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Rhodium(I)- and Palladium(0)-Catalyzed Carbonylation of Triarylbismuthines with Carbon Monoxide via a Possible Oxidative Addition of a Carbon–Bismuth Bond to Rhodium(I) and Palladium(0)

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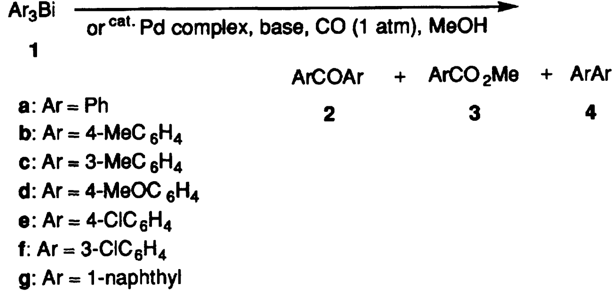
Triarylbismuthines react with carbon monoxide (CO) at atmospheric pressure in acetonitrile at 25 °C in the presence of a catalytic amount of a rhodium compound such as $[RhCl(CO)_2]_2$, $RhCl_3{\cdot}3H_2O$, and $[RhCl(COD)]_2$ to give the corresponding diaryl ketones in high yields. If methanol is used as the solvent, methyl benzoates are also produced. When similar reactions are carried out in methanol in the presence of a catalytic amount of palladium(II) acetate together with potassium carbonate in place of the rhodium compound, methyl benzoates are formed as the sole carbonylation products. The oxidative addition of a carbon–bismuth bond to rhodium(I) and palladium(0) is proposed as the key step of these carbonylation reactions.

The synthetic usefulness of organic and inorganic bismuth compounds has recently increased,[1)] because several carbon–carbon bond forming reactions have been developed. However, clear-cut examples of the conversion of a C–Bi bond to a C–C bond using triarylbismuthines seem as yet to be limited to biaryl formation by a self-coupling of Ar_3Bi,[2)] ketone formation from Ar_3Bi and acyl chlorides[2)] and Heck-type reaction of Ph_3Bi with alkenes,[3)] all catalyzed by palladium salts. On the other hand, we reported recently that a low valent rhodium(I) complex worked as a very efficient catalyst for the carbonylation of triarylbismuthines with atmospheric pressure carbon monoxide (CO) to afford diaryl ketones and methyl benzoates (the former being the major product) in high yields at room temperature.[4)] During the continuation of this work to clarify the reaction pathway and to look for other catalytic systems, we recently discovered that carbonylation also proceeded in the presence of a catalytic amount of palladium(II) salt together with a base to give methyl benzoates as the sole carbonylation products. This represents another example of a C–C bond forming reaction using triarylbismuthines. We report here the results of both catalytic carbonylation systems in detail. Among group 15 elements, only bismuth showed this characteristic reaction, and triarylarsines and triarylstibines afforded almost no carbonylation products under similar conditions. The pathway involving oxidative addition of a C–Bi bond to rhodium(I) and palladium(0) was proposed as the key step of these carbonylation reactions.

Results and Discussion

Rhodium(I)-Catalyzed Carbonylation of Triarylbismuthines (1). First, the carbonylation of triphenylbismuthine (**1a**) with atmospheric pressure carbon monoxide (CO) was investigated in a variety of aprotic solvents at 25 °C in the presence of a catalytic amount of $[RhCl(CO)_2]_2$ (5 mol%) for various reaction times (Scheme 1). Benzophenone (**2a**) was produced as the main product, together with a small amount of biphenyl. The yield of **2a** was increased by prolonging the reaction time up to 20 h (71%: 42% for 8 h, 67% for 17 h), but it was not improved for much longer times. Acetonitrile was the solvent of choice, and other solvents such as tetrahydrofuran (THF), dichloromethane, benzene, and ethyl acetate were moderately effective. The reaction proceeded even by the use of 1 mol% of $[RhCl(CO)_2]_2$ in acetonitrile, but the reac-



Scheme 1.
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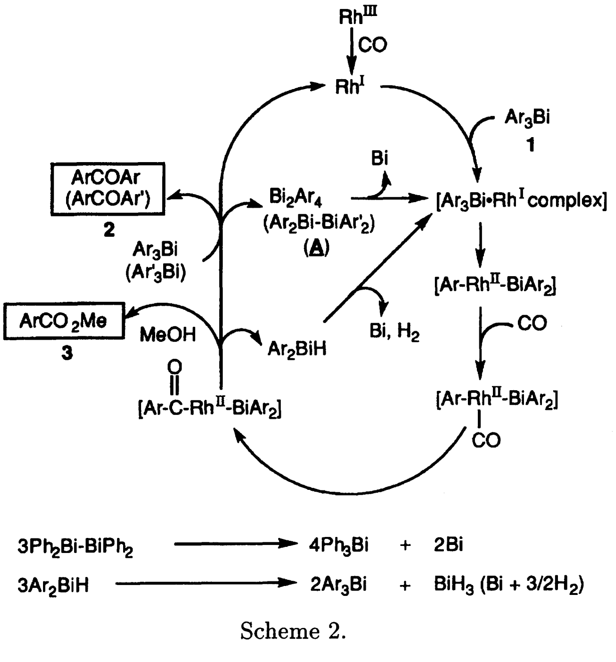
tion became slow (the yield of **2a** was 24%). Other rhodium complexes such as $RhCl(CO)(PPh_3)_2$, $RhH(CO)(PPh_3)_3$, and $RhCl(PPh_3)_3$ were moderately effective: thus 12—44% of **2a** was obtained in acetonitrile for a longer reaction time, but $Rh_2(OAc)_4$, $Rh(acac)_3$, and $Rh_6(CO)_{16}$ were ineffective. $RhCl_3{\cdot}3H_2O$ and $[RhCl(COD)]_2$ exhibited nearly the same catalytic activity as $[RhCl(CO)_2]_2$ under the employed reaction conditions. Typical results are summarized in Table 1. From other easily available triarylbismuthines **1**, the corresponding diaryl ketones **2** were also formed in good yields.

On the other hand, when the reaction was carried out in methanol using effective rhodium catalysts, the formation of methyl benzoates **3** was observed together with diaryl ketones **2**, the latter being the major product. In this case little **4** was formed. Representative results are summarized in Table 2.

Although the exact nature of the reaction is not certain and spectroscopic studies to look for intermediate species were unsuccessful, the most plausible reaction pathway seems to be that shown in Scheme 2. Thus, coordination of triarylbismuthines **1** to Rh^{I} followed by aryl migration from Bi to Rh produces an organorhodium compound, where CO coordination to Rh and then aryl migration from Rh to carbon of CO occurs to produce an aroylrhodium intermediate. The intermediate reacts with another Ar_3Bi to give the product ketone and a dibismuthine (**A**). It is known that other aryl compounds of group 15 elements such as triphenylphosphine and triphenylarsine react with $[RhCl(CO)_2]_2$ to give their coordination compounds $[(Ph_3M)_2Rh(CO)Cl]$ (M=P, As) by displacing a CO ligand.$^{5)}$ Rhodium(III) chloride (a catalytic amount) may be reduced to some rhodium(I) species under reaction conditions containing CO.$^{6)}$ The separately confirmed retardation of the $[RhCl(CO)_2]_2$-catalyzed carbonylation by addition of triphenylphosphine (e.g., the yield of **2a** decreased from 52 to 5% by addition of 2 mmol of Ph_3P in THF) is explained by considering preferred coordination to Rh^{I} of the stronger ligand Ph_3P rather than Ar_3Bi to afford a stable complex. In fact, the treatment of triphenylstibine with CO (1—20 atm) in the presence of a stoichiometric amount of $RhCl_3{\cdot}3H_2O$ in methanol or THF at 25 °C afforded the complex $RhCl_3(CO)(SbPh_3)_2$ in 71—94% yield, and no carbonylated products were formed. The result indicates that other compounds of group 15 elements such as triphenylstibine and triphenylarsine can not be activated at all in this rhodium-catalyzed system because of their strong coordination to Rh and/or because the mean bond dissociation energies of the Ph–Sb and Ph–As bonds are stronger than that of the Ph–Bi bond.$^{7)}$ The aryl migration process may be considered as an oxidative addition of a C–Bi bond to Rh^{I}, the precedent of which is found in the proposal of addition of a C–Hg bond to Rh^{I} in the Rh^{I}-mediated carbonylation of some vinyl- and aryl-mercury(II) chlorides.$^{8)}$ It is also noteworthy that the oxidative addition of a C–P bond to various transition metals, such as Ru^{0}, Os^{0}, Rh^{I}, Pd, and Pt, is well documented.$^{9)}$



Scheme 2.

When equimolar amounts of triphenylbismuthine (**1a**) (0.50 mmol) and tri-*p*-tolylbismuthine (**1b**) (0.50 mmol) were treated with CO (1 atm) in the presence of a catalytic amount of $[RhCl(CO)_2]_2$ (0.05 mmol) in acetonitrile (20 mL) at 25 °C for 25 h, a mixture of benzophenone (**2a**) (0.26 mmol), di-*p*-tolyl ketone (**2b**) (0.23 mmol) and phenyl *p*-tolyl ketone (0.47 mmol) was obtained, together with small amounts of the corresponding biaryls. Similar crossover reactions between other triarylbismuthines (**1d** and **1e**) and **1a** also afforded three different ketones, unsymmetrical ketones being always the main products (Table 3). The formation of three different ketones in these crossover reactions supports the assumption of intermolecular reactions between an intermediate aroylrhodium(II) compound and the triarylbismuthines shown in the catalytic cycle of Scheme 2.

As described above, even if the reaction was conducted in a protic media, the main carbonylation products were diaryl ketones **2**, and not methyl benzoates **3**. This fact may suggest that the coordination of triarylbismuthines **1** to aroylrhodium(II) compound leading to **2** via an aroylarylrhodium intermediate is faster than methanolysis of the species leading to **3** (Scheme 3).

In Scheme 2, we proposed the formation of tetraaryldibismuthines $Ar_2Bi–BiAr_2$ (**A**). We confirmed separately that $Ph_2Bi–BiPh_2$, prepared from $Ph_2BiCl^{10)}$ by the reported method,$^{11)}$ also reacted with CO in the presence of $[RhCl(CO)_2]_2$ catalyst to afford **2a** in 49% yield, based on the starting dibismuthine. Since it is known that the dibismuthine, unstable in air, disproportionates to triphenylbismuthine and metallic Bi

Table 1. Carbonylation of Triarylbismuthines **1** with CO (1 atm) in the Presence of a Rhodium Complex in Aprotic Solvent[a)]

Triarylbismuthine	Rh complex	Solvent	Time	Products and yield/%[b)]	
		10 mL	h	**2**	**4**
1a	$[RhCl(CO)_2]_2$	MeCN	20	71	5
1a	$[RhCl(CO)_2]_2$	THF	20	52	2
1a	$[RhCl(CO)_2]_2$	CH_2Cl_2	20	32	1
1a	$[RhCl(CO)_2]_2$	Benzene	20	45	0
1a	$[RhCl(CO)_2]_2$	EtOAc	20	31	10
1a	$RhCl_3 \cdot 3H_2O$	MeCN	24	52	Tr.
1a	$[RhCl(COD)]_2$	MeCN	20	67	7
1a	$RhCl(CO)(PPh_3)_2$	MeCN	42	39	8
1a	$RhH(CO)(PPh_3)_3$	MeCN	42	44	4
1a	$RhCl(PPh_3)_3$	MeCN	43	12	17
1a	$Rh_2(OAc)_4$	MeCN	49	4	29
1a	$Rh(acac)_3$	MeCN	24	Tr.	22
1a	$Rh_6(CO)_{16}$	MeCN	42	0	0
1b	$[RhCl(CO)_2]_2$	MeCN	20	72	15
1c	$[RhCl(CO)_2]_2$	MeCN	20	70(61)[c)]	3
1d	$[RhCl(CO)_2]_2$	MeCN	20	49	Tr.
1e	$[RhCl(CO)_2]_2$	MeCN	20	67	Tr.
1f	$[RhCl(CO)_2]_2$	MeCN	20	68(60)[c)]	Tr.
1g	$[RhCl(CO)_2]_2$	CH_2Cl_2	25	27[c)]	0

a) All the reactions were carried out with triarylbismuthine **1** (0.5 mmol) and rhodium complex (0.025 mmol) at 25 °C. b) GLC yield based on **1** unless otherwise stated: 0.75 mmol of **2** and **4** corresponds to 100% yield, respectively. c) Isolated yield.

Table 2. Carbonylation of Triarylbismuthines **1** with CO (1 atm) in the Presence of a Rhodium(I) Complex in Methanol[a)]

Triarylbismuthine	Rh complex	Time	Products and yield/%[b)]		
		h	**2**	**3**	**4**
1a	$[RhCl(CO)_2]_2$	20	73	26	0
1a	$[RhCl(CO)_2]_2$[c)]	45	55	12	0
1a	$RhCl_3 \cdot 3H_2O$	24	70	21	0
1a	$[RhCl(COD)]_2$	24	74	23	0
1b	$[RhCl(CO)_2]_2$	20	68	17	15
1b	$RhCl_3 \cdot 3H_2O$[d)]	24	68	16	15
1c	$[RhCl(CO)_2]_2$	20	77	20	2
1d	$[RhCl(CO)_2]_2$	20	11	19	0
1e	$[RhCl(CO)_2]_2$	20	76	22	0
1f	$[RhCl(CO)_2]_2$	20	70	25	0
1g	$[RhCl(CO)_2]_2$	20	0	0	0

a) All the reactions were carried out with triarylbismuthine **1** (0.5 mmol) and rhodium complex (0.025 mmol) in MeOH (10 mL) at 25 °C for 20 h unless otherwise stated. b) GLC yield based on **1** unless otherwise stated: 1.5 mmol of **3** and 0.75 mmol of **2** and **4** correspond to 100% yield, respectively. c) 1 mol%. d) 10 mol%.

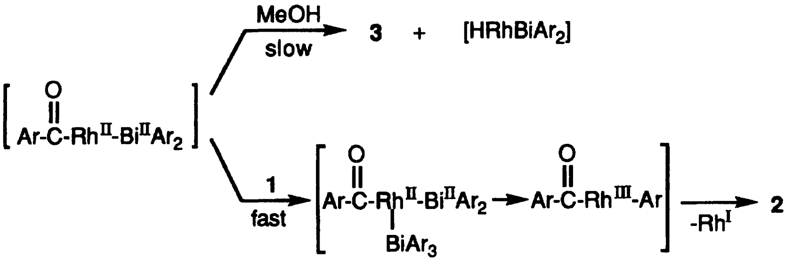
(Scheme 2), it might also be possible that triphenylbismuthine thus formed partly reacted in the control experiment.

The bismuth in organobismuth compounds in the present carbonylation seems to be changed to a metallic Bi, since, for example, the formation of 73 and 26% of **2a** and **3a** from 0.5 mmol of **1a** in methanol (Table 2) means the transfer of 1.49 out of 1.5 phenyl groups to the product. In the case of methanol as solvent, the formation of Ar_2BiH is expected, which might disproportionate to Ar_3Bi and BiH_3. The latter compound is known to be very unstable and it may decompose to Bi and H_2 (Scheme 2). Analysis of the precipitated gray-black solid showed, after thorough washing with $CHCl_3$ and diethyl ether, the absence of any organic groups by FT-IR and the presence of Bi and a trace of Rh as elements by X-ray fluorescence (XRF). On the other hand, analysis with X-ray photoelectron spectra (XPS) showed the presence of trivalent Bi (not zerovalent Bi) and divalent oxygen, suggesting that the precipitated

Table 3. Rhodium(I)-Catalyzed Crossover Carbonylation between **1a** and Tris(*p*-substituted aryl)bismuthines[a)]

Triarylbismuthine	Yield/mmol[b)]			
	PhCOPh	PhCOAr	ArCOAr	Total/mmol
1b	0.257(1)	0.471(1.83)	0.231(0.90)	0.959
1d	0.235(1)	0.312(1.33)	0.126(0.54)	0.673
1e	0.321(1)	0.417(1.30)	0.171(0.53)	0.909

a) All the reactions were carried out with **1a** (0.5 mmol), triarylbismuthine (0.5 mmol) and $[RhCl(CO)_2]_2$ (0.05 mmol) in MeCN (20 mL) at 25 °C for 25 h. b) By GLC. Relative ratio based on PhCOPh is shown in parentheses.



Scheme 3.

metallic Bi is very labile to be oxidized by air to afford Bi_2O_3 and/or other Bi^{3+} species (see Experimental).

Palladium(0)-Catalyzed Carbonylation of Triarylbismuthines (1). Next, we examined whether other transition metal complexes catalyze this carbonylation. We found that various palladium(II) salts catalyzed the reaction in the presence of a base (Scheme 1). Thus, on treatment of triphenylbismuthine (**1a**) with an atmospheric pressure of CO in the presence of a catalytic amount of palladium(II) acetate (5 mol%) in methanol at 25 °C for 20 h, only small amounts of methyl benzoate (**3a**) (9%) and benzophenone (**2a**) (2%) were obtained together with biphenyl (**4a**) (6%). However, when potassium carbonate (K_2CO_3) was added to this reaction system, a quite good yield of **3a** was obtained as the sole carbonylation product; thus, 24% for 10 h, 47% for 15 h, and 60—64% for 20—30 h. Among bases examined, K_2CO_3 was the most effective; other bases such as $NaHCO_3$, Na_2CO_3, NaOH, and KOH were moderately effective, but bases such as $Ca(OH)_2$, NaOAc, and Et_3N were ineffective for this carbonylation. With other readily available triarylbismuthines, **3** and **4** were also formed in good yields, but **2** was not obtained. Typical results are summarized in Table 4. On the other hand, when this Pd-catalyzed reaction was carried out in acetonitrile or THF as the solvent in place of methanol, almost no carbonylation occurred, in sharp contrast to the Rh(I)-catalyzed reaction system.

Table 4. Carbonylation of Triarylbismuthines **1** with CO (1 atm) in the Presence of Palladium(II) Acetate and a Base in Methanol[a)]

Triarylbismuthine	Base	Products and yield/%[b)]		
		2	**3**	**4**
1a	—	2	9	6
1a	K_2CO_3	0[c)]	60—64[c)]	20—22[c)]
1a	$NaHCO_3$	3	32	13
1a	Na_2CO_3	2	50	17
1a	NaOH	0	45	16
1a	KOH	1	46	21
1a	$Ca(OH)_2$	0	14	5
1a	NaOAc	3	14	15
1a	Et_3N	1	5	7
1b	K_2CO_3	0	67	24
1c	K_2CO_3	0	43(41)[d)]	14
1d	K_2CO_3	0	22	5
1e	K_2CO_3	0	60	33
1f	K_2CO_3	0	40[d)]	35[d)]
1g	K_2CO_3	0	0	0

a) All the reactions were carried out with triarylbismuthine **1** (0.5 mmol), $Pd(OAc)_2$ (0.025 mmol) and a base (1 mmol) in MeOH (10 mL) at 25 °C for 20 h. b) GLC yield based on **1** unless otherwise stated: 1.5 mmol of **3** and 0.75 mmol of **2** and **4** correspond to 100% yield, respectively. c) Several runs. d) Isolated yield.

As far as the reaction scheme is concerned, the following findings seem to support the pathway via an oxidative addition of a C–Bi bond to Pd^0. The reduction of $Pd(OAc)_2$ to Pd(0) can be derived from several routes in this reaction system; i. e., the aryl coupling reaction of arylpalladium(II) species [ArPdOAc] formed in situ by transmetallation between triarylbismuthine and palladium(II) acetate[3b)] and the oxidation of triarylbismuthine with $Pd(OAc)_2$, as is known between triphenylphosphine and $Pd(OAc)_2$.[12)] The following experimental observation is also worth noting as evidence for the presence of palladium(0) species in our catalytic system. When iodobenzene (1 mmol) was used in place of triphenylbismuthine (**1a**) in the reaction with CO (1 atm) at 25 °C for 20 h, **3a** was obtained in 43% yield. The reaction is easily expected to proceed via the oxidative addition of a C–I bond to Pd^0, since such a process is quite well-known.[13] A lower yield of **3a** obtained here than that from **1a** shows that the addition of a C–Bi bond to Pd^0 is faster than that of a C–I bond under the employed reaction conditions. Further, a similar carbonylation of **1a** using tris(dibenzylideneacetone)dipalladium(0) in place of $Pd(OAc)_2/K_2CO_3$ afforded methyl benzoate and benzophenone as carbonylated products in 25 and 2% yields, respectively (Table 5). Although the yield is low, this phenomenon also supports the assumption of oxidative addition of a C–Bi bond to Pd^0.

We presume that the reaction proceeds as in the case of the rhodium(I)-catalyzed carbonylation. Thus, the initial coordination of triarylbismuthine **1** to Pd^0, followed by aryl migration from Bi to Pd, produces an organopalladium compound. Subsequent reaction with CO, followed by aryl migration, affords an aroylpalladium compound such as $ArCOPdBiAr_2$ which reacts with methanol to give methyl benzoates and Ar_2BiH. The separately confirmed retardation of this palladium-catalyzed carbonylation by addition of phosphine ligand is also explicable in terms of preferred coordination to Pd of the stronger phosphine compound rather than Ar_3Bi (Table 5). In fact, while other palladium salts or complexes were moderately effective for this carbonylation, the complexes having triphenylphosphine as a ligand such as $Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$, and $Pd(CO)(PPh_3)_3$ were ineffective. The aryl migration process may also be considered as oxidative addition of a C–Bi bond to Pd^0, the precedents of which are found in the proposal of addition of a C–Hg bond and a C–B bond to Pd^0 in the palladium-catalyzed carbonylation of some vinylmercurials[14] and aryl and alkenylboronic acids and their esters,[15] respectively. As described in the former section, the oxidative addition of Pd^0 or Pd^{II} to a C–P bond is well documented.[9] In the reaction with trimesitylbismuthine (0.5 mmol) under $Pd(OAc)_2/K_2CO_3$ system, carbonylation products were not formed and only mesitylene was obtained in a small amount (0.06 mmol). This may be due to the difficulty of initial coordination of Bi to Pd because of its steric bulkiness.

Experimental

General Procedures. ^1H (270 MHz) and ^{13}C (67.8 MHz) NMR spectra were recorded on a JEOL GSX-270 spectrometer using Me_4Si as an internal standard in $CDCl_3$. Chemical shifts are reported in δ units downfield from Me_4Si. IR spectra were recorded on Hitachi EPI-G2 and JEOL JIR-7000 (FT) infrared spectrophotometers. X-Ray fluorescence (XRF) analyses were carried out on KEVEX (Delta XRF analyst system). X-Ray photoelectron spectra (XPS) were measured on a Shimadzu ESCA-1000 instrument irradiated with Mg $K\alpha$ and the observed binding energies were calibrated with 285.0 eV for C 1s electron. Melting points were determined on a Yanaco MP-J3 micro melting point apparatus and are uncorrected. GLC analyses were carried out with Hitachi 163 and Shimadzu GC-14A instruments equipped with a EGSS-X (10% on Chromosorb W, 60—80 mesh, 3 mm×2 m) and CBP 10-S25-050 (Shimadzu, fused silica capillary column, 0.33 mm×25 m, 5.0 μm film thickness) columns, respectively, using nitrogen as carrier gas. GLC yields were determined using suitable hydrocarbons as internal standards. The isolation of pure products was carried out with column chromatography (Wakogel C-200, 100—200 mesh, Wako Pure Chemical Ind., Ltd.) or thin-layer chromatography (silica gel 60 HF_{254}, Merck).

Materials. Solvents were freshly distilled prior to use: Acetonitrile was distilled from phosphorus pentaoxide; tetrahydrofuran was distilled from lithium aluminium hydride; methanol, dichloromethane, ethyl acetate, and benzene were distilled from calcium hydride. The following known triarylbismuthines were prepared by reported methods from the corresponding Grignard reagents and $BiCl_3$: $(4\text{-}MeC_6H_4)_3Bi$,[16] $(3\text{-}MeC_6H_4)_3Bi$,[16] $(4\text{-}MeOC_6H_4)_3Bi$,[16] $(4\text{-}ClC_6H_4)_3Bi$,[17] $(3\text{-}ClC_6H_4)_3Bi$,[17] tri-1-naphthylbismuthine,[18] tris(2,4,6-trimethylphenyl)bismuthine,[19] Commercial triphenylbismuthine and triphenylstibine were used without further purification. Unsymmetrical ketones such as phenyl *p*-tolyl ketone (mp 56—57 °C; lit,[20] mp 59.5 °C), *p*-methoxyphenyl phenyl ketone (mp 60.5—61.5 °C; lit,[21] mp 61—62 °C), and *p*-chlorophenyl phenyl ketone (mp 74—75 °C; lit,[22] mp 75—76 °C) were prepared separately in 65—80% yield by the treatment of the corresponding acid chlorides with sodium tetraphenylborate in the presence of $Pd(PPh_3)_4$.[23] They were used as authentic samples for GLC determination. Transition metal salts such as $RhCl_3\cdot 3H_2O$, $RhCl(PPh_3)_3$, $Rh_2(OAc)_4$, $Rh(acac)_3$, $Rh_6(CO)_{16}$, $[RhCl(COD)_2]_2$, $Pd(OAc)_2$, $PdCl_2$, Na_2PdCl_4, $Pd(PPh_3)_4$, and $Pd_2(dba)_3$ were commercial products. $[RhCl(CO)_2]_2$,[24] $RhCl(CO)(PPh_3)_2$,[6] $RhH(CO)(PPh_3)_3$,[25] $PdCl_2(PPh_3)_2$,[26] $PdCl_2(PhCN)_2$,[27] and $Pd(CO)(PPh_3)_3$[28] were synthesized by reported methods.

General Procedure for Rh(I)-Catalyzed Carbonylation of Triarylbismuthines with Carbon Monoxide. In a two-necked 30 mL round-bottom flask, equipped with a septum inlet and a three-way stopcock, were placed triarylbismuthine (0.5 mmol), metal salt (0.025 mmol), and bibenzyl (a suitable amount as an internal standard for GLC determination). The system was then flushed with CO from a CO-filled balloon connected to the flask; then dry solvent (10 mL) was injected by a syringe. After the mixture had been stirred for an appropriate time at 25 °C, a gray to black solid was filtered off. The filtrate was poured into brine (50 mL) and extracted with dichloromethane (30 mL×2). The extract was washed with water and dried over anhydrous Na_2SO_4. GLC analysis revealed the presence of methyl benzoates, diaryl ketones and biaryls. Some diaryl ketones were isolated by column or thin-layer chromatography using ethyl acetate–hexane as an eluent.

3,3′-Dimethylbenzophenone (2c): Mp 43—44 °C (lit,[29] mp 45 °C); IR ($CHCl_3$) 1655 cm^{-1}; ^1HNMR δ_H= 2.42 (6H, s), 7.32—7.41 (4H, m), and 7.55—7.63 (4H, m); ^{13}CNMR δ_C=21.4, 127.4, 128.0, 130.4, 133.1, 137.8, 138.1, and 197.2.

3,3′-Dichlorobenzophenone (2f): Mp 123.5—124.5 °C (lit,[30] mp 123.8—124.9 °C); IR ($CHCl_3$) 1660 cm^{-1}; ^1HNMR δ_H=7.27—7.46 (2H, m), 7.55—7.66 (4H, m), and

Table 5. Carbonylation of Triphenylbismuthine (**1a**) with CO (1 atm) in the Presence of a Palladium Complex in Methanol[a)]

Run	Palladium salt	Base or additive (mmol)	Products and yield/%[b)]		
			2a	**3a**	**4a**
1	$Pd(OAc)_2$	$PPh_3(0.1)$	1	1	7
2	$Pd(OAc)_2$	$K_2CO_3(1)/PPh_3(0.05)$	0	Tr.	6
3	$Pd(OAc)_2$	$K_2CO_3(1)$/dppp[c)](0.025)	0	13	15
4	$PdCl_2$	$K_2CO_3(1)$	0	43	15
5	$PdCl_2$	$K_2CO_3(1)/LiCl(1)$	3	41	19
6	$PdCl_2$	$KOH(1)/Et_3N(1)$	0	23	7
7	Li_2PdCl_4[d)]	$K_2CO_3(1)$	2	37	13
8	Na_2PdCl_4	$K_2CO_3(1)$	1	41	16
9	$PdCl_2(PhCN)_2$	$K_2CO_3(1)$	0	47	19
10	$PdCl_2(PPh_3)_2$	$K_2CO_3(1)$	0	7	1
11	$Pd(PPh_3)_4$	—	0	2	30
12	$Pd(PPh_3)_4$	$K_2CO_3(1)$	0	0	26
13	$Pd(CO)(PPh_3)_3$	—	0	1	Tr.
14	$Pd_2(dba)_3$	—	2	25	14

a) All the reactions were carried out with triphenylbismuthine (0.5 mmol) and palladium complex (0.025 mmol) in MeOH (10 mL) at 25 °C for 20 h. b) GLC yield based on **1a**. 1.5 mmol of **3a** and 0.75 mmol of **2a** and **4a** correspond to 100% yield, respectively. c) 1,3-Bis(diphenylphosphino)propane. d) Li_2PdCl_4 denotes a mixture of $PdCl_2$ and LiCl (1 : 2).

7.76—7.77 (2H, m); ^{13}C NMR δ_C=128.1, 129.8, 129.8, 132.8, 134.8, 138.6, and 193.7.

Di-1-naphthyl Ketone (2g): Mp 99—100 °C (lit,[31)] mp 99—100 °C); IR ($CHCl_3$) 1655 cm^{-1}; ^{1}H NMR δ_H= 7.38—7.44 (2H, m), 7.51—7.60 (6H, m), 7.89—8.02 (4H, m), and 8.53—8.57 (2H, m); ^{13}C NMR δ_C=124.4, 125.9, 126.6, 127.9, 128.5, 130.4, 131.2, 132.5, 133.9, 137.2, and 199.8.

Analysis of the Precipitated Gray-Black Solids. The gray black solids obtained from carbonylation of **1a** (0.440 g, 1 mmol) using $[RhCl(CO)_2]_2$ (0.019 g, 0.05 mmol) in MeOH (20 mL) were washed with $CHCl_3$ and then by diethyl ether and dried in vacuo (0.176 g). They were almost FT-IR inactive. XRF analysis showed the presence of bismuth element (ca. 50%) and a trace amount of rhodium element. In the analysis using XPS, the Bi $4f_{7/2}$ and O 1s binding energies were observed at 159.4 and 530.8 eV, in good agreement with literature values[32)] for Bi^{3+} and O^{2-}, respectively. A satellite at 157.2 eV, presumably assignable to metallic Bi, appeared by Ar^+-etching, but the major Bi $4f_{7/2}$ was still Bi^{3+} at 159.6 eV.

General Procedure for $[RhCl(CO)_2]_2$-Catalyzed Crossover Carbonylation between Triphenylbismuthine and Tris(*p*-substituted aryl)bismuthines with Carbon Monoxide. In a two-necked 30 mL round-bottom flask, equipped with a septum inlet and a three-way stopcock, were placed triphenylbismuthine (0.220 g, 0.5 mmol), tris(*p*-substituted aryl)bismuthine (0.5 mmol), $[RhCl(CO)_2]_2$ (0.019 g, 0.05 mmol) and bibenzyl (an internal standard for GLC). The system was then flushed with CO from a CO-filled balloon connected to the flask; then dry acetonitrile (20 mL) was injected by a syringe. After the mixture had been stirred at 25 °C for 24 h, the precipitated black solid was filtered off and the filtrate was poured into brine (100 mL) and extracted with dichloromethane (50 mL×2). The organic phase was washed with water and dried over anhydrous Na_2SO_4. GLC analysis revealed the presence of symmetrical and unsymmetrical ketones, together with minor amounts of biaryls.

$[RhCl(CO)_2]_2$-Catalyzed Carbonylation of Tetraphenyldibismuthine with Carbon Monoxide. In a two-necked 30 mL round-bottom flask with a septum inlet and a three-way stopcock were placed tetraphenyldibismuthine (0.363 g, 0.5 mmol, a brown solid; prepared from Ph_2BiCl[9)] and sodium in liquid NH_3[10)]), $[RhCl(CO)_2]_2$ (0.0097 g, 0.025 mmol) and bibenzyl (an internal standard for GLC). The system was then flushed with CO from a CO balloon connected to the flask at 25 °C, to which dry acetonitrile (10 mL) was added by a syringe. After an initial black suspension was stirred for 22 h at 25 °C, the resulting brown precipitates were filtered off. The colorless filtrate was poured into brine (50 mL) and extracted with dichloromethane (30 mL×2). The extract was washed with water and dried over anhydrous Na_2SO_4. GLC analysis of the extract revealed the presence of benzophenone (0.49 mmol, 49%) together with a trace amount of biphenyl.

A Facile Synthesis of $RhCl_3(CO)(SbPh_3)_2$. Treatment of triphenylstibine with CO (1—20 atm) in the presence of a stoichiometric amount of $RhCl_3 \cdot 3H_2O$ in methanol or THF at 25 °C afforded the complex $RhCl_3(CO)(SbPh_3)_2$ in 71—94% yields. A typical experimental procedure is as follows.

In a two-necked 30 mL round-bottom flask with a septum inlet and a three-way stopcock were placed $RhCl_3 \cdot 3H_2O$ (0.263 g, 1 mmol) and triphenylstibine (0.353 g, 1 mmol). The system was then flushed with CO from a CO balloon connected to the flask at 25 °C, to which dry methanol (10 mL) was added by a syringe. After an initial reddish brown suspension was stirred for 20 h at 25 °C, the resulting yellow orange precipitates were collected by filtration and washed with diethyl ether several times. The material was then dried in vacuo to give a yellow solid (0.429 g, 91%): IR (neat) 3057, 2069 (C=O), 1576, 1479, 1433, 1065, 997, 737, and 692 cm^{-1}. (Found: C, 47.11; H, 3.34%. Calcd for $C_{37}H_{30}Cl_3OSb_2Rh$: C, 47.06; H, 3.18%).

Such a complex has previously been prepared by adding chlorine in CCl_4 to the solution of $RhCl(CO)(SbPh_3)_2$ at 0 °C.[33)]

Typical Procedure for Palladium-Catalyzed Carbonylation of Triarylbismuthines with Carbon Monoxide. In a two-necked 30 mL round-bottom flask with a septum inlet and a three-way stopcock were placed triphenylbismuthine (0.220 g, 0.5 mmol), palladium(II) acetate (0.0056 g, 0.025 mmol), potassium carbonate (0.138 g, 1 mmol) and bibenzyl (an internal standard for GLC). The system was then flushed with CO from a CO balloon connected to the flask at 25 °C, to which dry methanol (10 mL) was added by a syringe. After the black suspension was stirred for 20 h at 25 °C, a black precipitate was filtered off. The colorless filtrate was poured into brine (50 mL) and extracted with dichloromethane (30 mL×2). The extract was washed with water and dried over anhydrous Na_2SO_4. GLC analysis revealed the presence of methyl benzoate (0.96 mmol, 64%) and biphenyl (0.17 mmol, 22%). The esters **3c** and **3f** were isolated by thin-layer chromatography using ethyl acetate–hexane (1 : 10) as an eluent; both were found to be identical with commercial products by GLC analysis.

Methyl 3-Methylbenzoate (3c): IR (neat) 1720 (C=O) cm^{-1}; ^{1}H NMR $\delta_H=2.40$ (3H, s), 3.90 (3H, s), 7.29—7.37 (2H, m), and 7.82—7.85 (2H, m); ^{13}C NMR $\delta_C=21.3$, 52.0, 126.7, 128.3, 130.1, 130.1, 133.7, 138.1, and 167.3.

Methyl 3-Chlorobenzoate (3f): IR (neat) 1725 (C=O) cm^{-1}; ^{1}H NMR $\delta_H=3.91$ (3H, s), 7.33—7.39 (1H, m), 7.49—7.53 (1H, m), 7.89—7.93 (1H, m), and 7.99—8.01 (1H, m); ^{13}C NMR $\delta_C=52.4$, 127.7, 129.7, 129.7, 131.9, 132.9, 134.5, and 165.8 (C=O).

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