

Palladium(II)- and Rhodium(III)-Catalyzed Carbonylation Reaction of Aryltin Compounds

Toshiyuki Ohe, Shin-ichi Motofusa, Kouichi Ohe, and Sakae Uemura*

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

(Received February 13, 2001)

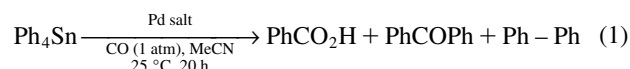
A variety of aryltin compounds can be employed for carbonylation reactions in the presence of a catalytic amount of palladium(II) salt with reoxidant in acetonitrile or acetic acid under an atmospheric pressure of carbon monoxide (CO) to afford arenecarboxylic acids and diaryl ketones. Similar reactions also proceed by using rhodium(III) salt as a catalyst, where the presence of reoxidant is sometimes not necessary. More than one of two, three, or four aryl groups of aryltin compounds, and almost all of them in some cases, can be transferred to the products in this catalytic carbonylation.

Organic transformations using organotin compounds have been powerful tools for organic synthesis in the last two decades.¹ Many examples of the conversion of C–Sn bond to C–C bond have been reported, such as Pd(0)-catalyzed cross coupling reaction with organic halides or acyl halides (the so-called Stille cross coupling),¹ Lewis acid-mediated or transition metal-catalyzed 1,2-addition reaction to carbonyl compounds and imines,² Heck-type dehydroarylation reaction of α,β -unsaturated carbonyl compounds,³ Michael-type hydroarylation reaction of α,β -unsaturated carbonyl compounds,⁴ organic transformations including radical intermediates,⁵ and so on. The carbonylation reactions of organotin compounds with carbon monoxide (CO) have been investigated for these three decades including Stille carbonylative cross coupling,^{1,6} but there are only very few examples of simple carbonylation as far as we know.⁷ In these reactions it was so far thought that at most only one of four organic groups of tetraorganotin compounds can be transferred to the products. However, the investigation to utilize more than one organic group of organoheteroatom compounds for organic reactions is of current interest from the viewpoint of atom economy.⁸ Actually, it has recently been disclosed that almost all organic groups can be utilized for some reactions, including our recent report of Pd-catalyzed Michael-type hydroarylation reaction using aryltin compounds.^{4d} As one of our series of studies of C–C bond forming reactions using organoheteroatom (B,⁹ Sb,¹⁰ Bi,¹¹ Sn^{4d}) compounds, we have now examined simple carbonylation reactions of tetra- to di-aryltins in detail from the viewpoint of atom economy of aryl groups. As a result, we found that more than one aryl group, and sometimes almost all of them, were transferred to the products, arenecarboxylic acids and diaryl ketones, in the presence of either a stoichiometric or a catalytic amount of Pd(II) or Rh(III) salt together with a suitable reoxidant in acetonitrile (MeCN) or acetic acid (AcOH). We report here the details of results of this carbonylation.

Results and Discussion

Pd(II)-Mediated and -Catalyzed Carbonylation of Aryl-

tin Compounds in MeCN. At first, we carried out the reaction of tetraphenyltin (Ph₄Sn) with an atmospheric pressure of CO in the presence of a stoichiometric amount of Pd(II) salt in order to confirm whether more than one of the four phenyl groups could be transferred to the products. Thus, a mixture of Ph₄Sn (0.5 mmol), PdCl₂ (0.5 mmol), and LiCl (4 mmol) was stirred in MeCN (5 mL) under CO (1 atm, 1 atm = 1.01325 × 10⁵ Pa) at 25 °C for 20 h. The reason for the addition of LiCl was to accelerate the carbonylation, as in the case of Michael-type hydroarylation reaction.^{4d,12} As a result, benzophenone was mainly obtained together with benzoic acid and a small amount of biphenyl as organic products, but only one of the four phenyl groups was transferred to the products (Eq. 1; Table 1, Entry 1).



As the stoichiometry for the formation of benzophenone and benzoic acid (benzoyl chloride is a precursor which is hydrolyzed to the acid by the work-up procedure) can be described as Eq. 2 and 3, respectively, it was thought that proper amounts of PdCl₂ to transfer all phenyl groups to the products are four-fold molar ones of Ph₄Sn.

Table 1. Carbonylation of Ph₄Sn in Presence of Stoichiometric Amount of Pd Salt in MeCN*

Entry	Pd salt	Additive	Isolated yield/% ^{a)}		
	mmol	mmol	PhCO ₂ H	PhCOPh	Ph-Ph
1	PdCl ₂ (0.5)	LiCl(4)	7	22	6
2	PdCl ₂ (2)	LiCl(4)	10	73	0
3	PdCl ₂ (2)	LiCl(8)	11	81	0
4	Na ₂ PdCl ₄ (0.5)	—	7	17	4
5	Na ₂ PdCl ₄ (2)	—	12	85	0

*CO (1 atm) and MeCN (5 mL) were used.

a) Based on Ph₄Sn employed (0.5 mmol): 2 mmol of PhCO₂H, 1 mmol of PhCOPh, and 1 mmol of Ph-Ph correspond to 100% yield, respectively.

Table 2. Pd(II)-Catalyzed Carbonylation of Aryltin Compounds in MeCN*

Entry	Ar _n SnCl _(4-n)	PdCl ₂	Reoxidant	Isolated yield/% ^{a)}		
	mmol	mmol	mmol	ArCO ₂ H	ArCOAr	Ar–Ar
1	Ph ₄ Sn(0.5)	0.1	— ^{b)}	4	1	2
2	Ph ₄ Sn(0.5)	0.1	CuCl ₂ (4) ^{b)}	30	1	7
3	Ph ₄ Sn(0.5)	0.1	CuCl ₂ (4)	57	< 1	< 1
4	Ph ₄ Sn(0.5)	0.02	CuCl ₂ (4)	23	24	0
5	Ph ₄ Sn(0.5)	0.1	CuSO ₄ (4) ^{b)}	23	40	6
6	Ph ₄ Sn(0.5)	0.1	CAN(2)	58	< 1	< 1
7	(<i>p</i> -CH ₃ C ₆ H ₄) ₄ Sn(0.5)	0.1	CuCl ₂ (4)	66	< 1	< 1
8	(<i>p</i> -CH ₃ OC ₆ H ₄) ₄ Sn(0.5)	0.1	CuCl ₂ (4)	43 ^{c)}	< 1	5
9	(<i>p</i> -ClC ₆ H ₄) ₄ Sn(0.5)	0.1	CuCl ₂ (4)	66	5	3
10	Ph ₃ SnCl(0.67)	0.1	CuCl ₂ (4)	84	5	4
11	Ph ₂ SnCl ₂ (1.0)	0.1	CuCl ₂ (4)	85	1	3
12	PhSnCl ₃ (2.0)	0.1	CuCl ₂ (4)	86	2	2

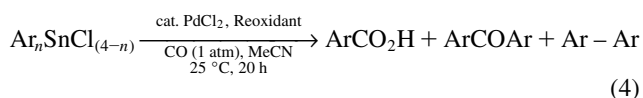
*CO (1 atm) and MeCN (5 mL) were used.

a) Based on Ar_nSnCl_(4-n) employed (2 mmol as Ar group): 2 mmol of ArCO₂H, 1 mmol of ArCOAr, and 1 mmol of Ar–Ar correspond to 100% yield, respectively. b) LiCl (4 mmol) was added. c) C₆H₅OCH₃(24% GLC yield) was also obtained.



Then, Ph₄Sn (0.5 mmol) was treated with CO in the presence of four-fold molar amounts of PdCl₂ (2.0 mmol; equimolar amounts to C–Sn bonds) and LiCl (4–8 mmol). The products were again benzophenone and benzoic acid together with a precipitation of palladium black, and in this case almost all phenyl groups were transferred to the products as expected (Table 1, Entries 2 and 3). This result shows that four phenyl groups of Ph₄Sn can be utilized for the carbonylation reaction under an atmospheric pressure of CO. The stoichiometric reaction using Na₂PdCl₄ instead of PdCl₂ and LiCl gave similar results (Table 1, Entries 4 and 5).

We next investigated the carbonylation of various aryltin compounds using a catalytic amount of Pd(II) salt together with a variety of reoxidants, such as CuCl₂, CuSO₄, Cu(OAc)₂, NaBrO₃, Na₂S₂O₈, *p*-benzoquinone (C₆H₄O₂), CAN[Ce(NH₄)₂(NO₃)₆], AgOAc, H₂O₂, I₂, and air, by considering reoxidation of Pd(0) to Pd(II) (Eq. 4).



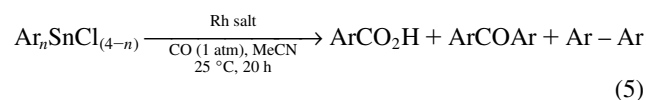
Thus, Ph₄Sn (0.5 mmol) was treated with CO (1 atm) in the presence of PdCl₂ (0.02–0.1 mmol) and one of these reoxidants with or without LiCl in MeCN (5 mL) at 25 °C for 20 h. As a result, the system using PdCl₂ and CuCl₂ (4 mmol, 8 molar equivalents to Ph₄Sn) without LiCl was revealed to be most efficient; between two and three out of the four phenyl groups of Ph₄Sn were transferred to the products, as shown in Table 2, Entries 1–3. The amount of PdCl₂ could be lowered to 0.02 mmol (0.04 molar amount to Ph₄Sn, and 0.01 molar amount to each C–Sn bond) where almost two out of the four phenyl groups were transferred to the products (Table 2, Entry 4). The reoxidants CuSO₄ and CAN were also effective, but other re-

oxidants were ineffective (Table 2, Entries 5 and 6). The Pd(0) compound [Pd₂(dba)₃] did not work as a catalyst.

In a similar treatment of other tetraaryltin compounds (Ar₄Sn) such as (*p*-CH₃C₆H₄)₄Sn, (*p*-CH₃OC₆H₄)₄Sn, and (*p*-ClC₆H₄)₄Sn in PdCl₂/CuCl₂ system, between two and three aryl groups out of the four aryl groups of Ar₄Sn could also be transferred to the products (Table 2, Entries 7–9). The maximum turnover number to palladium in these carbonylations was 13.7 (1.32 mmol of arenecarboxylic acid and 0.05 mmol of diaryl ketone were obtained using 0.1 mmol of PdCl₂; Table 2, Entry 9).

Carbonylation could also be applied to phenyltin chlorides such as Ph₃SnCl, Ph₂SnCl₂, and PhSnCl₃. Thus, treatment of Ph_nSnCl_(4-n) [2 mmol as phenyl group(s); i.e. 0.67 mmol of Ph₃SnCl, 1 mmol of Ph₂SnCl₂, and 2 mmol of PhSnCl₃, respectively] with CO (1 atm) in the presence of PdCl₂ (0.1 mmol) and CuCl₂ (4 mmol) as the reoxidant in MeCN (5 mL) at 25 °C for 20 h afforded almost exclusively benzoic acid, where slightly fewer than all phenyl groups were utilized in all cases (Table 2, Entries 10–12), the turnover number to palladium in these cases being more than 17.

Rh(III)-Mediated and -Catalyzed Carbonylation of Aryltin Compounds in MeCN. Similar carbonylation was next carried out using Rh(III) salt in place of Pd(II) salt. When Ph₄Sn (0.5 mmol) was treated with CO (1 atm) in MeCN (5 mL) in the presence of a stoichiometric amount of RhCl₃·3H₂O (0.5 mmol), benzophenone was mainly produced together with benzoic acid and biphenyl (Eq. 5).



Here, three fourths of the four phenyl groups were transferred to the products as shown in Table 3, Entry 1. Interestingly, the product yield (1.17 mmol of carbonylated products) is higher than 100% based on the amount of Rh(III) chloride used, showing that the Rh(III) salt itself worked as a catalyst

Table 3. Rh(III)-Catalyzed Carbonylation of Aryltin Compounds in MeCN*

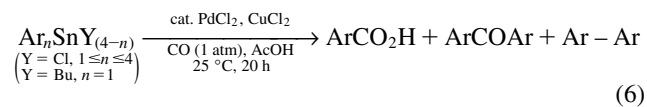
Entry	Ar _n SnCl _(4-n)	Rh species	Isolated yield/% ^{a)}		
	mmol	mmol	ArCO ₂ H	ArCOAr	Ar–Ar
1	Ph ₄ Sn(0.5)	RhCl ₃ ·3H ₂ O(0.5)	21	75	< 1
2	Ph ₄ Sn(0.5)	RhCl ₃ ·3H ₂ O(0.1)	13	29	< 1
3	Ph ₃ SnCl(0.67)	RhCl ₃ ·3H ₂ O(0.5)	10	64	4
4	Ph ₂ SnCl ₂ (1.0)	RhCl ₃ ·3H ₂ O(0.5)	16	38	9
5	(<i>p</i> -CH ₃ C ₆ H ₄) ₄ Sn(0.5) ^{b)}	RhCl ₃ ·3H ₂ O(0.5)	14	41	3
6	(<i>p</i> -ClC ₆ H ₄) ₄ Sn(0.5)	RhCl ₃ ·3H ₂ O(0.5)	4	57	7
7	Ph ₄ Sn(0.5)	[RhCl(CO) ₂] ₂ (0.05)	9	10	< 1

*CO (1 atm) and MeCN (5 mL) were used.

a) Based on Ar_nSnCl_(4-n) employed (2 mmol as Ar group): 2 mmol of ArCO₂H, 1 mmol of ArCOAr, and 1 mmol of Ar–Ar correspond to 100% yield, respectively. b) MeCN (20 ml) was used.

without the addition of reoxidant.^{7b} Similarly, by use of 0.1 mmol of RhCl₃·3H₂O, 0.55 mmol of carbonylated compounds were produced (Table 3, Entry 2). Different from the Pd(II) cases, the addition of oxidant such as CuCl₂ or Na₂S₂O₈ almost stopped the reaction. Results of carbonylation of several aryltin compounds are also shown in Table 3 (Entries 3–6), where a half and three fourths of two and three aryl groups were transferred, respectively, to the products. It is worth noting that Rh(I) salt such as rhodium(I) chlorocarbonyl complex also worked as a catalyst (Table 3, Entry 7).

Pd(II)-Catalyzed Carbonylation of Aryltin Compounds in AcOH. Palladium(II)-catalyzed carbonylation of various aryltin compounds using a system of PdCl₂/CuCl₂ was next carried out in AcOH in which a high efficiency of atom transfer has been observed in Pd(II)-catalyzed Michael-type hydroarylation of α,β -unsaturated carbonyl compounds with Ph₄Sn.^{4d} When Ph₄Sn (0.5 mmol) was treated with CO (1 atm) in the presence of PdCl₂ (0.1 mmol)/CuCl₂ (4 mmol) in AcOH (5 mL) at 25 °C for 20 h, benzoic acid was mainly produced, together with benzophenone and a trace amount of biphenyl (Eq. 6; Table 4, Entry 1) where about three out of four phenyl groups were transferred to the products.



Other reoxidants such as CuCl₂·2H₂O, CuSO₄, and CAN could also be used, but they were less effective. Carbonylation could be applied to various tetraaryltins (Table 4, Entries 3–5) as well as phenyltin compounds (Table 4, Entries 6–8) with a good atom economy of aryl groups in all cases except the case of tetrakis(*p*-methoxyphenyl)tin (Table 4, Entry 4) where anisole, a protodestannylation compound,¹³ was the major product. In the cases of aryltributyltins, the corresponding diaryl ketone became the main product (Table 4, Entries 9–12). The maximum turnover number to palladium was 14.1 (1.30 mmol of arenecarboxylic acid and 0.11 mmol of diaryl ketone were obtained using 0.1 mmol of PdCl₂; Table 4, Entry 1).

Rh(III)-Catalyzed Carbonylation of Aryltin Compounds in AcOH. As described above, RhCl₃·3H₂O itself worked as a catalyst without any reoxidant in the carbonylation reaction of Ph₄Sn in MeCN; the addition of reoxidant decreased the

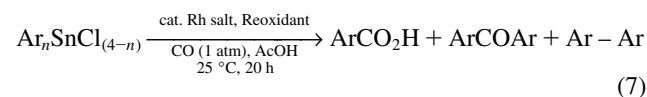
Table 4. Pd(II)-Catalyzed Carbonylation of Aryltin Compounds in AcOH*

Entry	Aryltins	Isolated yield/% ^{a)}		
	mmol	ArCO ₂ H	ArCOAr	Ar–Ar
1	Ph ₄ Sn(0.5)	65	11	< 1
2	Ph ₄ Sn(0.5) ^{b)}	20	17	1
3	(<i>p</i> -CH ₃ C ₆ H ₄) ₄ Sn(0.5)	56	6	< 1
4	(<i>p</i> -CH ₃ OC ₆ H ₄) ₄ Sn(0.5)	3 ^{c)}	7	< 1
5	(<i>p</i> -ClC ₆ H ₄) ₄ Sn(0.5)	36	39	< 1
6	Ph ₃ SnCl(0.67)	54	31	3
7	Ph ₂ SnCl ₂ (1.0)	62	16	5
8	PhSnCl ₃ (2.0)	31	2	2
9	PhSnBu ₃ (2.0)	3	53 ^{d)}	5
10	<i>p</i> -CH ₃ C ₆ H ₄ SnBu ₃ (2.0)	< 1	47 ^{d)}	3
11	<i>p</i> -CH ₃ OC ₆ H ₄ SnBu ₃ (2.0)	0	21 ^{e)}	— ^{f)}
12	<i>p</i> -ClC ₆ H ₄ SnBu ₃ (2.0)	2	45 ^{d)}	4

*PdCl₂ (0.1 mmol), CuCl₂ (4 mmol), CO (1 atm) and AcOH (5 mL) were used.

a) Based on aryltin compound employed (2 mmol as Ar group): 2 mmol of ArCO₂H, 1 mmol of ArCOAr, and 1 mmol of Ar–Ar correspond to 100% yield, respectively. b) CuCl₂ 2 mmol. c) C₆H₅OCH₃ (42% GLC yield) was also formed. d) A small amount of chlorinated arene (ArCl) was also formed. e) C₆H₅OCH₃ (63% GLC yield) and *p*-CH₃OC₆H₄Cl (8% GLC yield) were also formed. f) Not determined.

product yield. In AcOH as solvent, however, we found that several reoxidants worked well in rhodium(III)-catalyzed carbonylation (Eq. 7).



The carbonylation of Ph₄Sn in the presence of RhCl₃·3H₂O (0.1 mmol) afforded mainly benzoic acid (22%, 0.44 mmol) together with benzophenone (8%, 0.08 mmol) and a small amount of biphenyl (1%, 0.01 mmol) (Table 5, Entry 1). Here, it was also shown that the total amounts of these products were larger than the amount of RhCl₃·3H₂O employed, and that slightly more than one of four phenyl groups could be utilized for the carbonylation reaction. Addition of reoxidants such as Cu(OAc)₂ and AgOAc increased the product yield, as shown in

Table 5. Rh(III)-Catalyzed Carbonylation of Aryltin Compounds in AcOH*

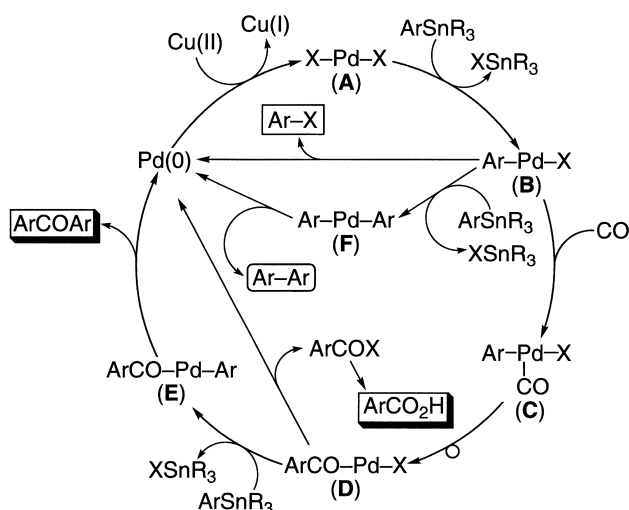
Entry	Ar _n SnCl _(4-n)	Rh species ^{a)}	Reoxidant	Isolated yield/% ^{b)}		
	mmol	mmol	mmol	ArCO ₂ H	ArCOAr	Ar–Ar
1	Ph ₄ Sn(0.5)	RhCl ₃ ·3H ₂ O(0.1)	—	22	8	1
2	Ph ₄ Sn(0.5)	RhCl ₃ ·3H ₂ O(0.1)	Cu(OAc) ₂ (2)	75	2	< 1
3	Ph ₄ Sn(0.5)	RhCl ₃ ·3H ₂ O(0.1)	CuSO ₄ (4)	33	2	< 1
4	Ph ₄ Sn(0.5)	RhCl ₃ ·3H ₂ O(0.1)	CuCl ₂ (4)	< 1	< 1	< 1
5	Ph ₄ Sn(0.5)	RhCl ₃ ·3H ₂ O(0.1)	AgOAc(4)	43	< 1	< 1
6	Ph ₄ Sn(0.5)	“Rh ₃ O”(0.034)	—	20	1	7
7	Ph ₄ Sn(0.5)	“Rh ₃ O”(0.034)	Cu(OAc) ₂ (4)	71	1	< 1
8	Ph ₃ SnCl(0.67)	RhCl ₃ ·3H ₂ O(0.1)	Cu(OAc) ₂ (2)	41	3	6
9	Ph ₂ SnCl ₂ (1.0)	RhCl ₃ ·3H ₂ O(0.1)	Cu(OAc) ₂ (2)	0	< 1	< 1
10	Ph ₃ SnCl(0.67)	“Rh ₃ O”(0.034)	Cu(OAc) ₂ (4)	41	4	6
11	Ph ₂ SnCl ₂ (1.0)	“Rh ₃ O”(0.034)	Cu(OAc) ₂ (4)	16	< 1	4
12	(<i>p</i> -CH ₃ C ₆ H ₄) ₄ Sn(0.5)	“Rh ₃ O”(0.034)	Cu(OAc) ₂ (4)	68	1	1
13	(<i>p</i> -CH ₃ OC ₆ H ₄) ₄ Sn(0.5)	“Rh ₃ O”(0.034)	Cu(OAc) ₂ (4)	27 ^{c)}	1	4
14	(<i>p</i> -ClC ₆ H ₄) ₄ Sn(0.5)	“Rh ₃ O”(0.034)	Cu(OAc) ₂ (4)	57	2	3
15	PhSnBu ₃ (2.0)	“Rh ₃ O”(0.034)	Cu(OAc) ₂ (4)	12	< 1	< 1

*CO (1 atm) and AcOH (5 mL) were used.

a) “Rh₃O” ≡ [Rh₃O(OAc)₆(H₂O)₃]OAc. b) Based on Ar_nSnCl_(4-n) employed (2 mmol as Ar group): 2 mmol of ArCO₂H, 1 mmol of ArCOAr, and 1 mmol of Ar–Ar correspond to 100% yield, respectively. c) C₆H₅OCH₃ (26% GLC yield) was also formed.

Table 5, Entries 2 and 5, respectively. In this case, however, CuCl₂ stopped the reaction (Table 5, Entry 4), probably because this carbonylation disfavors the presence of excess chloride anions as the addition of LiCl also stopped the reaction completely. As one chloride-free rhodium(III) salt, we noticed oxo-centered trinuclear rhodium(III) acetate {[Rh₃O(OAc)₆(H₂O)₃]OAc}¹⁴ which was actually effective as a catalyst (Table 5, Entries 6 and 7). Carbonylation of other tetraaryltins than Ph₄Sn in the presence of RhCl₃·3H₂O almost failed, while the Rh(III) acetate was shown to be effective (Table 5, Entries 12–14). Results of the application to various aryltin compounds using this acetate are shown in Table 5. The maximum turnover number to rhodium was 15.2 (1.50 mmol of benzoic acid and 0.02 mmol of benzophenone were obtained; Table 5, Entry 2). The characteristic feature in Rh(III)-catalyzed carbonylation is that arenecarboxylic acid is almost the sole product, in contrast to similar reactions in MeCN where diaryl ketone is the major product.

Plausible Reaction Scheme. We propose the reaction pathway for this catalytic carbonylation reaction as shown in Scheme 1. The transmetalation of Sn(IV) moiety of aryltin(IV) compounds by palladium(II) salt [A: X = Cl or OAc] occurs to give an Ar–Pd–X species (B), to which CO coordinates to afford a metal carbonyl species (C). Then, this carbonyl species gives an acylpalladium(II) species (D) to which the other organotin(IV) compound attacks to afford an acylarylpalladium species (E), which gives diaryl ketone and Pd(0) species by reductive elimination. Palladium(0) is oxidized by the oxidant such as Cu(II) salt to regenerate the species A. Reductive elimination from the species D might give acyl chloride (in MeCN) or unsymmetrical acid anhydride (in AcOH) (abbreviated to ArCOX), followed by aqueous work-up to give arenecarboxylic acid: this expectation is based on the formation of arenecarboxamide when NH₄Cl was added under incomplete hydrolysis (see Experimental). The second transmetalation of Sn(IV) moiety of aryltin(IV) compounds by the spe-



Scheme 1. Plausible reaction scheme.

cies B occurs to give Ar–Pd(II)–Ar species (F), reductive elimination from which gives biaryl. A similar reaction pathway can be considered to occur in Rh(III)-catalyzed carbonylation in AcOH. Partially dearylated aryltins (XSnR₃) produced by the first cycle also enter this catalytic cycle, resulting in the transfer of more than one aryl group to products.

In the case of carbonylation using Rh(III) chloride in MeCN, a pathway of oxidative addition of aryltin(IV) compounds to the produced Rh(I) species to generate Ar–Rh(III)–SnR₃ species might be considered, though the details are not yet clear.

The formation of a small amount of chlorinated arene (Ar–X) from the carbonylation of ArSnBu₃ may be explained by reductive elimination of Pd(0) from the species B.

Experimental

General Procedure. Melting points were determined on a Yanako MP-J3 micro melting point apparatus and are uncorrected.

The ^1H NMR spectra were recorded with JEOL JNM-AL300. GLC analyses were carried out with a Shimadzu GC-14A with flame ionization detectors equipped with an OV-17 (7 mm ϕ \times 2 m) column using nitrogen as carrier gas. The GLC yields were determined using chlorobenzene (PhCl) as an internal standard. The isolation of a pure product was carried out with column chromatography on SiO_2 (Merck 60, 230–400 mesh, Merck KGaA.).

Materials. Solvents except AcOH were freshly distilled under N_2 prior to use: THF was distilled from sodium diphenylketyl; C_6H_6 was distilled from calcium hydride; MeCN was distilled twice under ambient pressure, first from phosphorus pentoxide and next from calcium hydride. Tetraaryltins such as (*p*- $\text{CH}_3\text{C}_6\text{H}_4$) $_4\text{Sn}$, (*p*- $\text{CH}_3\text{OC}_6\text{H}_4$) $_4\text{Sn}$, and (*p*- ClC_6H_4) $_4\text{Sn}$ were prepared from the corresponding Grignard reagents and SnCl_4 (as C_6H_6 solution) in THF, followed by recrystallization.¹⁵ Aryltributyltins such as PhSnBu_3 , *p*- $\text{CH}_3\text{C}_6\text{H}_4\text{SnBu}_3$, *p*- $\text{CH}_3\text{OC}_6\text{H}_4\text{SnBu}_3$, and *p*- $\text{ClC}_6\text{H}_4\text{SnBu}_3$ were prepared from phenylmagnesium bromide and Bu_3SnCl in THF, followed by distillation under reduced pressure.¹⁶ The compound $[\text{Rh}_3\text{O}(\text{OAc})_6(\text{H}_2\text{O})_3]\text{OAc}$ was prepared by the literature method from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and AgOAc in aqueous AcOH.¹⁴ The authentic samples (for characterization using ^1H NMR) such as (*p*- $\text{CH}_3\text{C}_6\text{H}_4$) $_2$, (*p*- $\text{CH}_3\text{OC}_6\text{H}_4$) $_2$, and (*p*- ClC_6H_4) $_2$ were synthesized by the reaction of the corresponding Grignard reagent with aryl bromide or iodide in the presence of $[\text{Pd}(\text{PPh}_3)_4]$. Other organic and inorganic reagents including products biaryls, diaryl ketones, and arenecarboxylic acids were commercial products and were used without further purification.

Tetra(*p*-tolyl)tin. [(*p*- $\text{CH}_3\text{C}_6\text{H}_4$) $_4\text{Sn}$]: Recrystallized from benzene–ethyl acetate, mp 242–242.5 $^\circ\text{C}$ (lit. 238 $^\circ\text{C}^{15c}$); ^1H NMR (CDCl_3) δ 2.35 (s, 12H), 7.18–7.21 (d, $J = 7.9$ Hz, 8H), 7.45–7.49 (d, $J = 7.7$ Hz, 8H).

Tetrakis(*p*-methoxyphenyl)tin. [(*p*- $\text{CH}_3\text{OC}_6\text{H}_4$) $_4\text{Sn}$]: Recrystallized from ethyl acetate, mp 135.5–136.5 $^\circ\text{C}$ (lit. 134.8 $^\circ\text{C}^{15c}$); ^1H NMR (CDCl_3) δ 3.81 (s, 12H), 6.93–6.98 (d, $J = 8.6$ Hz, 8H), 7.47–7.51 (d, $J = 8.4$ Hz, 8H).

Tetrakis(*p*-chlorophenyl)tin. [(*p*- ClC_6H_4) $_4\text{Sn}$]: Recrystallized from benzene–petroleum ether, mp 198–201 $^\circ\text{C}$ (lit. 199 $^\circ\text{C}^{15c}$); ^1H NMR (CDCl_3) δ 7.36–7.58 (m, 16H).

Tributyl-*p*-tolyltin. (*p*- $\text{CH}_3\text{C}_6\text{H}_4\text{SnBu}_3$): Obtained as colorless oil; ^1H NMR (CDCl_3) δ 0.85–0.91 (t, $J = 7.1$ Hz, 9H), 1.00–1.05 (t, $J = 8.1$ Hz, 6H), 1.25–1.40 (sext, $J = 7.2$ Hz, 6H), 1.45–1.60 (m, 6H), 2.33 (s, 3H), 7.13–7.17 (d, $J = 7.5$ Hz, 2H), 7.30–7.40 (d, $J = 7.3$ Hz, 2H).

Tributyl-*p*-methoxyphenyltin. (*p*- $\text{CH}_3\text{OC}_6\text{H}_4\text{SnBu}_3$): Obtained as colorless oil; ^1H NMR (CDCl_3) δ 0.84–0.91 (t, $J = 7.3$ Hz, 9H), 0.99–1.05 (t, $J = 7.6$ Hz, 6H), 1.26–1.39 (sext, $J = 7.2$ Hz, 6H), 1.47–1.59 (m, 6H), 3.80 (s, 3H), 6.88–6.92 (d, $J = 7.4$ Hz, 2H), 7.30–7.40 (d, $J = 7.3$ Hz, 2H).

Tributyl-*p*-chlorophenyltin. (*p*- $\text{ClC}_6\text{H}_4\text{SnBu}_3$): Obtained as colorless oil; ^1H NMR (CDCl_3) δ 0.85–0.91 (t, $J = 7.2$ Hz, 9H), 1.01–1.08 (t, $J = 8.0$ Hz, 6H), 1.25–1.38 (sext, $J = 7.3$ Hz, 6H), 1.46–1.56 (m, 6H), 7.26–7.50 (m, 4H).

4,4'-Dimethoxybiphenyl. [(*p*- $\text{CH}_3\text{OC}_6\text{H}_4$) $_2$]: Obtained as white crystal; ^1H NMR (CDCl_3 , recrystallized from THF) δ 3.84 (s, 6H), 6.94–6.97 (d, $J = 8.8$ Hz, 4H), 7.46–7.50 (d, $J = 8.8$ Hz, 4H).

4,4'-Dichlorobiphenyl. [(*p*- ClC_6H_4) $_2$]: Obtained as white crystal; ^1H NMR (CDCl_3 , recrystallized from ethanol) δ 7.35–7.55 (m, 8H).

General Procedure for Palladium(II)- or Rhodium(III)-Catalyzed Carbonylation of Aryltin Compounds. In a two-necked 30 mL round-bottom flask, equipped with a septum inlet

and a three-way stopcock, were placed aryltin [0.5–2 mmol, 2 mmol as aryl group(s)], transition metal species (0.02–2 mmol as the metal) and additive(s). The system was then evacuated and flushed with CO from a CO-filled balloon connected to the flask several times; then solvent (5 mL) was injected by a syringe. The resulting mixture was stirred at 25 $^\circ\text{C}$ for 20 h and then the mixture was poured into an aqueous solution of NaOH (10% for the case of MeCN, 20% for the case of AcOH, 50 mL) and the solution was stirred for 30–60 min and then filtered through celite. [When ArSnBu_3 was used as an aryltin reagent, 30% aqueous solution of KF (10 mL) was added in order to remove Bu_3Sn species and the mixture was stirred for 1 h prior to the addition of aqueous NaOH. If H_2O_2 , NaBrO_3 , or $\text{Na}_2\text{S}_2\text{O}_8$ were present in the reaction mixture, Na_2SO_3 was also added to aqueous NaOH in order to reduce these oxidants. If Cu(II) salt was present in the reaction mixture, NH_4Cl was added and the mixture was stirred additionally for 15–30 min before filtration.] The celite was washed with 10% aqueous NaOH (50 mL) and diethyl ether (30 mL). The organic layer of this filtrate was separated from the aqueous layer; then the aqueous layer was extracted with diethyl ether (25 mL \times 4). The organic layer was washed with saturated aqueous solution of NaHCO_3 (30 mL \times 2) and then dried over anhydrous MgSO_4 . To the aqueous layer were added sodium chloride and concentrated hydrochloric acid (50–60 mL). After the mixture was cooled in an ice bath, the aqueous layer was extracted with diethyl ether (25 mL \times 4) and the extract was washed with dilute HCl (ca. 3 mol dm^{-3} , 30 mL \times 3) and brine (30 mL), and then dried over anhydrous MgSO_4 . After removal of the solvent under reduced pressure, the products in the residue were separated by column chromatography.

References

- For reviews, see for example: a) I. P. Beletskaya, *J. Organomet. Chem.*, **250**, 551 (1983). b) J. K. Stille, *Angew. Chem., Int. Ed. Engl.*, **25**, 508 (1986). c) T. N. Mitchell, *Synthesis*, **1992**, 803. d) V. Farina, *Pure Appl. Chem.*, **68**, 73 (1996). e) V. Farina, V. Krishnamurthy, and W. J. Scott, *Org. React.*, **50**, 1 (1997). f) S. P. Stanforth, *Tetrahedron Lett.*, **54**, 263 (1998). g) M. A. J. Dunston and G. Pattenden, *J. Chem. Soc., Perkin Trans. 1*, **1999**, 1235. h) K. Afarinkia, *J. Chem. Soc., Perkin Trans. 1*, **1999**, 2025. i) L. Haughton and J. M. J. Williams, *J. Chem. Soc., Perkin Trans. 1*, **1999**, 2645. j) E. Shirakawa and T. Hiyama, *J. Organomet. Chem.*, **576**, 169 (1999). k) E. Negishi, *J. Organomet. Chem.*, **576**, 179 (1999). l) B. A. Lorsbach and M. J. Kurth, *Chem. Rev.*, **99**, 1549 (1999). m) R. Franzen, *Can. J. Chem.*, **78**, 957 (2000).
- Recent examples of Lewis acid-mediated reactions: a) J. A. Marshall and K. Hinkle, *J. Org. Chem.*, **60**, 1920 (1995). b) J. A. Marshall, R. H. Yu, and J. F. Perkins, *J. Org. Chem.*, **60**, 5550 (1995). c) M. Yasuda, T. Miyai, I. Shibata, A. Baba, R. Nomura, and H. Matsuda, *Tetrahedron Lett.*, **36**, 9497 (1995). d) J. A. Marshall and M. Chen, *J. Org. Chem.*, **62**, 5996 (1997). e) D. A. Evans, D. P. Halstead, and B. D. Allison, *Tetrahedron Lett.*, **40**, 4461 (1999). f) N. H. Taylor and E. J. Thomas, *Tetrahedron*, **55**, 8757 (1999). g) J. A. Marshall and C. M. Grant, *J. Org. Chem.*, **64**, 8214 (1999). Recent examples of transition metal-catalyzed reactions: h) J. M. Nuss and R. A. Rennels, *Chem. Lett.*, **1993**, 197. i) H. Nakamura, N. Sadayori, M. Sekido, and Y. Yamamoto, *J. Chem. Soc., Chem. Commun.*, **1994**, 2581. j) H. Nakamura, H. Iwata, and Y. Yamamoto, *J. Am. Chem. Soc.*, **118**, 6641 (1996). k) S. Oi, M. Moro, and Y. Inoue, *Chem. Commun.*, **1997**, 1621. l) H. Nakamura and Y. Yamamoto, *Coll. Czech. Chem. Commun.*, **64**,

829 (1999); *Chem. Abstr.* **131**: 133024v (1999).

3 a) K. Hirabayashi, J. Ando, Y. Nishihara, A. Mori, and T. Hiyama, *Synlett*, **1999**, 99. b) K. Hirabayashi, J. Ando, J. Kawashima, Y. Nishihara, A. Mori, and T. Hiyama, *Bull. Chem. Soc. Jpn.*, **73**, 1409 (2000).

4 a) S. Cacchi, F. La Torre, and D. Misiti, *Tetrahedron Lett.*, **1979**, 4591. b) S. Oi, M. Moro, S. Ono, and Y. Inoue, *Chem. Lett.*, **1998**, 82. c) E. Piers, E. J. McEachern, and P. A. Burns, *Tetrahedron*, **56**, 2753 (2000). d) T. Ohe, T. Wakita, S. Motofusa, C. S. Cho, K. Ohe, and S. Uemura, *Bull. Chem. Soc. Jpn.*, **73**, 2149 (2000).

5 For recent examples: a) E. Fouquet, M. Pereyre, A. L. Rodriguez, and T. Roulet, *Bull. Soc. Chim. Fr.*, **134**, 959 (1997). b) I. Ryu, T. Niguma, S. Minakata, M. Komatsu, Z. Luo, and D. P. Curran, *Tetrahedron Lett.*, **40**, 2367 (1999). c) T. Mikami, M. Harada, and K. Narasaka, *Chem. Lett.*, **1999**, 425.

6 For recent examples of traditional Stille carbonylative coupling: a) E. Morera and G. Ortar, *Bioorg. Med. Chem. Lett.*, **10**, 1815 (2000). b) S. Ceccarelli, U. Piarulli, and C. Gennari, *J. Org. Chem.*, **65**, 6254 (2000). For recent examples of modified Stille-type carbonylative coupling: c) S.-K. Kang, H.-C. Ryu, and S.-W. Lee, *J. Chem. Soc., Perkin Trans. 1*, **1999**, 2661. d) S.-K. Kang, S.-W. Lee, and H.-C. Ryu, *Chem. Commun.*, **1999**, 2117. e) M. H. Al-Qahtani and V. W. Pyke, *J. Chem. Soc., Perkin Trans. 1*, **2000**, 1033. f) M. H. Al-Qahtani and V. W. Pyke, *J. Labelled Compd. Radiopharm.*, **43**, 825 (2000); *Chem. Abstr.* **133**: 222395m (2000).

7 a) P. M. Henry, *Tetrahedron Lett.*, **1968**, 2285. b) R. F. Heck, *J. Am. Chem. Soc.*, **90**, 5546 (1968).

8 Organotin: a) K. Fugami, S. Ohnuma, M. Kameyama, T. Saotome, and M. Kosugi, *Synlett*, **1999**, 63. b) S. Kobayashi, K. Sugita, and H. Oyamada, *Synlett*, **1999**, 138. c) G. Harada, M. Yoshida, and M. Iyoda, *Chem. Lett.*, **2000**, 160. Organoborons: d) N. A. Bumagin and D. N. Korolev, *Tetrahedron Lett.*, **40**, 3057 (1999). Organoindiums: e) I. Pérez, J. P. Sestelo, and L. A. Sarandeces, *Org. Lett.*, **1**, 1267 (1999).

9 a) C. S. Cho, S. Motofusa, and S. Uemura, *Tetrahedron Lett.*, **35**, 1739 (1994). b) C. S. Cho, S. Motofusa, K. Ohe, S. Uemura, and S. C. Shim, *J. Org. Chem.*, **60**, 883 (1995).

10 a) C. S. Cho, K. Tanabe, and S. Uemura, *Tetrahedron Lett.*, **35**, 1275 (1994). b) C. S. Cho, K. Tanabe, O. Itoh, and S. Uemura, *J. Org. Chem.*, **60**, 274 (1995). c) C. S. Cho, S. Motofusa, K. Ohe, and S. Uemura, *Bull. Chem. Soc. Jpn.*, **69**, 2341 (1996). d) K. Matoba, S. Motofusa, C. S. Cho, K. Ohe, and S. Uemura, *J. Organomet. Chem.*, **574**, 3 (1999).

11 a) C. S. Cho, T. Ohe, O. Itoh, and S. Uemura, *J. Chem. Soc., Chem. Commun.*, **1992**, 453. b) C. S. Cho, Y. Yoshimori, and S. Uemura, *Bull. Chem. Soc. Jpn.*, **68**, 950 (1995). c) T. Ohe, T. Tanaka, M. Kuroda, C. S. Cho, K. Ohe, and S. Uemura, *Bull. Chem. Soc. Jpn.*, **72**, 1851 (1999).

12 Examples of acceleration of transmetalation from tin to transition metal by halide anion: LiCl: a) M. Fujita, H. Oka, and K. Ogura, *Tetrahedron Lett.*, **36**, 5247 (1995). NaCl: b) S.-K. Kang, J.-S. Kim, and S.-C. Choi, *J. Org. Chem.*, **62**, 4208 (1997). LiBr: c) E. Shirakawa, K. Yamasaki, and T. Hiyama, *Synthesis*, **1998**, 1544. Bu₄NF: d) E. Fouquet, M. Pereyre, and A. L. Rodriguez, *J. Org. Chem.*, **62**, 5242 (1997). e) E. Fouquet and A. L. Rodriguez, *Synlett*, **1997**, 1323. f) A. L. Rodriguez, G. Peron, C. Duprat, M. Vallier, E. Fouquet, and F. Fages, *Tetrahedron Lett.*, **39**, 1179 (1998). g) G. A. Grasa and S. P. Nolan, *Org. Lett.*, **3**, 119 (2001). See also Refs. 5a and 8a.

13 a) R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds," Elsevier, Amsterdam (1965), p. 243. b) W. Kitching, H. A. Olszowy, I. Schott, W. Adcock, and D. P. Cox, *J. Organomet. Chem.*, **310**, 269 (1986).

14 a) I. B. Baranovskii, G. Ya. Mazo, and L. M. Dikareva, *Russ. J. Inorg. Chem.*, **16**, 1388 (1971); *Chem. Abstr.*, **75**, 147280y (1971). b) S. Uemura, A. Spencer, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, **1973**, 2565.

15 For example: a) M. Kira, "Shin-Jikken Kagaku Koza," vol. 12, ed by H. Sakurai, Maruzen, Tokyo (1965), p. 395. b) P. Pfeiffer and K. Schunurnann, *Ber. Dtsch. Chem. Ges.*, **37**, 319 (1904). c) R. K. Ingham, S. D. Rosenberg, and H. Gilman, *Chem. Rev.*, **60**, 459 (1960).

16 For example: W. P. Neumann, "The Organic Chemistry of Tin," John Wiley & Sons, London (1970).