2(dba)_3$	(0.0025)	Air	2	90
$Pd_2(dba)_3$	(0.0025)	N_2	2	8
$Pd(O_2)(PPh_3)_2$	(0.005)	Air	2	46—49
$Pd(O_2)(PPh_3)_2$	(0.005)	Air	5	87—89
$Pd(O_2)(PPh_3)_2$	(0.375)	N_2	2	84—87

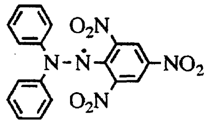
a) All reactions were carried out at 25 °C, using 0.5 mmol of **1a** and 20 mL of MeOH. b) 0.75 mmol of Ph–Ph corresponds to 100%.

Table 4. Effect of the Additive[a)]

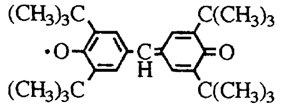
Additive	mmol	GLC Yield (%)[b)]
—	—	89—92
4	0.25	27
4	0.05	37
5[c)]	0.25	13
5[c)]	0.05	30
6[d)]	0.5	80
6[d)]	0.25	77
6[d)]	0.05	89
7	0.5	65
7	0.25	88
7	0.1	86

a) All reactions were carried out at 25 °C for 2 h under air, using 0.5 mmol of **1a** and 20 mL of MeOH. b) 0.75 mmol of Ph–Ph corresponds to 100%,

c)



d)



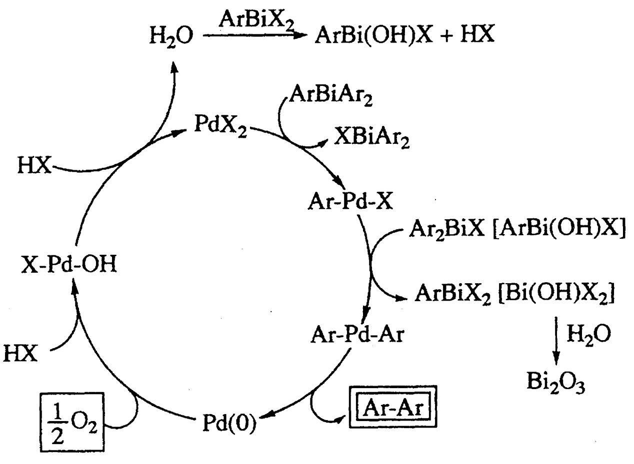
6 and **7** did not. Here, the compounds **4**—**6** are known as radical scavengers, and the compound **7** is known as a chain-radical scavenger. Although the details are not known, this result shows that the reaction may involve a free carbon radical species. Alternatively, the compounds **4** and **5** may disturb the interaction between Pd(0) species and oxygen for regeneration of Pd(II) species.

$Pd(OAc)_2$-Catalyzed Phenyl-Coupling of $Ph_3Bi(OAc)_2$ in MeOH. The properties and the reactions of organobismuth(V) compounds have been widely investigated[1a,3,5,7] and it has been known that aryl coupling of Ar_3BiX_2 proceeded in the presence of a catalytic amount of Pd(0) in THF.[3] Since there is a possibility in the above-described coupling to proceed via arylbismuth(V) compounds, we separately prepared $Ph_3Bi(OAc)_2$ (**8**) and treated it under conditions similar to those described so far. Typical results are shown in Table 5. Treatment of **8** (0.5 mmol) without catalyst in MeOH under air at 25 °C for 2 h scarcely afforded biphenyl (**2a**) and even in the presence of $Pd(OAc)_2$ (0.005 mmol) the yield of **2a** was quite low compared with the case of the coupling reaction using **1a** under the same conditions. More prolonged reaction time was necessary for completion of the phenyl coupling. In contrast, the treatment of **8** (0.5 mmol) with $Pd(OAc)_2$ (0.005 mmol) in MeOH under N_2 afforded **2a** in a slightly higher yield than the case of **1a** under N_2. Here, the compound **8** itself may work as a re-oxidant of the produced Pd(0).

Table 5. Coupling of the Ph-Group of $Ph_3Bi(OAc)_2$ (**8**)[a)]

Atmosphere	MeOH	Reaction time	GLC Yield[b)]
(1 atm)	mL	h	%
Air	20	2	0.4[c)]
Air	20	2	16—25
Air	20	5	75
Air	20	15	87
Air	50	2	61
Air	50	15	89
N_2	20	2	43
N_2	20	15	90

a) All reactions were carried out at 25 °C, using 0.5 mmol of **8** and 0.005 mmol of $Pd(OAc)_2$. b) 0.75 mmol of Ph–Ph corresponds to 100%. c) Without $Pd(OAc)_2$.



(X = OAc, OMe)

Scheme 5.

Plausible Reaction Scheme. Although the details are not yet known for a reaction pathway, we propose Scheme 5 for this catalytic coupling reaction. The transmetallation of Bi(III) moiety of arylbismuth(III) compounds by Pd(II) occurs twice to give Ar–Pd–Ar species, from which reductive elimination occurs to afford biaryl (Ar–Ar) and Pd(0). Then, Pd(0) is re-oxidized by the appropriate amount of oxygen to regenerate Pd(II), probably via a Pd-oxygen complex,[8] since this complex was revealed to be also effective for this reaction as described above. The efficiency of Pd(0) complex, $Pd_2(dba)_3$, can also be explained by this scheme involving the oxidation step of Pd(0) species by oxygen. Although the oxidative addition of the C–Bi bond of Ar_3Bi to the Pd(0) has been proposed[3,4] and this coupling might proceed through this pathway, the experimental results of a very slow reaction and a low product yield under N_2 exclude this possibility.

Experimental

General Procedure. Melting points were determined on a Yanako MP-J3 micro melting point apparatus and are uncorrected. GLC analyses were carried out with a Shimadzu GC-14A with flame ionization detectors equipped with an SE-30 (7 mmϕ × 2 m) column using nitrogen as carrier gas. The GLC yields were determined using appropriate aromatics as internal standards. The isolation of pure products was carried out with column chromatography on SiO_2 (Wakogel C300, about 300 mesh, Wako Pure Chemical Ind., Ltd.).

Materials. Solvents were freshly distilled under N_2 prior to use: MeOH was distilled from in situ prepared $Mg(OMe)_2$ (Mg metal+I_2); THF was distilled from sodium diphenylketyl; dichloromethane (CH_2Cl_2) and benzene were distilled from calcium hydride. Bismuth(III) chloride ($BiCl_3$) was washed by thionyl chloride and dried in vacuo prior to use. Each Ar_3Bi (**1a**: recrystallized from petroleum ether, mp 77—78 °C, lit, 77—78 °C,[9] 78—78.5 °C;[10] **1b**: from ethyl acetate, mp 194—196 °C, lit, 185 °C;[11] **1c**: from EtOH, mp 116—117 °C, lit, 116—117 °C,[12] 119—120 °C;[12] **1d**: from EtOH, mp 79—81 °C, lit, 92—94 °C;[10] **1e**: from petroleum ether, mp 115—116 °C, lit, 115.4 °C;[10] **1f**: from EtOH, mp 55—57 °C, lit, 68 °C;[13] **1g**: from petroleum ether, mp 132—133 °C, lit, 130—131 °C;[12] **1h**: from EtOH, mp 136—137 °C, lit, 136—138 °C,[14] 134—135 °C[15]) was prepared from the corresponding Grignard reagent and $BiCl_3$ in THF. The authentic samples for GLC analyses such as **2b** (from THF, mp 178—180 °C, lit, 175—176 °C[16]), **2c** (from EtOH, mp 121—122 °C, lit, 121—122 °C[9]), **2d** (from MeOH, mp 87—89 °C, lit, 94—95 °C[9]), **2e** (from EtOH, mp 148—149 °C, lit, 148 °C[9]), **2g** [bp 98—99 °C/3 mmHg (1 mmHg = 133.322 Pa)], and 4-MeC_6H_4–Ph (from MeOH, mp 43 °C, lit, 47—48 °C[9]) were synthesized by the cross-coupling reaction between arylmagnesium bromide and aryl iodide (for **2b** and **2e**) or aryl bromide (for others) catalyzed by $Pd(PPh_3)_4$ in THF under N_2. $Pd(PPh_3)_4$[17] and $Pd(O_2)(PPh_3)_2$[18] were synthesized by the literature method. The compound **4** was recrystallized from benzene-acetone prior to use. $Pd(OAc)_2$, $PdCl_2$, $Pd_2(dba)_3$, Na_2PdCl_4, Pd black, **2a**, **5**, **6**, and **7** were commercial products and were used without purification.

Synthesis of Triphenylbismuthine Diacetate (8). The compound was prepared by slightly modifying the reported methods of Suzuki[19] and Barton.[20] To a solution of **1a** (4.40 g, 10 mmol) in CH_2Cl_2 (30 mL), cooled in an ice bath, was added sulfuryl chloride (0.85 mL, $d = 1.67$, 10.5 mmol) by a syringe under N_2. After stirring for 30 min at room temperature, the resulting solution was evaporated in vacuo. The white residue (triphenylbismuthine dichloride) was dissolved in acetone (40 mL, without purification), to which a solution of potassium carbonate (1.62 g, 11.7 mmol) in distilled water (12 mL) was added under air. The solution turned white gradually. After stirring for 5 min at room temperature, the precipitated white powder was collected by filtration, washed by distilled water and acetone, and then dried under vacuum for 2.5 h to give 4.95 g of triphenylbismuthine carbonate, mp 152 °C [decomp, lit, 155 °C (decomp),[20] 164—165 °C[9]].

This carbonate was completely dissolved in a mixture of acetic acid (50 mL) and acetic anhydride (1 mL), where the color of the solution changed to pale yellow with the emission of CO_2. The resulting solution was evaporated in vacuo to give the pale yellow solid. The solid was recrystallized from a mixture of acetic acid (65 mL) and acetone (65 mL) to give 3.14 g (56% yield based on **1a**) of **8**, mp 147 °C (decomp, lit, 152—153 °C,[11] 186 °C,[11] 173 °C[21]). Found: C, 47.02; H, 3.82%. Calcd for $C_{22}H_{21}BiO_4$: C, 47.32; H, 3.79%.

General Procedure for Palladium(II)-Catalyzed Aryl-Coupling of Triarylbismuthines and 8 under Air. In a two-necked flask with a septum inlet and a drying tube filled with silica gel were placed an organobismuth compound (0.5 mmol) and $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) at 25 °C, to which dry MeOH (20 mL) was added by a syringe. After stirring for 2 h at 25 °C, the mixture was poured into water (100 mL), and extracted with CH_2Cl_2 (30 mL×4). The appropriate internal standard was added to the extract. Then the products were analyzed and determined by gas chromatography.

General Procedure for Measurement of the Absorption of Oxygen. In a two-necked flask with a septum inlet and a three-way stopcock connected to an O_2 balloon were placed **1a** (0.5 mmol) and $Pd(OAc)_2$ (1.1 mg, 0.005 mmol) at 25 °C. The system was then flushed with O_2 from the O_2 balloon at room temperature, to which dry MeOH (20 mL) bubbled with O_2 for 1 h was added by a syringe. After the addition of MeOH, the stopcock was closed as soon as possible, and the syringe charged by O_2 was connected through the septum inlet. After stirring for 4 h at 25 °C, the mixture was poured into water (100 mL), and extracted with CH_2Cl_2 (30 mL×4). The extract was added with *trans*-stilbene as an internal standard, and the produced biphenyl (0.54 mmol) was analyzed and determined by gas chromatography. The true volume of the absorbed O_2 was 7 mL (0.28 mmol).

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